

Dedication

*A mis padres y hermanos
con un gran amor y por su
impulso en mis estudios*

A Felipe por su compañía

THE SPECTRA OF THE DICYANOBENZENES

THE SPECTRA OF THE DICYANOBENZENES

By

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SCOPE AND CONTENTS:

This work is concerned with the assignment of the fundamental frequencies of the three dicyanobenzenes (para-, meta- and ortho-) and their deuterated species using infra-red data for the region $4000-30\text{ cm}^{-1}$ and Raman spectra, and interpretations are given for all the observed bands not chosen as fundamentals.

From a comparative analysis of the spectra, together with those of other related molecules assignments have been made for the 36 normal frequencies of vibration of the molecules.

The assignments for these compounds constitute the basis for the interpretation of the spectra of more complex and less symmetrical disubstituted derivatives.

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CHAPTER I
INTRODUCTION

Molecular vibrations are due classically to the periodic displacements of the nuclei in the molecule from their equilibrium positions. These displacements can be analysed into normal modes of vibration, each normal mode corresponding to harmonic motion with respect to a normal coordinate (1).

Quantum-mechanically, the molecule possesses different vibrational eigenstates, in which the normal modes are individually or collectively excited with different quanta of energy.

The electric dipole moment of a molecule may change periodically during vibration along a particular normal coordinate. Classically this produces a line in the infrared spectrum at the normal frequency of vibration. Similarly changes in the polarizability of the molecule with vibration produce a vibrational Raman line (2).

According to quantum mechanical theory, infrared transitions between two vibrational energy levels with wave functions ψ_v^I and ψ_v^{II} can occur if the transition moment integral $\int \psi_v^I |P| \psi_v^{II} dz$ is non-zero, where P is the dipole moment operator. A Raman transition is allowed if $\int \psi_v | \mu_i^0 | \psi_v dz$ is non-zero, where μ_i^0 is the induced electric dipole vector.

Basis spectroscopic theory is not reviewed here. The theory of molecular vibrations has been treated by Herzberg (3), King (1), Wilson, Decius and Cross (4) and Woodward (3). The analyses of the Raman and infrared spectra of a molecule provide useful information about the bonding and dynamics of complex organic molecules.

Much attention has been paid to the vibrational spectrum of benzene in order to clarify the structure of this compound. It is one of the few molecules with a comparatively large number of nuclei for which a complete vibrational analysis has been possible, and for which all the theoretically expected bands, both in the infrared and in the Raman spectrum, could be identified. With the results obtained for benzene itself, it is possible to interpret the spectra of benzene derivatives, especially the ring substitution products.

The assignments previously made for benzene can serve as a useful guide for analysing the vibrations of the substituted benzenes. The fundamental frequencies, for different modes of benzene rings with various types of substituents have been collected in charts by Thompson (6), Williams (7) and other authors.

The aim of the present work is to study the vibrational spectra of three disubstituted organic compounds. These compounds are the dicyanobenzenes, also called phthalonitriles or phthalic acids: Ortho-, meta- and para $C_6H_4(CN)_2$ and their deuterated isotopes ortho- $C_6D_4(CN)_2$, meta- $C_6H_3D(CN)_2$ and para- $C_6D_4(CN)_2$.

These compounds will be referred to below as ortho-DCB ..., and so on. Most of the thirty fundamentals of the ring parts (ϕ) of these molecules, have been assigned here for each of these compounds by analogy with previously reported studies on other benzene derivatives.

Previously, Jakobsen and Bentley (8) assigned the frequency range between 540-552 cm^{-1} to the out-of-plane ring deformation 16b in para-DCB; and Shmulyakovskii, Oranskaya and Baranova (9) gave frequency values for the "umbrella" vibration in each DCB. No other research has been done on these compounds to date.

The three DCB-h's were obtained commercially from Eastman Organic Chemical Co. The method of preparation for these compounds will also be described in this thesis.

N.M.R., mass spectroscopy and thin layer chromatography techniques were used to determine the purities of the compounds, which were found to be approximately 90% for all three substances.

The deuterated DCB's were prepared for the first time, under the guidance of Drs. R. Bell and N. H. Werstiuk of this department. The normal modes of these compounds have been completely determined and classified into three different groups which can be described as follows; tangential, radial and out-of-plane modes.

CHAPTER II

EXPERIMENTAL METHODS

2.1 Synthesis of the Dicyanobenzenes

For the preparation of ortho, meta and para $C_6H_4(CN)_2$, the reaction of aryl chlorides and bromides with cuprous cyanide to yield nitriles is a suitable reaction. This can be carried out in the presence or absence of solvents.

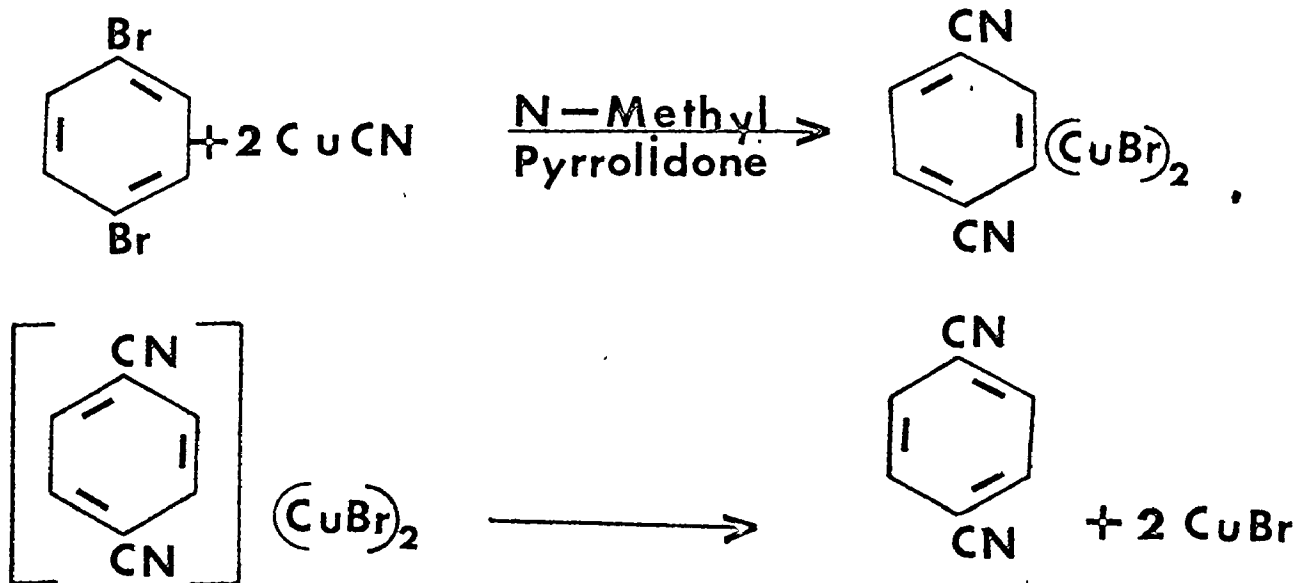
Each dicyanobenzene was prepared from 7.08 gm (0.03 moles) of the corresponding dibromobenzene and 10.73 gm (0.12 moles) of CuCN. These compounds were allowed to react under nitrogen, in 30 ml of N-methyl pyrrolidone as solvent, for a period of 10 hrs at a temperature of $170^\circ C$. As the reaction proceeded the mixture became dark brown. The complex formed from the nitrile and cuprous halide remained in solution, while copper, uncomplexed copper halides and excess cuprous cyanide formed as precipitates. The reaction mixture was allowed to cool, then added to a solution of 10.78 gm (0.176 moles) NaCN in 200 ml of H_2O . The aqueous NaCN rapidly destroys the complex with cuprous halide by formation of soluble sodium cuprocyanide, with simultaneous liberation of the organic nitrile.

The mixture was then stirred for 2 hrs. The organic solvent layer was separated, washed with 200 ml of 10% NaCN plus some

saturated Na_2CO_3 , and then with 300 ml H_2O in portions. The organic layer was separated again and the solvents were removed on a rotary evaporator.

The yields of dicyanobenzenes were generally around 60%. The melting point of ortho-, meta- and para- DCBs were: 138-139°C, 161-162°C and 221-222°C respectively.

The above reaction proceeds in a satisfactory manner to give the corresponding nitriles, in N-methyl pyrrolidone as solvent. This method was initially developed by Melvin S. Newman (10) and Dr. R. Bell.



2.2 Synthesis of the Deuterated Dicyanobenzenes

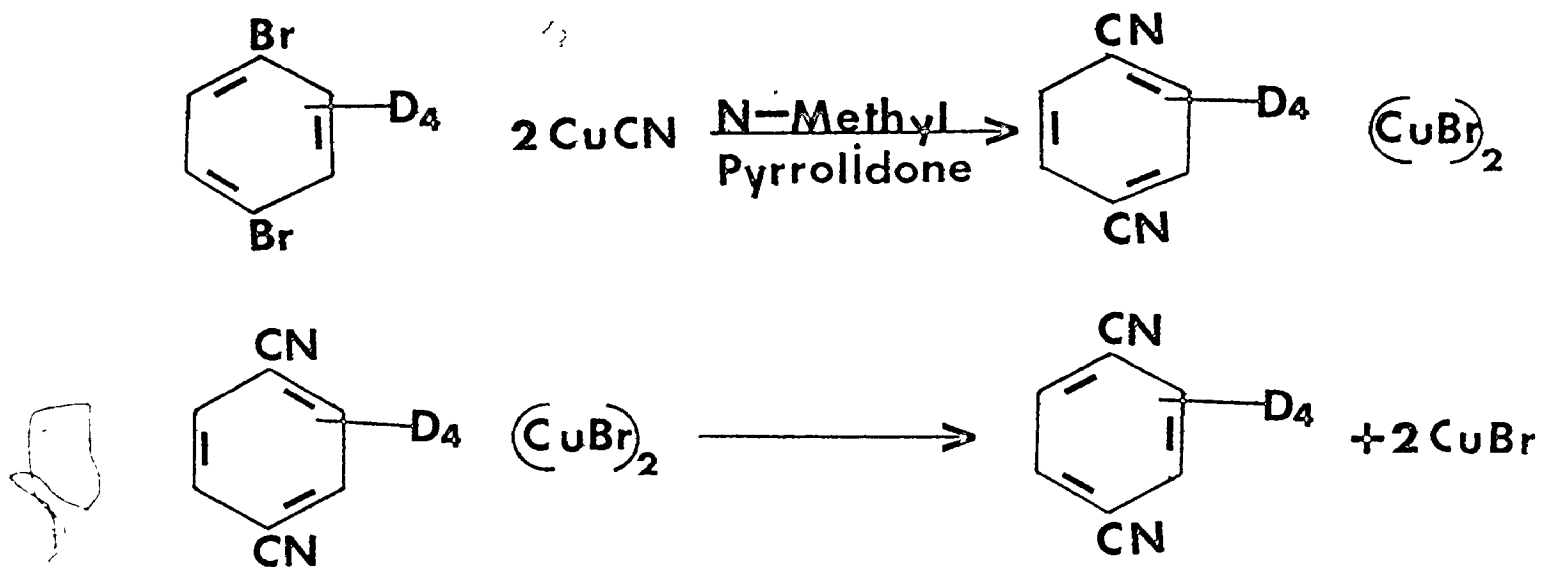
A new method was developed by Dr. N. H. Werstiuk (11,12), for the preparation of the deuterated-DCBs, ortho- $C_6d_4(CN)_2$, meta- $C_6hd_3(CN)_2^*$ and para- $C_6d_4(CN)_2$.

This method entailed ring hydrogen-deuteration of the dibromobenzenes by exchange with D_2O under acid conditions at high temperatures. The reaction was carried out with a mixture of 7.5 gm of the corresponding dibromobenzene, 46.5 ml D_2O and 3.5 ml DCl . These were sealed in a thick walled glass tube (10 in \times 2 in O.D.). The tubes were kept at 250°C in a Parr autoclave pressure apparatus, Model 4914, for 72 hrs. The pressure reached inside the tubes was approximately 800-1000 psi. The reaction product was analysed by nuclear magnetic resonance and also by mass spectroscopy.

The results of the proton spectrum showed that all aromatic positions had been substituted to the extent of 97% overall exchange.

The ortho- $C_6d_4(Br)_2$, meta- $hd_3(Br)_2$ and para- $C_6d_4(Br)_2$ were then subjected to the reaction with $CuCN$ and N-methyl pyrrolidone as described previously.

* Incomplete deuteration occurred for this species due to the deactivation caused by the bromines in the meta position.



The nitriles are solids of low solubility in all common solvents.

The molecular weight of the hydrogenic molecules is 128.

2.3 Instrumentation

A - The Near Infrared Spectra

All near infrared spectra of the isotopic species of the DCBs were recorded with a Perkin-Elmer model 521 double beam grating spectrophotometer in the 250 to 4000 cm^{-1} region. The frequency calibration of the instrument was checked against the spectrum of polystyrene film. The wave number accuracy of intense sharp bands in the spectra of the DCBs is about $\pm 1 \text{ cm}^{-1}$ and ± 2 to $\pm 5 \text{ cm}^{-1}$ for broad/or weak signals.

The compounds under investigation are solids with low solubility in the usual I.R. solvents. Hence they were suspended in pressed KBr discs made from optically pure crystalline KBr, previously ground up and dried for 48 hr at 125°C and then at 500°C for 30 min. Discs of each DCB were prepared by mixing 0.005 mg of the isomer with 0.15 mg of KBr. This mixture was

ground for 5 min in a "Wig- ℓ -Bug" grinder.

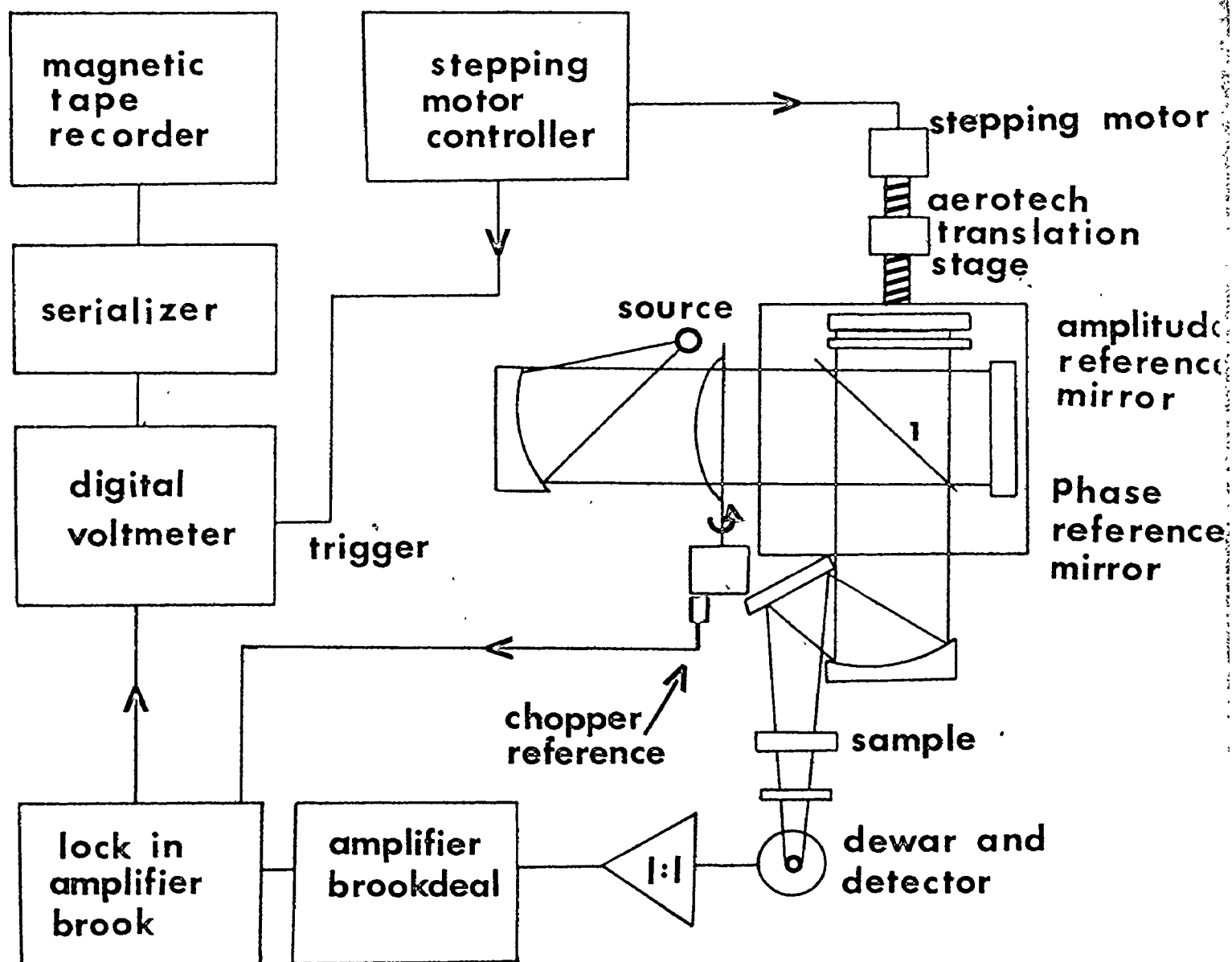
The mixture was transferred to a die (diameter 7 mm) and pressed at 7 t/cm² for 10 min. The thickness was not identical for each of the discs, because of variations in pressing, but was approximately 1 mm.

B - The Far Infrared Spectra

In order to examine the 300-40 cm⁻¹ region, an RIIC Fourier spectrophotometer FS-720 was used.

In use the instrument was evacuated to 1 torr. This eliminated the intense rotational absorption transitions due to atmospheric water vapor. The instrument was equipped with a 125 watts high pressure Hg vapour lamp as source and a low temperature bolometer detector. Figure (2.3.1).

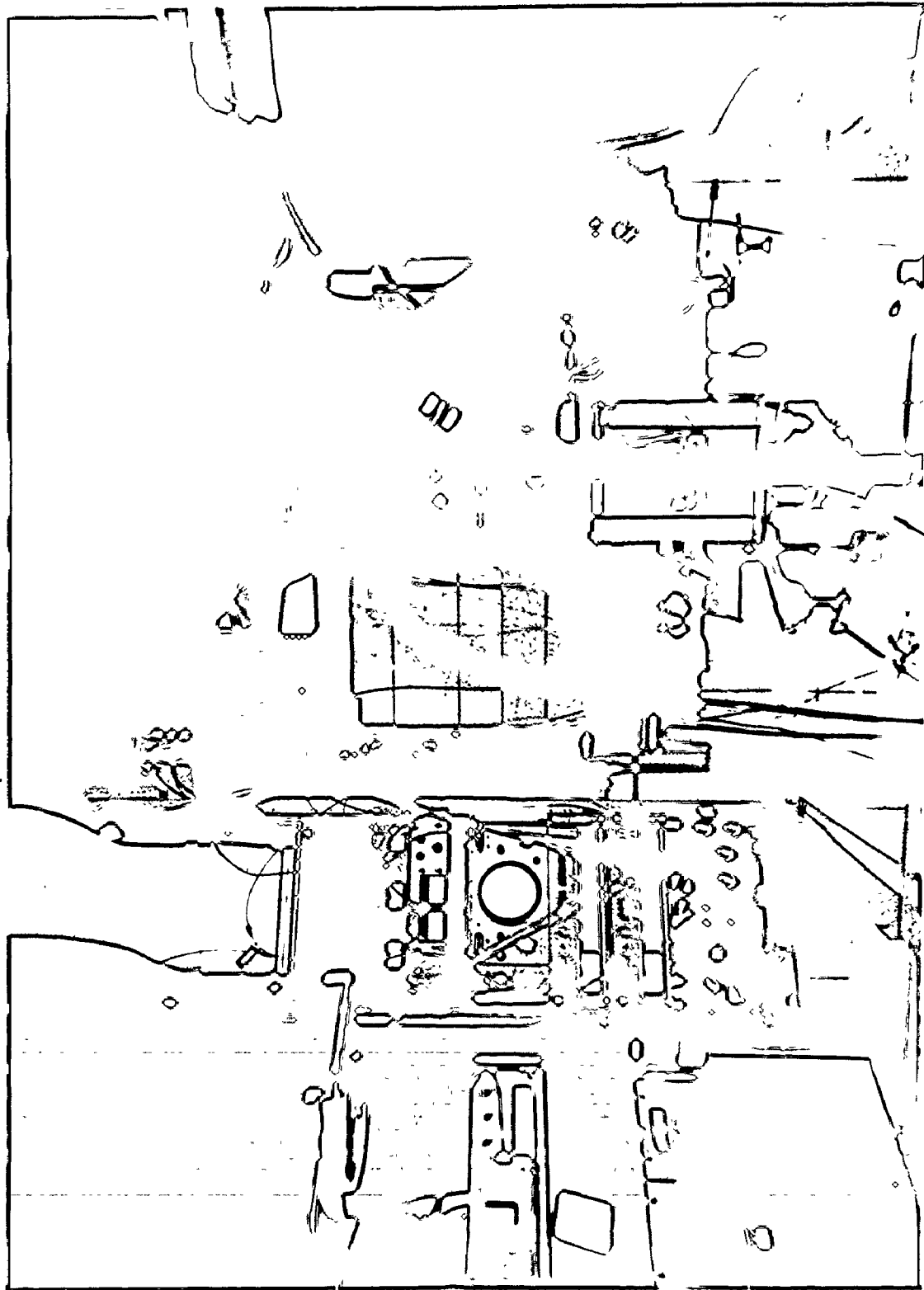
Basically the instrument functions as follows. It contains an interferometer of the Michaelson type, in which light from a mercury lamp is split into two beams by a beam splitter. One beam is reflected by a fixed mirror and the other beam by a movable mirror driven by a stepper motor. These two beams are recombined by the beam splitter, passed through the sample and are detected by a bolometer. The signal is amplified and synchronously detected at the chopper reference frequency. The resultant DC analogue voltage is then digitized by a digital voltmeter, indexed to the mirror displacement by a serializer and stored on magnetic tape. Finally, the frequency spectrum is calculated from the digitized interferogram by standard Fourier transform techniques (13,14).



1. beam splitter

Fig. 2.3.1 Modified FS-720 Fourier Spectrometer

Fig. 2.3.2 Fourier Spectrophotometer FS-720



The spectra of the solid samples were recorded in the far infrared, using a disc technique. Each disc of DCB was prepared by mixing 0.012 mg of isomer with 0.300 mg of polyethylene as support. Each mixture was pressed at 7 t/cm^2 for 5 min. The thickness of each disc was approximately 1 mm. A blank, also of powdered polyethylene, was pressed to similar dimensions and used to balance the reference channel.

C - The Raman Spectra

The Raman spectra of the solid dicyanobenzenes were recorded with a laser Raman spectrophotometer.

Two light sources were available, a Spectra Physics Model 125-He/Ne gas laser and a Spectra Physics Model 164 Argon ion laser. The former provided exciting radiation in the red at 6328 \AA and the latter in the green at 5145 \AA and blue at 4880 \AA , with variable out-put from 20 to 800 milliwatts. The Raman bands were recorded on a Spex grating monochromator unit with photo-electronic recording. The instrument was calibrated for wavelength using a Fe/Ne hollow cathode tube. The estimated uncertainty in the measured frequencies is ± 2 to $\pm 5 \text{ cm}^{-1}$.

Samples were sealed in pyrex capillary tubes (about 1.5 mm o.d. and 4 cm long).

Depolarization Ratios

Discussion:- The Raman scattered light emanating from a sample is polarized to a certain extent. For a given line, the degree of polarization is dependent upon symmetry of the molecular

vibration which gives rise to the band. Hence measurements of the degree of polarization (or its converse, the depolarization ratio), provide information about vibrational symmetries.

Proper measurement of depolarization ratios can only be made on gases and liquids. In the case of ortho-DCB-h₄, hot benzene was used as a solvent, while for the deuterated DCBs, methanol was used. The measurements were taken at high concentrations. However, it was not possible to obtain depolarization ratios for the hydrogenic para- and meta-DCBs, because the molecular fluorescence was found to be relatively very high and partially obscured the Raman spectra.

The measurements taken were the intensities of Raman line with a polarising analyzer, both parallel and perpendicular to the direction of polarization of the exciting laser radiation. These are denoted as $I_{||}$ and I_{\perp} respectively. The ratio of I_{\perp} to $I_{||}$ is called the depolarization ratio of the Raman line. A depolarization ratio, ρ , of 0.75 or less indicates a polarized band, that is, one which arises from a totally symmetric vibration. A depolarization ratio of 0.75 indicates a depolarized line, that is one which does not arise from a totally symmetric vibration (15).

CHAPTER III

THE VIBRATIONAL SPECTRA OF THE DICYANOBENZENES

The complete analysis of the fundamental vibrations of the ortho, meta and para DCB's derives mainly from three types of experimental evidence. The first of these is the infrared spectra of the molecules; the second is the Raman spectra, including depolarization ratios for the bands where measurable; the third type of data consists of the changes in both infrared and Raman band frequencies upon isotope substitution, i.e. when the ring hydrogen atoms are substituted by deuterium atoms.

For simplicity, the experimental results are presented in the following manner. In this chapter, the symmetry of the DCBs is described. The infrared spectra of the three hydrogenic compounds are examined, and the observed frequencies compared with those which have been previously assigned for related molecules by other workers. The emphasis in this chapter is on the description and comparison of the normal modes of DCB's with other molecules. In Chapter IV, the Raman spectra are discussed, and it is shown how they provide additional confirmation of the assignments given for the infrared spectra. Also, the infrared and Raman spectra of the deuterated species are given, and the frequency shifts which have been observed for these are further employed to justify the given assignments.

3.1 Symmetry Classifications of Dicyanobenzenes

The analysis of symmetry properties is based on the idea of symmetry operations. These are coordinate transformations of the parts of a body which produce a figure that is indistinguishable from the original (1).

Symmetry classifications are of great importance in the theory of molecular structure and spectra. With them it is possible to determine the number of fundamental vibrational frequencies, their degeneracies, the selection rules for the infrared and Raman spectra, the polarization properties of the Raman lines and other useful information (4).

These properties will now be derived for each of the DCB's. The deuterated compounds examined in this work have the same symmetries as the corresponding undeuterated compounds. p-DCB-d₄, belongs to the $D_{2h} (V_h)$ point group. This molecule has seven symmetry elements in addition to the identity element, namely, three two-fold rotation axis, the inversion operation i and three reflection planes. These symmetry elements are shown in figure (3.1.1). The definition of the coordinates (x, y, z) and the numbering of the carbon atoms for p-DCB are shown in the same figure.

The symmetry operations which can be performed upon the p-DCBs are:

$C_2(z)$, rotation about the z-axis through π .

$C_2(y)$, rotation about the y-axis through π .

$C_2(x)$, rotation about the x-axis through π .

i inversion

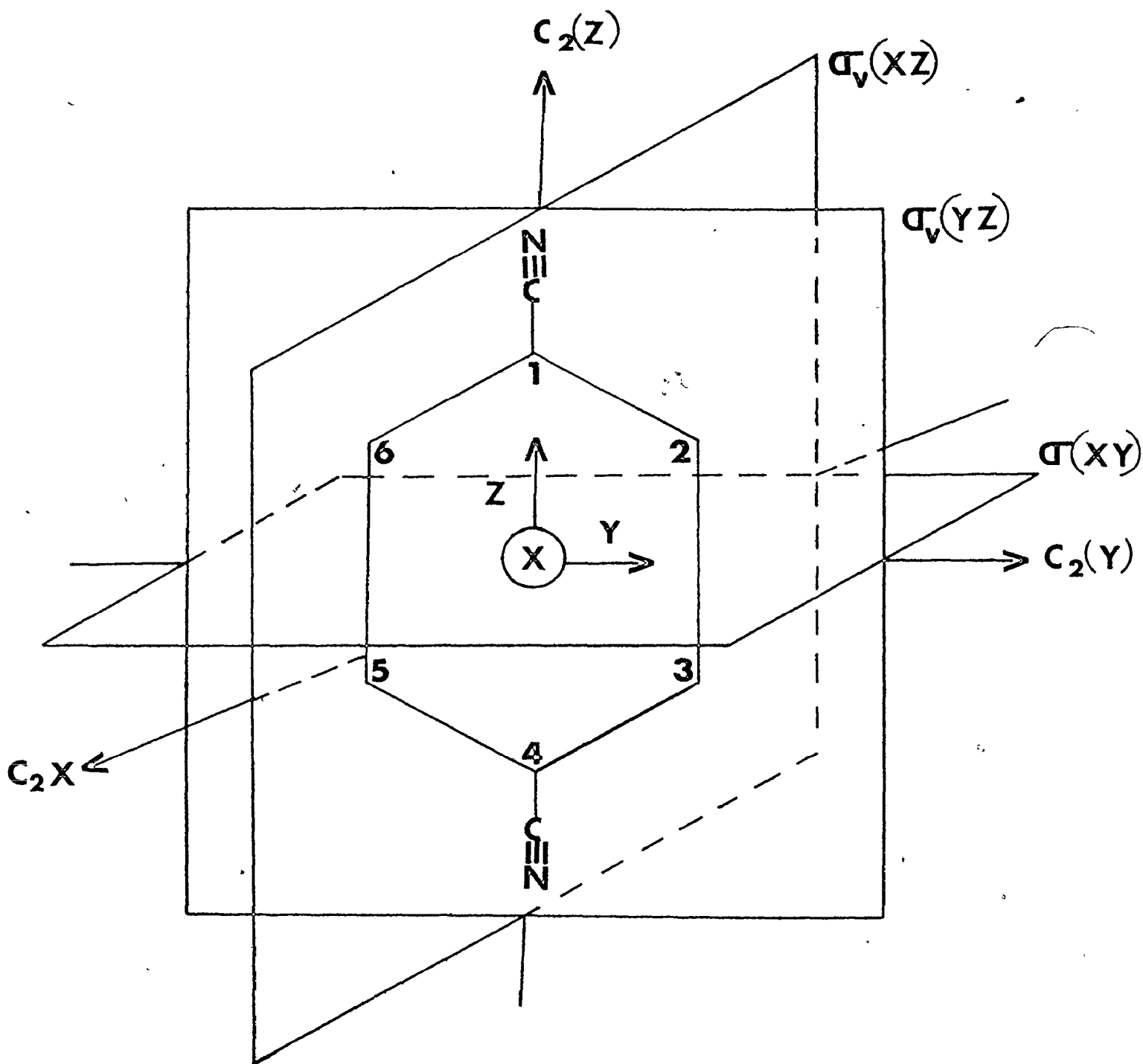


Fig. 3.1.1 Symmetry elements, coordinates and numbering of the atoms for para-DCB

- $\sigma(xy)$ reflection in a plane horizontal to the molecular plane.
 $\sigma(xz)$ reflection in a plane perpendicular to the molecular plane.
 $\sigma(yz)$ reflection in the molecular plane.

These seven symmetry operations together with the identity E comprise the D_{2h} (V_h) point group. The character table of this group is given in table (3.1.1)

Table (3.1.1) . Character Table of the D_{2h} Point Group

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

The meta compound and its deuterated isotope belong to the point group C_{2v} . Deuteration upon the carbons 1, 3 and 5 does not alter the symmetry of this molecule.

The meta-DCB molecule has three symmetry elements in addition to the identity element; these are, a two fold rotation axes and two reflection planes. The corresponding symmetry operations

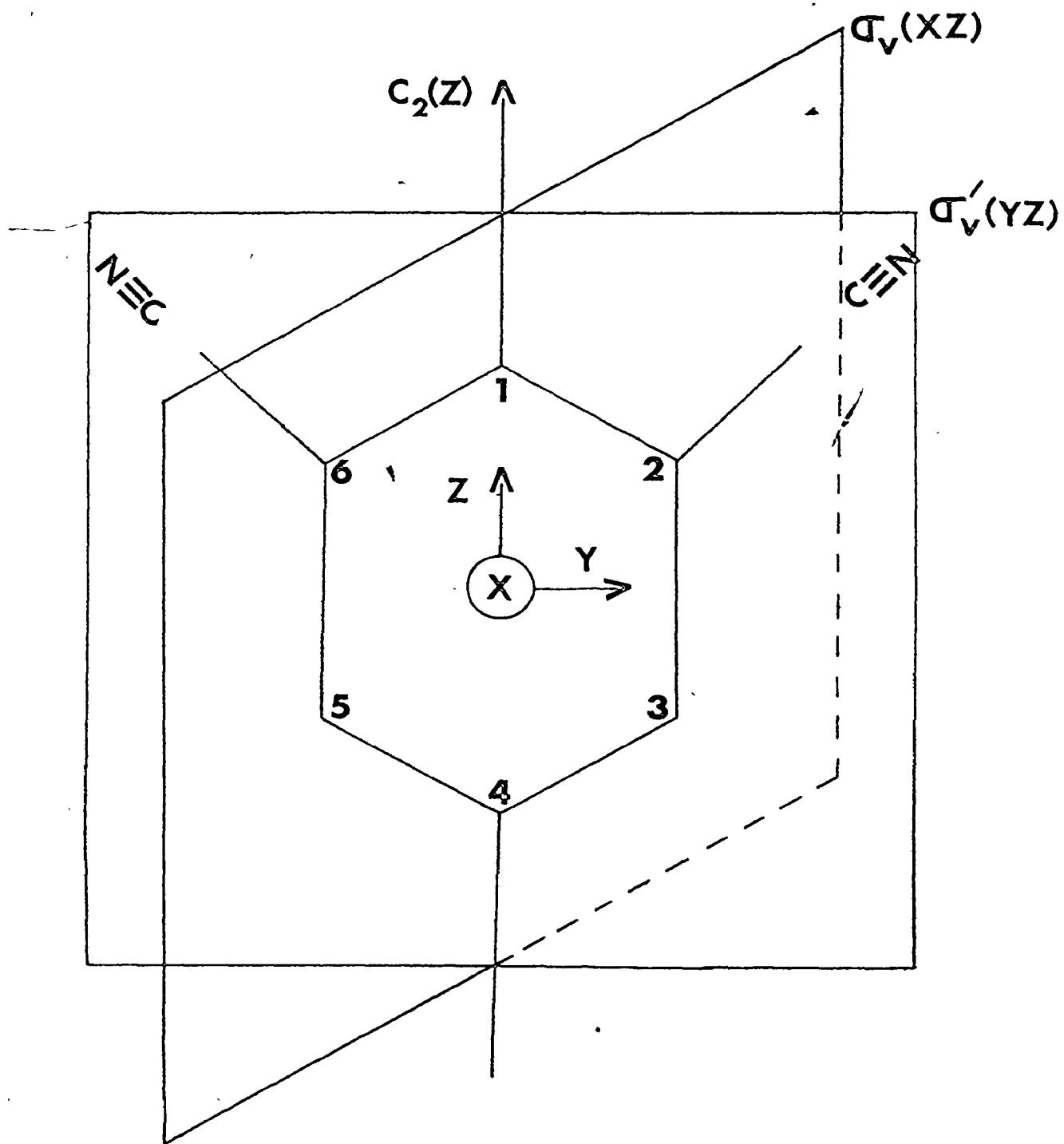


Fig. 3.1.2 Symmetry elements, coordinates and numbering of the atoms for meta-DCB

are:

$C_2(z)$, rotation about the z-axis through π ,

$\sigma_v(xz)$, reflection in a plane perpendicular to the molecular plane,

$\sigma_v(yz)$, reflection in the molecular plane.

These symmetry elements are shown in figure (3.1.2). The definition of the coordinates (x, y, z) and numbering of the carbon atoms for this molecule are also given in the figure. The character table of the C_{2v} group is given in Table (3.1.2)

Table (3.1.2). Character Table of the C_{2v} Point Group

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Ortho-DCB also belongs to the C_{2v} point group, and has the same symmetry elements that are given in Table (3.1.2). However in this molecule, the $C_2(z)$ axis does not pass through ring atoms, but instead bisects opposite ring bonds, see Fig. (3.1.3). For this reason, the point group for this molecule will be distinguished by an asterisk, and written as C_{2v}^* .

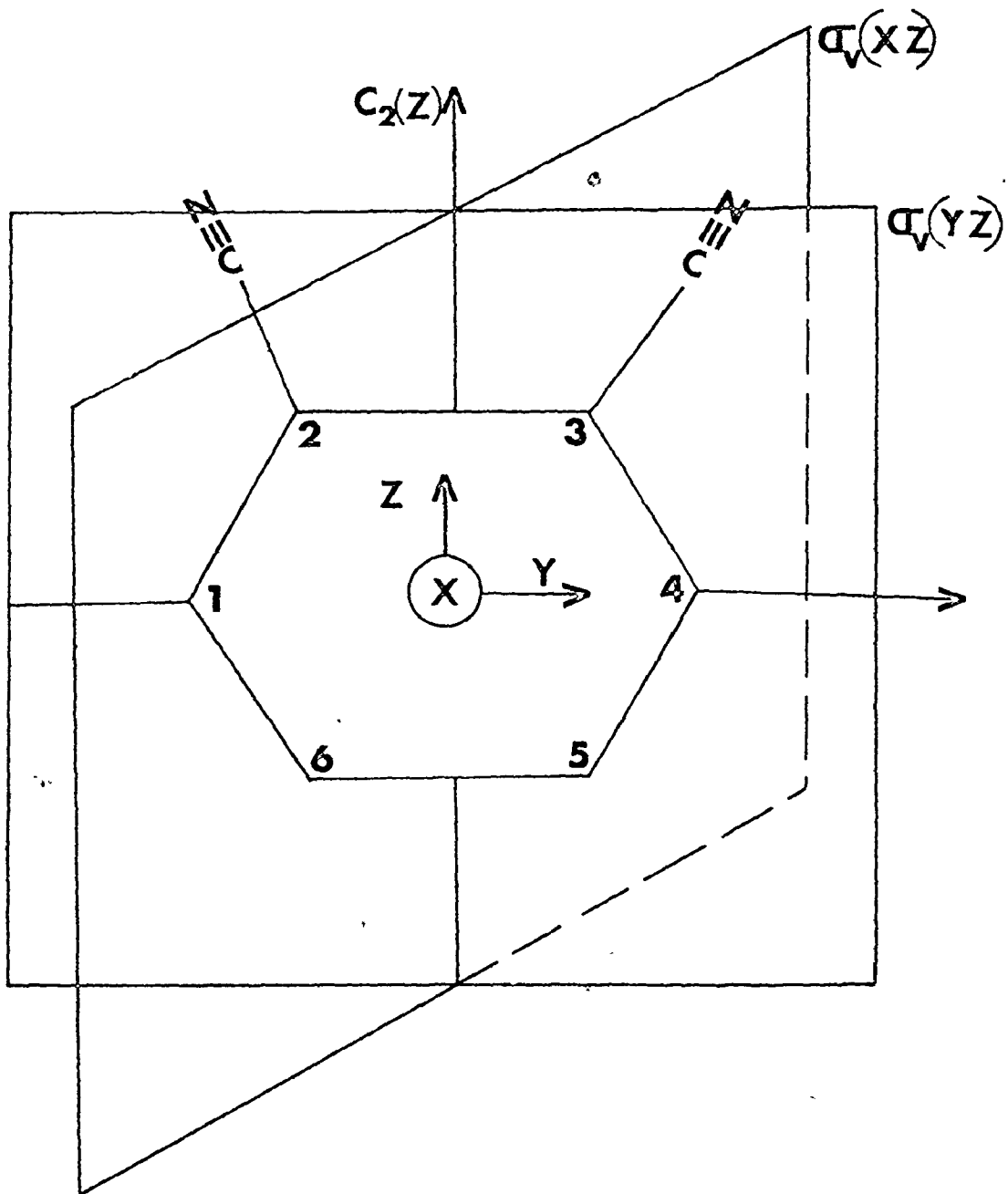


Fig. 3.1.3 Symmetry elements, coordinates and numbering of the atoms for ortho-DCB

3.2 The Normal Modes of the Dicyanobenzenes

Descriptions of the fundamental modes of vibration for the three dicyanobenzenes (DCBs) are presented in this section.

Each dicyanobenzene has a total of thirty-six normal modes of vibration. These correspond to the 30 normal vibrations of benzene plus six derived from the motions of the nitrile groups.

Under the D_{2h} point group, para-DCB has the following normal vibrations:

$$7a_g + b_{1g} + 4b_{2g} + 6b_{3g} + 2a_u + 6b_{1u} + 6b_{2u} + 4b_{3u}.$$

According to the selection rules, the a_g , b_{1g} , b_{2g} , b_{3g} modes are Raman active only, the a_u bands are infrared and Raman inactive, and the b_{1u} , b_{2u} and b_{3u} give only infrared bands; the meta-DCB under the C_{2v} point group has

$$12a_1 + 4a_2 + 7b_1 + 12b_2.$$

For ortho-DCB, under the C_{2v}^* point group, the vibrations can be divided into

$$13a_1 + 6a_2 + 5b_1 + 12b_2.$$

The a_1 , b_1 and b_2 modes are both infrared and Raman active, and the a_2 bands are Raman active only. However the selection rules which predict this are rigorous only for isolated molecules in the gas phase, and can be abrogated in the liquid and solid phases. This was found to be true for some modes of the DCBs.

Varsányi further classifies the normal vibrations as (1) tangential, (2) radial and (3) out-of-plane. The numbering of the thirty ring (ϕ) modes and the appropriate displacement vectors, see figs. (3.2.1, 3.2.2, 3.2.3), follow Varsányi's and Wilson's notation (16). We emphasize at this point that there are two notations used for describing the normal vibrations of substituted benzenes. In Wilson's notation, the ring vibrations are numbered to correspond to the normal vibrations of benzene itself and letters are used to denote the vibrations primarily located in the substituents. The other notation is the conventional spectroscopic one by which the vibrations are labelled ν_i , with $i = 1, 2, \dots$ according to decreasing frequency in each symmetry class.

In each DCB there are eleven out-of-plane vibrations, twelve radial vibrations and thirteen tangential ones. The abbreviations used for these are explained in table (3.2.1). The symmetries of the fundamental modes of benzene and of the DCBs are given in table (3.2.2), according to the symmetry point group under which they are classified. This information is reorganized in table (3.2.3) according to the spectroscopic convention of listing and numbering the vibrations in order of decreasing symmetry and frequency. The abbreviations T, R and O, have the following meaning; the letter T represents the tangential vibrations, which are characterized by displacements perpendicular to the lines connecting opposite nuclei; R, radial modes that involve only displacements along the lines connecting opposite nuclei of the benzene ring, and the letter O represents

Table (3.2.1) Description of the vibrations of benzene ring and the nitrile substituents

Abbreviation	Description
ν C-C	C-C stretching
α C-C-C	Ring in plane vibration
ϕ C-C	Ring out-of-plane def.
ν C-H	C-H stretching
β C-H	C-H in plane deformation
γ C-H	C-H out-of-plane deformation
ν C-CN	C-X stretching vibration
β C-CN	C-X in plane vibration
γ C-CN	C-X out-of-plane vibration
ν C \equiv N	C \equiv N stretching
β C \equiv N	C \equiv N in plane
γ C \equiv N	C \equiv N out-of-plane

Table (3.2.2) Description of the benzene and nitrile modes. Symmetries of benzene and the DCBs. An asterisk against a vibration indicates a substituent-sensitive vibration

Design	D_{6h}	D_{2h}	C_{2v}	C_{2v}^*	Description
1	a_{1g}	a_g	a_1	a_1	γ (C-C)
2	a_{1g}	a_g	a_1	a_1	γ (C-H)
3	a_{2g}	b_{3g}	b_2	b_2	β (C-H)
4	b_{2g}	b_{2g}	b_1	a_2	ϕ (C-C)
5	b_{2g}	b_{2g}^*	b_1	a_2^*	γ (C-H)
6a		a_g	a_1	a_1	
	e_{2g}				α (C-C-C)
6b		b_{3g}	b_2	b_2	
7a		a_g	a_1^*	a_1^*	
	e_{2g}				ν (C-H)
7b		b_{3g}	b_2	b_2	
8a		a_g	a_1	a_1	
	e_{2g}				ν (C-C)
8b		b_{3g}	b_2	b_2	
9a		a_g	a_1^*	a_1^*	
	e_{2g}				β (C-H)
9b		b_{3g}	b_2	b_2	
10a		b_{1g}	a_2	b_1	
	e_{1g}				γ (C-H)
10b		b_{2g}	b_1	a_2	
11		b_{3u}	b_1	b_1	γ (C-H)
	a_{2u}				

(continued next page)

Design	D_{6h}	D_{2h}	C_{2v}	C_{2v}^*	Description
12		b_{1u}	a_1	b_2	α (C-C-C)
	b_{1u}				
13		b_{1u}^*	a_1^*	b_2^*	ν (C-H)
	b_{1u}				
14		b_{2u}	b_2	a_1	ν (C-C)
	b_{2u}				
15		b_{2u}^*	b_2^*	a_1	β (C-H)
	b_{2u}				
16a		a_u	a_2	a_2	
	e_{2u}				ϕ (C-C)
16b		b_{3u}	b_1	b_1	
17a		a_u	a_2^*	a_2	
	e_{2u}				γ (C-H)
17b		b_{3u}	b_1^*	b_1^*	
18a		b_{1u}	a_1	b_2^*	
	e_{1u}				β (C-H)
18b		b_{2u}	b_2	a_1	
19a		b_{1u}	a_1	b_2	
	e_{1u}				ν (C-C)
19b		b_{2u}	b_2	a_1	
20a		b_{1u}	a_1	b_2	
	e_{1u}				ν (C-H)
20b		b_{2u}	b_2	a_1	

(continued next page)

Design	D_{6h}	D_{2h}	C_{2v}	C_{2v}^*	Description
A		a_g	a_1	a_1	$\nu(C\equiv N)$
B		b_{1u}	b_2	b_2	
C		b_{3g}	b_2	b_2	$\beta(C\equiv N)$
D		b_{2u}	a_1	a_1	
E		b_{2g}	a_2	a_2	$\gamma(C\equiv N)$
F		b_{3u}	b_1	b_1	

Table (3.2.3) The classification of the normal modes of vibration

ν	para-DCB (D_{2h})	meta-DCB (C_{2v})	ortho-DCB (C_{2v}^*)
1	2 ν (C-H) R	20a ν (C-H)R	2 ν (C-H)R
2	A ν (C \equiv N)R	2 ν (C-H)R	20b ν (C-H)R
3	8a ν (C-C)T	7a ν (C-H)R	A ν (C \equiv N)R
4	7a ν (C-CN)R a_g	A ν (C \equiv N)R	8a ν (C-C)T
5	9a ν (C-H)T	8a ν (C-C)T	19b ν (C-C)T a_1
6	1 ν (C-CN)R	19a ν (C-C)T	14 ν (C-C)T
7	6a α (C-C-C)R	13 ν (C-CN)R	7a ν (C-CN)R
8	10a γ (C-H)O b_{1g}	18a β (C-H)T a_1	9a β (C-H)T
9	10b γ (C-H)O	12 ν (C-CN)R	18b β (C-H)T
10	4 ϕ (C-C)O b_{2g}	1 ν (C-CN)R	1 ν (C-CN)R
11	E γ (C \equiv N)O	C β (C \equiv N)T	6a α (C-C-C)R
12	5 γ (C-CN)	6a α (C-C-C)R	C β (C \equiv N)T
13	7b ν (C-H)R	9a β (C-CN)T	15 β (C \equiv CN)T
14	8b ν (C-C)T	10a γ (C-H)O	17a γ (C-H)O
15	3 β (C-H)T b_{3g}	16a ϕ (C-C)O a_2	10b γ (C-H)O
16	6b α (C-C-C)R	E γ (C \equiv N)O	4 ϕ (C-C)O
17	9b β (C-CN)T	17a γ (C-CN)O	16a ϕ (C-C)O a_2
18	C β (C \equiv N)T	5 γ (C-H)O	E γ (C \equiv N)O
19	17a γ (C-H)O	10b γ (C-H)O	5 γ (C-CN)O
20	16a ϕ (C-C)O a_u	11 γ (C-H)O	10a γ (C-H)O
21	20a ν (C-H)R	4 ϕ (C-C)O b_1	11 γ (C-H)O
22	B ν (C \equiv N)R	16b ϕ (C-C)O	16b ϕ (C-C)O b_1
23	19a ν (C-C)T b_{1u}	F γ (C \equiv N)O	F γ (C \equiv N)O
24	13 ν (C-CN)R	17b γ (C-CN)O	17b γ (C-CN)O
25	18a β (C-H)T	20b ν (C-H)R	20a ν (C-H)R
26	12 ν (C-CN)R	B ν (C \equiv N)R	7b ν (C-H)R
27	20b ν (C-H)R	8b ν (C-C)T b_2	B ν (C \equiv N)R b_2
28	19b ν (C-C)T b_{2u}	19b ν (C-C)T	8b ν (C-C)T
29	14 ν (C-C)T	3 β (C-H)T	19a ν (C-C)T
30	15 β (C-H)T	14 ν (C-C)T	3 β (C-H)T
31	D β (C \equiv N)T	9b β (C-H)T	13 ν (C-CN)R
32	18b β (C-CN)T	18b β (C-H)T	9b β (C-H)T
33	11 γ (C-H)O	7b ν (C-CN)R	12 ν (C-CN)R
34	16b ϕ (C-C)O	D β (C \equiv N)T	D β (C \equiv N)T
35	F γ (C \equiv N)O	6b α (C-C-C)R	6b α (C-C-C)R
36	17b γ (C-CN)O	15 β (C-CN)T	18a β (C-CN)T

the out-of-plane vibrations.

Tangential Normal Modes

A detailed discussion of the thirteen tangential normal vibrations is given in this section.

The tangential vibrations are first grouped according to their symmetry species, see table (3.2.3). Displacement vectors are given in fig. (3.2.1).

The tangential vibrations are numbers 3, 14, 15 and the degenerate pairs 8, 9, 18, 19 plus the C and D vibrations of the nitrile group. The majority of these vibrations have been readily assigned by analogy with other monosubstituted and disubstituted organic compounds, for which complete vibrational analysis have already been done.

The Carbon-carbon Stretching Vibrations

The $\nu(\text{C-C})$ stretching vibrations will be discussed first. They are the vibrations 14 and the degenerate pairs 8 and 19.

Most aromatic compounds display four or five infrared bands that are considered to be relatively pure C-C stretching modes. These modes fall in the range from 1386 cm^{-1} to 1628 cm^{-1} for disubstituted benzene compounds.

Para-disubstituted Compounds

Wilson and Bloor (17) have observed that in para-substituted benzonitriles, the less symmetric vibrations are usually quite weak, appearing as shoulders. The band with A_g symmetry is generally found near 1600 cm^{-1} while the other with b_{3g} symmetry is about 25 cm^{-1} lower in frequency.

Table (3.2.4) Tangential vibrations and their symmetries

para-DCB		meta-DCB		ortho-DCB	
8a ν (C-C)] a_{1g}	8a ν (C-C)] a_1	8a ν (C-C)] a_1
9a β (C-H)		19a ν (C-C)		19b ν (C-H)	
9b β (C-CN)] b_{3g}	18a β (C-H)] b_2	14 ν (C-C)] b_2
8b ν (C-C)		C β (C \equiv N)		9a β (C-H)	
C β (C \equiv N)		9a β (C-CN)		18b β (C-H)	
3 β (C-H)] b_{1u}	19b ν (C-C)] b_2	C β (C \equiv N)] a_1
19a ν (C-C)		18b β (C-H)		15 β (C-CN)	
18a β (C-H)] b_{2u}	D β (C \equiv N)] b_2	8b ν (C-C)] b_2
D β (C \equiv N)		9b β (C-H)		19a ν (C-C)	
19b ν (C-C)		8b ν (C-C)		9b β (C-H)	
18 β (C-CN)		3 β (C-H)		18a β (C-CN)	
14 ν (C-C)		14 ν (C-C)		D β (C-CN)	
15 β (C-H)		15 β (C-CN)		3 β (C-H)	

This was found to be true also for para-DCB-h₄. The $\nu(\text{C-C})$ modes 8a and 8b appear as a weak broad shoulder and as a weak band respectively in the infrared spectrum, with frequencies at 1623 and 1602 cm^{-1} respectively. The weakness of the bands is ascribed to the fact that these fundamentals are infrared inactive according to the selection rules.

Two other $\nu(\text{C-C})$ stretching modes 19a and 19b, fall in the range from 1400 to 1510 cm^{-1} in para compounds (17,18,19). In para-DCB, bands at 1502 cm^{-1} and 1403 cm^{-1} are assigned with certainty to the b_{1u} and b_{2u} fundamentals respectively. These modes both derive from a degenerate benzene fundamental at 1485 cm^{-1} (20).

Stojiljkovic and Whiffen (19) state that the vibration of symmetry b_{1u} should be raised in frequency from the benzene value of 1485 cm^{-1} by interaction with the lowest frequency C-X stretching mode.

The vibration 14 is called the cyclohexatriene or Kekulé vibration. It is inactive both in the infrared and in the Raman spectra of benzene*.

Several research workers have sought to identify vibration 14 for benzene derivatives. Saeki (21) chose a frequency of 1393 cm^{-1} in the spectrum of para-dichlorobenzene, which is a relatively high value. In contrast to this, Ferguson et al (22) give.

*There is a historically interesting fact in connection with this mode; its frequency was the last to be determined (1949). This vibration was the subject of much polemics up till the early sixties.

two different values at 1049 cm^{-1} and 1110 cm^{-1} . Gates, Radcliffe and Steele (18) gave 1285 cm^{-1} for para-difluorobenzene. Since the band assigned to vibration 14 is also rather weak in para-disubstituted molecules, its identification is not easy. The frequency value assigned to vibration 14 of 1294 cm^{-1} in the infrared spectrum of para-DCB is in agreement with the value given by Gates et al (18). This fundamental is also found to have a low intensity. The frequency is also in agreement with the assignment given by Stojiljkovic and Whiffen (19). They give 1285 cm^{-1} for para-difluorobenzene and a frequency of about 1300 cm^{-1} for para-fluorotoluene.

The Meta-disubstituted Compounds

According to Green (23) the 8a and 8b modes, for meta-xylene are located at 1595 cm^{-1} and 1613 cm^{-1} respectively. The same author gives an assignment at approximately 1580 cm^{-1} for both modes in meta-dichlorobenzene.

The medium intensity bands at 1580 and at 1600 cm^{-1} are respectively assigned to the totally symmetric 8a mode and the non totally symmetric 8b in meta-DCB.

For both components of the degenerate mode 19, two strong bands are identified at 1421 cm^{-1} and 1475 cm^{-1} in meta-DCB. A similar situation has been found in the infrared spectra of meta-xylene, meta-dichlorobenzene and meta-dibromobenzene (23).

In meta disubstituted benzene derivatives, the assignment of vibration 14 is not easy. This problem has been discussed

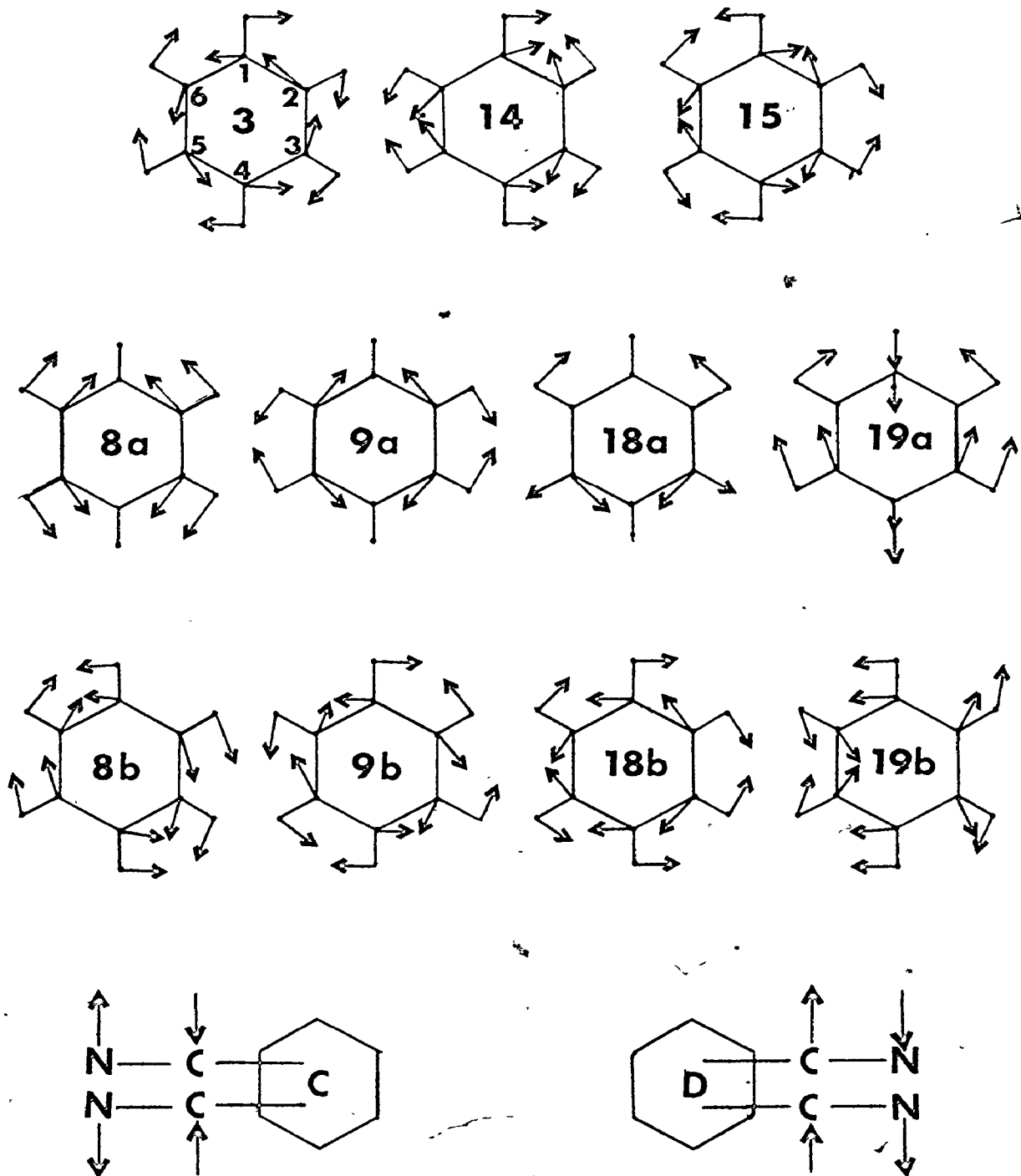


Fig. 3.2.1 Schematic representation of the tangential modes of vibration

above for para-DCB. Scherer and Evans (24) place this fundamental at 1330 cm^{-1} in the i.r. spectrum of meta-dichlorobenzenes.

Varsányi (16) assigned to it a frequency range from 1250 cm^{-1} to 1350 cm^{-1} . By similar arguments, the vibration 14 is assigned to a weak band at 1329 cm^{-1} in the i.r. spectrum of meta-DCB.

The Ortho-disubstituted Compounds

In ortho-DCB, the frequencies of the vibrations 8a and 8b are 1570 and 1589 cm^{-1} respectively. These results agree with those for ortho-bromotoluene in which the (ν_4) 8a vibration falls at 1570 cm^{-1} and the (ν_{28}) 8b mode falls at 1589 cm^{-1} .

Green (25) gives the frequencies of vibrations 8a and 8b in ortho-disubstituted compounds as lying at around 1570 cm^{-1} for both modes.

The $\nu(\text{C-C})$ 19a and 19b modes can be identified in the spectra by analogy with the ortho-dihalogenobenzenes. Green (25) assigned the fundamentals 19a and 19b as at 1472 and 1508 cm^{-1} for difluorobenzene; 1469 cm^{-1} and 1508 cm^{-1} respectively for ortho-xylene; 1438 and 1452 cm^{-1} respectively for dichlorobenzenes. In this study are assigned frequencies of 1450 cm^{-1} and 1486 cm^{-1} , these values corresponding to strong and medium intensity bands due to the vibrations 19a and 19b respectively.

In ortho-disubstituted compounds the symmetry of vibration 14 is different from what it is in the para- and meta- compounds, since the change in direction of the main symmetry axis (C_2), makes the vibration a totally symmetric one, see (fig. 3.1.3). This fundamental could be seen easily in the spectrum of ortho-DCB

as a strong band falling at 1230 cm^{-1} . This agrees with the frequency assignments for mode 14 in other ortho-disubstituted compounds (24,25,26,27).

The C-X In Plane Bending Vibrations

Herzberg (3) gives the frequency range for a $\beta(\text{C-CN})$ in-plane bending vibration in aromatic and aliphatic as from $385\text{--}350\text{ cm}^{-1}$. Jakobsen (28) assigns the value of 381 cm^{-1} for $\beta(\text{C-CN})$ in benzonitrile, and Wilson and Bloor (17) observed a band at around 370 cm^{-1} in many para-substituted benzonitriles. Hidalgo (29) also observed this band in various nitriles. The in plane C-X modes in the three dicyanobenzenes are therefore assigned as follows.

Para-DCB. The fundamentals 9b and 18b are identified at 375 cm^{-1} and 360 cm^{-1} , as weak and medium bands respectively.

Meta-DCB. The normal modes 9a and 15 are identified at 380 cm^{-1} and 343 cm^{-1} as medium intensity bands.

Ortho-DCB. The normal modes 15 and 18a are identified as weak bands at 360 cm^{-1} and 380 cm^{-1} respectively.

The C-H In Plane Bending Vibrations

The other type of tangential vibrations are the C-H in plane bending vibrations. In general the in-plane $\beta(\text{C-H})$ bands are often not separately resolved for disubstituted benzenes and this makes their identification difficult (17). The normal frequencies of the four $\beta(\text{C-H})$ modes have been found in the region from 1300 cm^{-1} down to 1000 cm^{-1} .

The Para-disubstituted Compounds

The four C-H in-plane deformation modes for para-DCB are assigned as follows; the totally symmetric β (C-H) mode 9a should appear in the Raman spectrum only. A strong Raman line at 1184 cm^{-1} is assigned to this fundamental for the hydrogenic compound; this corresponds to a strong polarised line at 895 cm^{-1} for the deuterated compound. (The 1184 cm^{-1} line is also the only candidate for the ν (C-CN) mode 7a of para-DCB- h_4 , and so 7a and 9a are assumed to have almost the same frequency in this species.) There is also a strong infrared band at about the same frequency. This could be due to either 7a or 9a or both appearing in violation of the strict infrared selection rules; alternatively it could be a combination band, such as $10a + 16a$ which has b_{1u} symmetry, and can borrow intensity from the strong b_{1u} fundamental 13 at 1278 cm^{-1} . The b_{3g} mode 3 could be identified in the deuterated Raman spectra at 1035 cm^{-1} with weak intensity. The b_{1u} fundamental 18a is assigned to a medium infrared band at 1025 cm^{-1} and the b_{2u} mode 15 to a weak one at 1120 cm^{-1} . These values agree with the assignments proposed by Stojiljkovic and Whiffen (19), Gates et al (18) and Green (30) for para-halogenobenzenes and with Wilson and Bloor (17) for para-substituted benzonitriles. The confirmation of these normal modes are given in Chapter IV.

The Meta-disubstituted Compounds

The vibrations 18a, 18b, 9b and 3 are considered to be the C-H in plane bending vibrations of meta-disubstituted benzenes.

Varsányi (16) gives the following calculated and experimental frequency data for in-plane C-H vibrations of meta-disubstituted compounds. The frequency range of vibration 18a falls at 1061-1091 cm^{-1} ; 18b, 1082-1123 cm^{-1} , 9b, 1145-1175 cm^{-1} and 3, 1262 to 1297 cm^{-1} . The totally symmetric C-H bending deformation in meta-DCB did not give rise to a strong polarized Raman band as was expected; only a weak band is found at 1104 cm^{-1} and also a weak band is found in the i.r. spectrum for this fundamental the same as occurs in diethynylbenzenes (31). The non-totally symmetric vibrations 18b, 9b and 3 have been assigned to medium bands at 1148 cm^{-1} , 1170 cm^{-1} and 1271 cm^{-1} respectively. The assignments of these modes have been facilitated by the frequency shifts that occur upon ring deuteration. This is discussed in detail below.

The Ortho-disubstituted Compounds

The vibrations 9a, 18b, 3 and 9b are the C-H in-plane bending normal modes of the ortho-disubstituted benzenes.

Varsányi (16) also gives the frequency limits for the above vibrations. The vibration 3 has a frequency range of 1272-1294 cm^{-1} , 9b, 1090-1148 cm^{-1} , 9a, 1150-1168 cm^{-1} and 18b at 1011-1056 cm^{-1} .

The totally symmetric fundamentals in ortho-DCB fall at 1177 cm^{-1} and 1038 cm^{-1} as polarized bands in the Raman spectrum. These fundamentals also give rise to two bands at 1178 cm^{-1} and 1030 cm^{-1} in the i.r. spectrum for the vibrations 9a and 18b respectively. The 3 and 9b fundamentals with b_2 symmetry, show

weak and medium bands in both i.r. and Raman spectra at 1295 cm^{-1} and 1092 cm^{-1} . In Chapter IV there is discussed the shifts in frequency upon deuterations for the above vibrations.

The In-plane CN Normal Modes

The assignment of the tangential fundamentals for the three dicyanobenzenes is completed by assigning a medium and a weak signal near 530 cm^{-1} , to the C and D, $\beta(\text{C}\equiv\text{N})$ modes in the infrared spectra. Jacobsen (28) found that the $\beta(\text{C}\equiv\text{N})$ band falls at 551 cm^{-1} in benzonitrile. The in-plane $\text{C}\equiv\text{C}$ stretch of ethynylbenzene which is isoelectronic with benzonitrile, has a frequency of 512 cm^{-1} according to So (32). Also by analogy with ϕCN and ϕCCH , Van Putten (31) assigned the $\beta(\text{C}\equiv\text{C})$ bands in the diethynylbenzenes at around 500 cm^{-1} .

Para-DCB. The Raman active C fundamental falls as a weak band at 525 cm^{-1} . No data on the polarization could be obtained. The infrared active D fundamental falls at 535 cm^{-1} , also with weak intensity.

Meta-DCB. The totally symmetric and non-totally symmetric C and D fundamentals have been assigned to the infrared bands at 524 and 580 cm^{-1} . The former mode appears with very low intensity and the latter is a weak band.

Ortho-DCB. In this molecule the C fundamental is seen as a medium intensity polarized band at 565 cm^{-1} in the Raman spectrum, a weak

is observed in the i.r. spectrum at 565 cm^{-1} and has been assigned to the D fundamental. The shifts in frequency upon ring deuteration are given in Chapter IV.

Radial Normal Modes

The radial normal modes are numbers 1, 2, 12, 13, the degenerate pairs, 6, 7, 20 and the A,B, stretching of the cyano group.

Displacement vectors and symmetry species for the radial modes are given in figure (3.2.2) and table (3.2.5).

The $\nu(\text{C-H})$ Stretching Vibrations

There are four essentially $\nu(\text{C-H})$ stretching modes for each DCB, whose frequencies must lie in the range from 3029 to 3120 cm^{-1} by analogy with other aromatic C-H frequencies (23,25,30). However precise assignments are difficult to make since the bands tend to mask each other. Additional information is obtained from the frequency shifts upon ring deuteration and Raman depolarization ratios for the $\nu(\text{C-H})$ assignments. This is discussed in detail in the following section. Summation bands for in-plane C-C stretching modes also lie around $2600\text{-}3000\text{ cm}^{-1}$, and vibrational perturbations may occur as in benzene (33).

The Para-disubstituted Compounds

In para-DCB, the vibration 2 with symmetry A_g is weak in both the infrared and Raman spectra. Its frequency is 3085 cm^{-1} in the i.r. absorption and 3090 cm^{-1} in the Raman. In the Raman spectra of para-diethynylbenzenes (31) this band also occurs with weak intensity at 3064 cm^{-1} in both infrared and Raman spectra. The normal vibration 7b is also weakly active.

Table (3.2.5) Radial vibrations and their symmetries

para-DCB		meta-DCB		ortho-DCB	
2 ν (C-H)] a_g	20a ν (C-H)] a_1	2 ν (C-H)] a_1
A ν (C \equiv N)		2 ν (C-H)		20b ν (C-H)	
7a ν (C-CN)		7a ν (C-H)		A ν (C \equiv N)	
1 ν (C-CN)		A ν (C \equiv N)		7a ν (C-CN)	
6a α (C-C-C)] b_{3g}	13 ν (C-CN)] b_2	1 ν (C-CN)] b_2
7b ν (C-H)		12 ν (C-CN)		6a α (C-C-C)	
6b α (C-C-C)		1 ν (C-CN)		20a ν (C-H)	
20a ν (C-H)] b_{1u}	6a α (C-C-C)] b_2	7b ν (C-H)] b_2
B ν (C \equiv N)		20b ν (C-H)		B ν (C \equiv N)	
13 ν (C-CN)		B ν (C \equiv N)		13 ν (C-CN)	
12 ν (C-CN)		7b ν (C-CN)		12 ν (C-CN)	
20b ν (C-H)] b_{2u}	6b α (C-C-C)		6b α (C-C-C)	

Its frequency is 3029 cm^{-1} . Lebas et. al. (34) studied this vibration in para-disubstituted benzenes and the same low intensity was found. The normal modes 20a and 20b give intense infrared bands in the spectrum of para-DCB. They fall at 3060 cm^{-1} and 3102 cm^{-1} .

The Meta-disubstituted Compounds

The aromatic C-H stretching bands overlap in the infrared and Raman spectra of meta-DCB. A very strong band occurs at 3090 cm^{-1} in the i.r. spectrum, and at 3089 cm^{-1} in the Raman spectrum. It is believed that this band corresponds to both, the vibrations 20a and 2. The remaining totally symmetric mode 7a has an infrared frequency of 3058 cm^{-1} , and has weak intensity. Another weak band is found at 3119 cm^{-1} and is assigned to the non-totally symmetric fundamental 20b.

Green (23), Scherer and Evans (24), established that for the $\nu(\text{C-H})$ stretching vibrations in both the i.r. and Raman spectra in meta-dihalogenobenzenes vibrations 2 and 20a appear between 3049 and 3095 cm^{-1} ; the normal vibration 7a falls between 3046 and 3048 cm^{-1} and vibration 20b has the same range given for vibrations 2 and 20a.

Ortho-disubstituted Compounds

The aromatic C-H stretches in the ortho-DCB are also only partially resolved in the i.r. and Raman spectra. The totally symmetric vibrations 2 and 20b appear as a very strong polarized band in the Raman spectrum at 3095 cm^{-1} . These normal modes are

resolved in the i.r. spectrum, at 3103 and 3094 cm^{-1} . Van Putten (31) and Scherer and Evans (24) found a band between 3090 and 3078 cm^{-1} , which was assigned to the vibrations 2 and 20b in the diethynylbenzenes and the dichlorobenzenes. The remaining non-totally symmetric 20a and 7b models also are unresolved in the i.r. spectrum, appearing as a medium band at 3040 cm^{-1} .

The C-X Stretching Vibrations

The other type of radial vibrations correspond to C-X stretching vibrations. However it is impossible to isolate $\nu(\text{C-CN})$ vibrations which are localised purely in the substituents, because such motions are, in practice, strongly coupled to the C-C-C bending vibrations of the benzene ring.

When substituents are added to a benzene ring, the normal frequencies of benzene are modified by such coupling between the motions of the ring nuclei and those of the substituent nuclei.

In particular the C-X stretching modes interact considerably with the ring vibrations and some of the C-X modes are shifted to lower frequencies. Van Putten (31) has discussed this coupling in the case of the diethynylbenzenes.

Para-disubstituted Compounds

Varsányi (16) has found that in para-disubstituted compounds both vibrations 1 and 12 have "substituent-sensitive" frequencies. When both substituents are light, as is the case in dicyanobenzenes, the two vibrations couple with certain of

the C-X stretching vibrations. This results in a frequency decrease for both modes. In the case where both substituents are heavy, the change of frequencies is smaller because of the smaller amplitude and hence weaker coupling.

On the basis of the Raman and i.r. spectra, it is possible to decide which frequencies correspond to the vibrations 1 and 12. When the two substituents are identical, the fundamental vibration 1 should only appear in the Raman spectrum while vibrational mode 12 should be found only in the i.r. spectrum (16,31).

In para-DCB the mode 1 has been assigned a frequency of 817 cm^{-1} , and has strong intensity in the Raman spectrum with a small value for the depolarization ratio. The mode 12 falls at 643 cm^{-1} , with strong intensity in the i.r. spectrum.

The other two C-X vibrations are the 7a and 13 modes. The totally symmetric 7a mode is assumed to have almost the same frequency as the in-plane $\beta(\text{C-H})$ 9a vibration, with a value of 1184 cm^{-1} . The vibration 13 of symmetry b_{1u} has a frequency of 1278 cm^{-1} .

Meta-disubstituted Compounds

Varsányi (16) found that in meta-disubstituted compounds the in phase C-X stretching vibration of two light substituents couples with the normal mode 1 of benzene while the out-of-phase mode couples with the benzene normal vibration 6b.

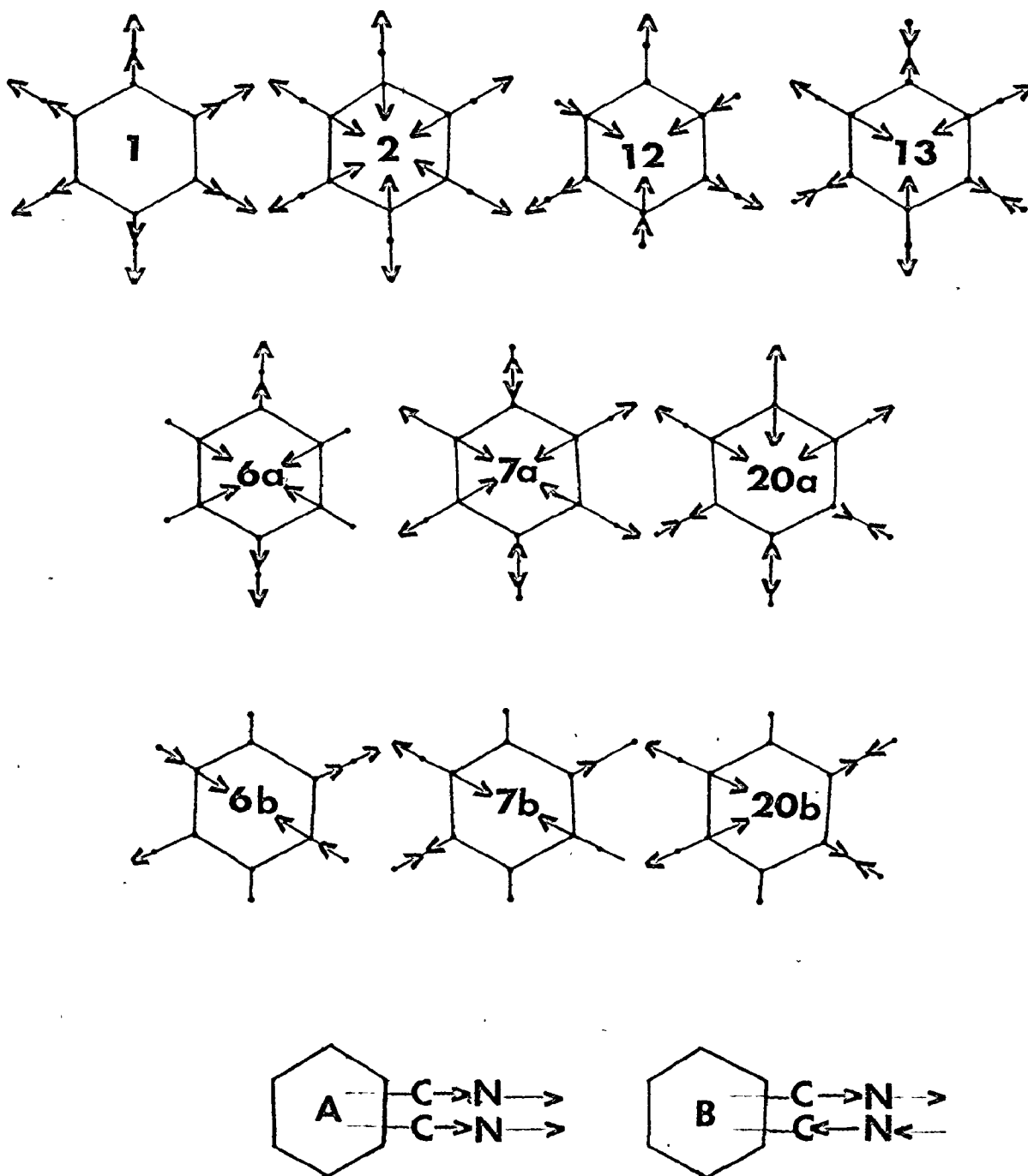


Fig. 3.2.2 Schematic representation of the radial modes of vibration

The in phase $\nu(\text{C-CN})$ mode 1, has been assigned for meta-DCB at 701 cm^{-1} , and the out of phase $7b$ mode at 900 cm^{-1} . These vibrations appear in the i.r. spectra as medium and weak bands respectively. The totally symmetric mode 1 appears as a polarized band in the Raman spectrum of the deuterated molecule.

Varsányi reported also that for benzene derivatives with mono-, meta-di- and symmetric trisubstitution, there is always a strong polarized band very close to 1000 cm^{-1} , whose frequency is left uninfluenced by the type of substituent. The vibration is localized on the unsubstituted carbon nuclei 2, 4 and 6 of trigonal symmetry. (The symmetry species b_{1u} implies trigonal symmetry. see fig. # (3.2.3)).

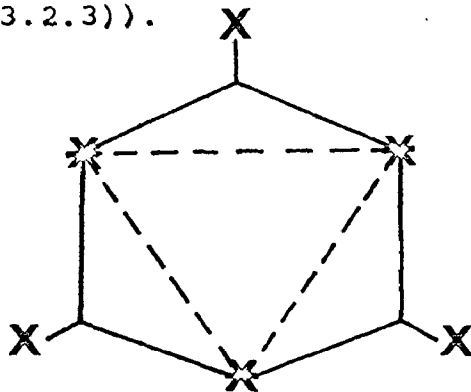


Fig. (3.2.3) Trigonal Symmetry Vibration

This trigonal ring vibration 12 only involves the movements of three carbon nuclei, the remaining ones being at rest. This means that normal vibration 12 in mono, meta-di, and symmetric trisubstituted molecules is close to the benzene value of 1010 cm^{-1} .

The mode 12 for meta-DCB appears as a very strong polarized band at 1005 cm^{-1} in the Raman spectra and as a weak band at 1012 in the i.r. spectrum.*

The vibration 13 with A_1 symmetry is assigned at 1248 cm^{-1} in the Raman spectrum.

The Ortho-disubstituted Compounds

In the case of two light substituents the frequency of both vibrations 1 and 12 is lower than 850 cm^{-1} . Bogomolov (35) determined the frequencies of ortho-xylene via normal coordinate analysis. On this basis, he assigned 750 cm^{-1} to normal mode 1, and 827 cm^{-1} to normal mode 12. On the other hand Green (25) assigned in the same compound the vibrations 1 and 12 as being at 733 cm^{-1} and 826 cm^{-1} .

In the case of ortho-DCB, the vibrations 1 and 12 have been assigned to strong infrared bands at 700 cm^{-1} and 804 cm^{-1} respectively.

Green also has given frequencies for vibrations 7a and 13 as at 1222 cm^{-1} and 1185 cm^{-1} respectively in ortho-xylene. Similar frequency values are found for diethynylbenzenes (31). Therefore the totally symmetric normal mode 7a is assigned to the strong i.r. band at 1205 cm^{-1} . The non-totally symmetric

* In ortho and para-disubstituted ring compounds, vibration 12 involves motion of substituted ring carbon nuclei, and it is therefore described as $\nu(\text{C-X})$: it is "substituent sensitive". Vibration 12 is usually described as $\nu(\text{C-X})$ for meta-compounds also, although it is not substituent sensitive in these.

vibration 13 is assigned to a weak band at 1190 cm^{-1} .

The In-plane Ring α (C-C-C) Vibrations

Jakobsen and Bentley (8) have pointed out that the frequency of the vibrations 6a in disubstituted compounds covers a wide range, 580 to $< 250 \text{ cm}^{-1}$, depending on the substituent. Its precise mechanical description is uncertain, except that it is a strongly coupled vibration, probably a mixture of ring-substituent stretching motion, and in-plane ring deformation and a ring stretching motion. The vibration 6b has a similar frequency range as above from 206 to 546 cm^{-1} according to Green (23,25,30).

Para-disubstituted Compounds

For mono- and para-substituted benzenes, the in-plane ring deformation can be identified as the only strong polarized Raman band in the 650 - 200 cm^{-1} spectral region (18).

In this study, the mode 6a is found at 213 cm^{-1} in the Raman spectrum, see Chapter IV. No signal was recorded in the i.r. spectrum.

Also the vibration 6b was only found at 653 cm^{-1} in the Raman spectrum.

Meta-disubstituted Compounds

Jakobsen and Bentley (8) established that in the infrared spectrum, the mode 6a appears as a medium intensity band in meta- and ortho-compounds, while in the spectra of para-substituted benzenes the intensity is variable. Jakobsen and Bentley also noted that mode 6a decreases in frequency as the mass of the substituents increase. In meta-DCB, this mode appears as

medium Raman band at 460 cm^{-1} .

The fundamental 6b produces a very strong band at 502 cm^{-1} in the i.r. spectrum of meta-DCB. This frequency can be supported by the frequency assignments for vibrations 6b given by Green (23); for meta-xylene it is at 515 cm^{-1} and at 514 cm^{-1} for meta-fluorobenzene.

Ortho-disubstituted Compounds

Green (25) gives the frequency range for vibration 6a from 566 cm^{-1} to 317 cm^{-1} in ortho-disubstituted benzene derivatives. For vibration 6a Jakobsen (8) also proposed the same arguments as for meta to the ortho compound.

In ortho-DCB, this normal mode is assigned to a medium intensity band at 472 cm^{-1} in the i.r. spectrum. The fundamental 6b is found at 530 cm^{-1} , and also has medium intensity in the i.r. spectrum. Green (25) has given the frequencies at 546 cm^{-1} for ortho-difluorobenzene and at 505 cm^{-1} for ortho-xylene. These values are reasonably close to the frequency given for ortho-DCB. The above frequency also falls in the frequency range given by Varsányi, from 220 to 560 cm^{-1} .

The C-N Stretching Vibrations

The remaining radial frequencies are the $\text{C}\equiv\text{N}$ stretching modes A and B.

The $\text{C}\equiv\text{N}$ group stretch is normally identified in either aromatic or aliphatic compounds as a strong, sharp band lying between 2200 cm^{-1} and 2300 cm^{-1} .

The triple band stretching frequencies found in various types of nitriles are listed by Dollish et al (36).

It has been shown that the nitrile band is not greatly affected by vibrational interactions. In the Raman spectrum this mode occurs as an intense band but in the infrared its intensity is quite variable from compound to compound.

The presence of an unsaturated non aromatic group adjacent to the $C\equiv N$ band shifts the nitrile stretching band slightly to lower frequencies and enhances the Raman intensity.

The Raman intensity is found to increase in intensity almost threefold compared to that in the saturated nitriles (36).

Derivatives in which the nitrile group is attached to an aromatic ring have $C\equiv N$ stretching bands, in the range from 2240 to 2221 cm^{-1} .

The normal mode A was found at between 2220 and 2228 cm^{-1} in the three DCBs.

The other $C\equiv N$ stretch band, namely A could not be identified with certainty. The weak infrared bands observed near 2200 cm^{-1} are the only possibilities for this fundamental.

The Out-of-Plane Normal Modes

All of the eleven out-of-plane vibrations have been assigned for each dicyanobenzene, namely 4, 5, 11, the degenerate pairs 10, 16, 17 and E, F for the nitrile group.

The out-of-plane vibrations are grouped according to their symmetry species in table (3.2.6). Displacement vectors are given in fig. (3.2.4).

These vibrations are the out-of-plane skeleton deformations ϕ (C-C), the out-of-plane C-H formations γ (C-H) and, completing the normal modes, the E and F out-of-plane deformations of the nitrile groups.

The Skeleton Deformation Vibrations

The para-disubstituted compounds.

The out-of-plane skeleton deformation ϕ (C-C) 16a in para-disubstituted compounds (30, 18, 17, 19) has a_{1u} symmetry, and does not involve motion of the substituent nuclei (see ref. 19). Its value should be close to that for benzene, namely 404 cm^{-1} . In para-DCB the vibration 16a has been assigned to a weak band observed at 395 cm^{-1} . This band appears weakly in both the i.r. and Raman spectrum, violating the rigorous selection rules.

The b_{3u} vibration 16b also derives from the same degenerate benzene mode. Bentley and Wolfarth (37) assigned vibration 16b to between 480 and 570 cm^{-1} in the i.r. spectra of several para-dialkylbenzenes. They also observed that the frequency generally increases upon increasing the size of the alkyl side-chain. Green (30) also assigned this mode at around 500 cm^{-1} for many

Table (3.2.6). Out-of-plane vibrations and their symmetry

Para-DCB		Meta-DCB		Ortho-DCB
10a γ (C-H)] b_{1g}	10a γ (C-H)] a_2	17a γ (C-H)
10b γ (C-H)		16a ϕ (C-C)		10b γ (C-H)
4 ϕ (C-C)] b_{2g}	E γ (C \equiv N)] a_2	4 ϕ (C-C)
E γ (C \equiv N)		17a γ (C-CN)		16a ϕ (C-C)
5 γ (C-CN)] a_u	5 γ (C-H)] b_1	E γ (C \equiv N)
17a γ (C-H)		10b γ (C-H)		5 γ (C-CN)
16a ϕ (C-C)] b_{3u}	11 γ (C-H)] b_1	10a γ (C-H)
11 γ (C-H)		4 ϕ (C-C)		11 γ (C-H)
16b ϕ (C-C)		16b ϕ (C-C)		16b ϕ (C-C)
F γ (C \equiv N)		F γ (C \equiv N)		F γ (C \equiv N)
17b γ (C-CN)		17b γ (C-CN)		17b γ (C-CN)

other para-disubstituted compounds. In the present study, the fundamental gives rise to a very strong band at 563 cm^{-1} in the i.r. spectrum. Stojiljkovic and Whiffen (19) point out that this mode is strongly infrared active, because some C-X out-of-plane motion is involved, causing a large dipole moment change. Further information about this vibration is given by Jakobsen and Bentley (8) who state that high frequency values for the 16b mode ($540\text{-}560\text{ cm}^{-1}$) always occur when one (or both) of the substituents is a cyano group. When one of the substituents is an electron donor and the other substituent is not a cyano group, the frequency of this vibration falls to between 490 and 520 cm^{-1} (8).

Wilson and Bloor (17) put the normal $\phi(\text{C-C})$ vibration 4 between $668\text{-}704\text{ cm}^{-1}$ for para-substituted benzonitriles. The fundamental 4 in para-DCB, has been assigned to a weak band at 662 cm^{-1} in the Raman spectrum, falling very close to the frequency given by (17).

The meta-disubstituted compounds

The b_1 normal mode 16b in meta-disubstituted compounds falls into a narrow frequency range of $400\text{-}490\text{ cm}^{-1}$.

Shimanouchi et al (38) from their normal coordinate analysis have calculated the vibration 16b for several meta-disubstituted benzenes as being at approximate 424 cm^{-1} . The frequency obtained for meta-DCB of 460 cm^{-1} falls into the above range, and is also very close to the Shimanouchi's value.

The vibration 16a with a_2 symmetry in meta-DCB is observed in the Raman spectrum as a medium intensity band at 625 cm^{-1} .

This value agrees with other meta-disubstituted benzenes (23,24). The mode is not infrared active.

Green (23) has given frequencies for mode 4 in different meta-disubstituted compounds. He assigned this mode for meta-xylene at 690 cm^{-1} , for meta-difluorobenzene at 672 cm^{-1} , in meta-dichlorobenzene at 672 cm^{-1} , in meta-dibromo and diiodobenzene at 669 cm^{-1} and 670 cm^{-1} respectively. Meta-DCB shows similarly a very strong band in the i.r. spectrum at 672 cm^{-1} .

The ortho-disubstituted compounds

In ortho-DCB the vibration 16b is found as a weak intensity band at 410 cm^{-1} in the i.r. spectrum. In ortho-disubstituted compounds the frequency range for vibration 16b is given as $410\text{-}470\text{ cm}^{-1}$ (16).

The vibration 16a is left unassigned because no band was found within the frequency limits given by many authors which are from $480\text{ to }530\text{ cm}^{-1}$ (16,24,25).

The remaining $\phi(\text{C-C})$ vibration in ortho-DCB is the mode 4 with symmetry a_2 . This vibration is infrared-inactive and Raman allowed, see Chapter IV. A weak band is observed for this vibration at 735 cm^{-1} in the Raman spectrum. The range of frequencies observed for this mode is given by Varsányi as $685\text{-}735\text{ cm}^{-1}$ (16).

The C-H Out-of-plane Vibrations

Young et al (39) and Bellamy (40) have used the bands observed in the $1650\text{-}2000\text{ cm}^{-1}$ absorption region to characterise

the C-H deformation modes of disubstituted benzenes. Some of these fundamentals are forbidden in the infrared spectrum. Very often weak absorption does occur as a result of violation of the selection rules (41).

The observed bands in the 1650-2000 cm^{-1} "fingerprint" region appear to be summation bands of the out-of-plane C-H deformation fundamentals. This adds interest to the region, since it is not always easy to obtain a complete set of C-H deformation frequencies directly from fundamental bands.

The para-disubstituted compounds

In para-disubstituted compounds with light substituents (such as CN), the following notation is used; the C-H out-of-plane vibration of symmetry b_{1g} is denoted by 10a, the same type of vibration of symmetry b_{2g} is 10b, the a_u vibration is 17a and the b_{3u} one is mode 11.

Green et al (30) observed that in para-disubstituted benzenes with the possible exception of the "umbrella" motion 11, it is difficult in most instances to assign unambiguously all four out-of-plane bending modes in the range from 750 to 1000 cm^{-1} . Similar difficulties were found for the spectrum of para-DCB. All the C-H out-of-plane bands are weak with the exception of the "umbrella" band. Green (30) and Stojilkovic and Whiffen (19) gave frequency ranges for para-disubstituted compounds of the γ C-H vibrations as; 10a at 800-835 cm^{-1} ; 10b, 928-970 cm^{-1} ; 17a, 927-961 cm^{-1} and 11 at 795-833 cm^{-1} . In

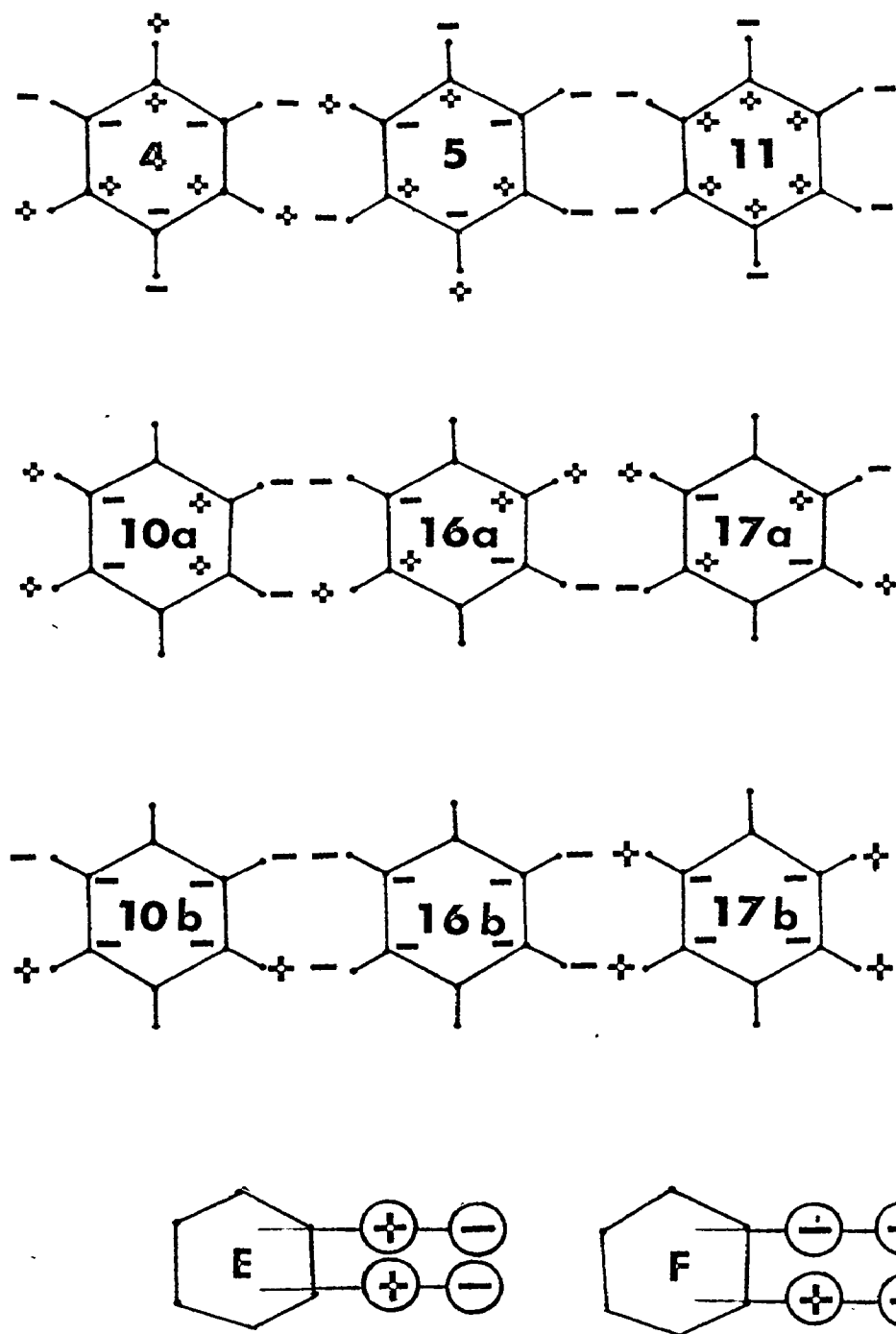


Fig. 3.2.4 Schematic representation of the out-of-plane modes of vibration

para-DCB the frequencies found are: the Raman active mode 10a at 794 cm^{-1} ; 10b, 975 cm^{-1} ; 17a appears weakly in the i.r. spectrum at 880 cm^{-1} and the i.r. active 11 at 840 cm^{-1} . These bands also show other characteristics of C-H bands such as large isotopic shifts described later, and their identification rests partly on these factors. Nonetheless, the assignments in this region are among the most uncertain attempted and should be regarded as tentative.

The meta-disubstituted compounds

In the case of light substituents, the vibrations 10a, 5, 10b and 11 are regarded as C-H out-of-plane vibrations. Nonnenmacher and Mecke (42) gave the following frequency values for the C-H out-of-plane vibrations of meta-disubstituted benzene derivatives; for meta-xylene: 5, 981 cm^{-1} (calc) 968 cm^{-1} (obs); 10b, 906 cm^{-1} (calc), 876 cm^{-1} (obs); 11, 791 cm^{-1} (calc), 768 cm^{-1} (obs); 10a, 923 (calc) 905 cm^{-1} (obs). The frequencies for resorcinol are; 5, 981 cm^{-1} (calc), 962 cm^{-1} (obs); 10b, 907 cm^{-1} (calc), 843 cm^{-1} (obs); 11, 793 cm^{-1} (calc), 773 cm^{-1} (obs), 10a, 923 cm^{-1} (calc), 929 cm^{-1} (obs); and for meta-difluorobenzene 5, 981 cm^{-1} (calc), 968 cm^{-1} (obs); 10b, 906 cm^{-1} (calc), 850 cm^{-1} (obs); 11, 793 cm^{-1} (calc), 770 cm^{-1} (obs); 10a, 924 cm^{-1} (calc), 871 cm^{-1} (obs); other frequency values for C-H vibrations in meta-disubstituted compounds are given by Nonnenmacher and Mecke (42) and Davydova et al (43).

The frequencies observed for the γ (C-H) vibrations for

meta-DCB are: 10b, 865 cm^{-1} , 11, 793 cm^{-1} , 5, 988 cm^{-1} , these modes observed in the i.r. spectrum and 10a at 910 cm^{-1} in the Raman spectrum.

The ortho-disubstituted compounds

The C-H out-of-plane vibrations in ortho-disubstituted compounds with light substituents are numbered, 17a, 10b, 10a and 11. Kohlrausch (44) assigned the following vibrations of some ortho-disubstituted benzene derivatives to the following intervals: 11, 742-759 cm^{-1} ; 10b, 841-864 cm^{-1} . Katritzky (45) gave the frequency range of vibration 10a as 932-949 cm^{-1} . He also assigned the vibration 17a as between 906 cm^{-1} and 916 cm^{-1} in the case where both substituents are electron donors to the ring. The i.r. frequencies assigned to these vibrations in ortho-DCB are; 17a at 970 cm^{-1} ; 10b, 846 cm^{-1} ; these normal modes appear in the i.r. spectrum violating the selection rules, 10a, 922 cm^{-1} and 11 at 770 cm^{-1} . Also the infrared band at 970 cm^{-1} seems too strong to arise from the a_2 γ (C-H) mode 17a. It could be a summation band, e.g. 11+17b ($\nu_{21} + \nu_{24}$).

The C-X Out-of-plane Vibrations

The para-disubstituted compounds

In this study both γ (C-X) fundamentals have been assigned for each dicyanobenzene. In para-disubstituted benzene derivatives these are two out-of-plane C-X vibrations, one mode in which the two substituents are moving in phase and one out-of-phase mode in which they are moving against each other. The

in-phase vibration is denoted by 17b, while the out-of-phase one is denoted by 5. The infrared active mode 17b has been assigned at 109 cm^{-1} in the far-infrared for para-DCB. Green (30) Scherer and Evans have given similar frequency value for this mode in para-halogenobenzenes while the Raman active mode 5 is assigned as a weak Raman band at 206 cm^{-1} . This value is also supported by Green and agrees with that given by Van Putten (31) at 197 cm^{-1} .

The meta-disubstituted compounds

In meta-disubstituted molecules with light substituents, the normal mode of vibration 17b is generated when both substituents oscillate out-of-phase with each other. Varsányi (16) reported that in meta-disubstituted compounds the vibrational pair 16 of benzene are coupled to the $\gamma(\text{C-CN})$ motion of the substituents. In meta-DCB the in-phase mode is found at a very low frequency, at 62 cm^{-1} in the i.r. spectrum. The frequency of the mode 17a is assigned at 215 cm^{-1} in the Raman spectrum. Varsányi gave the frequency range for vibration 17a in meta-disubstitution as $196\text{-}271\text{ cm}^{-1}$.

The ortho-disubstituted compounds

In ortho-disubstituted rings with light substituents, the in-phase out-of-phase C-X vibration is normal mode 17b and the out-of-phase one is vibration 5. These vibrations give medium intensity bands in the spectrum of ortho-DCB.

The vibration 17b which is infrared active, is assigned at 206 cm^{-1} in the far-infrared spectrum, while the Raman active vibration 5 is placed at 144 cm^{-1} in the spectrum, appearing weakly in the i.r. spectrum at 148 cm^{-1} . Similar frequencies values are found by Green (25) for both vibrations 5 and 17b, at 152 and 239 cm^{-1} respectively for ortho-dichlorobenzene. He also assigned these vibrations at 136 and 217 cm^{-1} respectively in ortho-dibromobenzene. Additional support for these assignments is given by Van Putten (31).

The Out-of-plane CN Vibrations

The assignment of the out-of-plane $\text{C}\equiv\text{N}$ modes completes the discussion of the out-of-plane vibrations. These vibrations are named E and F in this work. Detailed studies on these modes show that the out-of-plane CN bending mode falls to a very low frequency, about 170 cm^{-1} . Jakobsen (28) assigned this mode in the Raman spectrum of benzonitrile at 170 cm^{-1} . Varsányi (16) has established that the low frequency value can be explained as due to the coupling of the substituent motion with vibration 16b of benzene. In the three dicyanobenzenes the E and F vibrations both have frequency at around 170 cm^{-1} .

Para-DCB. The Raman active E fundamental has been assigned to a weak band at 165 cm^{-1} . The infrared active mode is assigned to a strong band at the same frequency in the far-infrared spectrum.

Meta-DCB. This molecule shows a strong band at 158 cm^{-1} in the far-infrared spectrum, being assigned to the b_1 fundamental F.

The Raman active E fundamental is localized as a very strong band at 148 cm^{-1} in the Raman spectrum.

Ortho-DCB. The Raman active fundamental E is assigned to a weak band at 174 cm^{-1} in the spectrum, while the F fundamental is assigned a medium band at 180 cm^{-1} in the far-infrared spectrum.

CHAPTER IV

THE RAMAN SPECTRA AND ISOTOPIC EFFECT OF THE DICYANOBENZENES

In this chapter the Raman spectra and isotope effects for the DCBs are discussed. As is mentioned in the introduction of Chapter III, the Raman spectra of the hydrogenic species and the infrared and Raman spectra of the deuterated species are analysed and used to support and further justify the assignments already proposed for the fundamentals on the basis of the infrared spectra.

Since the infrared spectra could only be obtained for solid samples, the Raman spectra in the same phase are employed for purposes of analysis. But since Raman depolarization ratios cannot be obtained from solid samples, solution spectra were used for this purpose. A list of the band frequencies and their depolarization ratios obtained with samples in solution is given in the following tables. Only a limited number of bands could be observed in the solution spectra, because of interference by the Raman bands of the solvent. Also, the relative intensity of molecular fluorescence was found to be much higher for solution than for solid Raman spectra.

The isotope effect is defined as follows: When one or more nuclei in a molecule are replaced by heavier isotopes, vibrations which involve motion of such nuclei will drop in frequency.

The changes in frequency of vibrations upon deuteration reflect the amplitudes of motion for the substituted nuclei during the vibration. Thus a normal mode in which a hydrogen atom is oscillating with a large relative amplitude will suffer a greater isotopic change in frequency than a normal mode in which this hydrogen is moving with small relative amplitude.

In the present case, deuteration of the ring hydrogens of the DCBs will cause the frequencies of the normal modes which involve motions of the ring hydrogens to drop, while substituent modes remain almost unchanged in frequency. The deuterated compounds used were:

para-C₆d₄(CN)₂, meta-C₆hd₃(CN)₂ and ortho-C₆d₄(CN)₂.

As has been mentioned previously no change in symmetry occurs for each such deuterated molecule.

The majority of the bands shown in the spectrum of the deuterated species, have about the same relative intensities as the corresponding bands of the hydrogenic DCBs.

It is important to note, that many of the normal modes of the solid DCBs appear in both i.r. and Raman spectra violating the selection rules.

The Raman spectra of the three DCBs and their deuterated species will be discussed in the same order as was used in the previous section, but in a more compact manner.

1.1 The carbon-carbon stretching vibrations

Para-disubstituted compounds

In the Raman spectrum of para-DCB-h₄ an intense band is located at 1615 cm⁻¹. This strong band is assigned to the totally symmetric (C-C) stretch 8a vibration. This band was only observed as a weak broad band in the i.r. spectrum.

In para-dialkylbenzenes, Aleksanian et al (46) determined the frequencies of vibration 8a in the Raman spectra for Me-Me, at 1618 cm⁻¹, Et-Et at 1613 cm⁻¹, i-Pr-i-Pr at 1616 cm⁻¹.

In para-DCB-d₄ the mode 8a is found as a polarized band with slightly lower frequency, at 1593 cm⁻¹. The normal mode 8b (b_{3g}) appears as a strong band at 1610 cm⁻¹. The depolarization ratios obtained for the deuterated para-DCB, reveal that this 8b band is polarized.

Upon ring deuteration both 8a and 8b bands are found at around 30 cm⁻¹ lower in frequency. In the analysis of the diethynylbenzenes (31) a shift of around 30 cm⁻¹ is also found for these bands, reinforcing the assignments proposed.

In para-DCB-h₄ the ν (C-C) vibrations 19a and 19b have been assigned in the infrared at 1502 cm⁻¹ and 1403 cm⁻¹ respectively. Both bands are Raman inactive according to the selection rules.

Deuterium substitution results in a decrease in frequency of about 100 cm⁻¹ in vibrations 19a and 19b.

Both the 19a and 19b normal modes show similar changes in frequency upon deuteration, as in the diethylnylbenzenes (31), this also justifies the assignments proposed.

The vibration $\nu(\text{C-C})$ 14, is also Raman inactive, see Chapter III. This mode occurs as a weak band at 1294 cm^{-1} in the i.r. spectrum and the assignment is confirmed by the frequency found upon deuteration, that is, 1294 cm^{-1} . The infrared-active $\nu(\text{C-C})$ vibration shows a similar decrease in frequency upon ring deuteration to the halogenobenzenes (24).

The Meta-disubstituted Compounds

Meta-DCB- h_4 and meta-DCB- hd_3 each possess two Raman bands at around 1600 cm^{-1} .

Surveying the Raman spectra of meta-disubstituted benzene derivatives, Herz (47) made the general observation that the bands belonging to vibrational pair 8 have high depolarization ratios. In the spectrum of meta-xylene, for example, he found the value 0.73. This has been established as a property of the vibrational pair 8a and 8b. The fact that some workers overlooked this property explains several false assignments.

Green (23) examined meta-xylene, meta-dichlorobenzene, meta-dibromobenzene and meta-diiodobenzene; He found that the bands belonging to vibrations 8a and 8b fall between 1553 and 1613 cm^{-1} in the Raman spectra. These bands are depolarized.

A similar frequency pattern is found for meta-DCB- h_4 with values of 1580 cm^{-1} for the 8a and 1605 cm^{-1} for the 8b mode. The 8a and 8b modes have been found to be depolarized in the deuterated

spectrum with frequencies at 1550 cm^{-1} and 1584 cm^{-1} . No comparative data is available for ring deuterated isotopes of other meta-disubstituted compounds.

In the Raman spectrum of meta-DCB- h_4 , the totally symmetric component of the pair 19 is at 1430 cm^{-1} . This frequency assignment agrees with the results of Herz (47). He examined the Raman spectra of meta-disubstituted toluenes and found the following frequencies for vibrations 19a and 19b: $1409\text{--}1435\text{ cm}^{-1}$ and $1470\text{--}1486\text{ cm}^{-1}$ respectively. The analogos of these bands are found in the Raman and i.r. spectra of meta-DCB- hd_3 , with frequencies of 1369 cm^{-1} for the totally symmetric vibration and at 1420 cm^{-1} for the non-totally symmetric vibration.

As was mentioned in Chapter III, the vibration 14 is not easy to assign. Weak infrared and Raman bands are observed in the region at $1330\text{--}1161\text{ cm}^{-1}$ where this band should fall. The mode is tentatively assigned to a very weak band in the Raman spectrum of meta-DCB at 1328 cm^{-1} . No data for other ring deuterated compounds is available. However a weak band, the only candidate, is assigned at 1286 cm^{-1} in meta-DCB- hd_3 . This assignment is supported by Scherer and Evans (24) who assign the Kekulé vibration 14 as being at 1340 cm^{-1} in meta-dichlorobenzene.

Ortho-disubstituted Compounds

The 8a vibration of ortho-DCB- h_4 appears as a polarized, medium intense Raman band with frequency of 1575 cm^{-1} . In the i.r. spectrum the observed frequency is 1570 cm^{-1} . Green (25) assigned this band in ortho-dihalogenated benzenes as being between

1558 cm^{-1} and 1605 cm^{-1} .

The vibration 8b with i.r. value of 1589 cm^{-1} is observed as a strong band, depolarized, with frequency at 1590 cm^{-1} in ortho-DCB.

Green (25) gives values for the latter mode from 1556 cm^{-1} to 1618 cm^{-1} in dihalogenated compounds. The Raman and infrared bands in ortho-DCB show between 30 cm^{-1} and 35 cm^{-1} decrease in frequency upon deuteration.

A medium polarized band is found at 1485 cm^{-1} in the Raman spectrum of ortho-DCB- h_4 . This signal is attributed to the totally symmetric $\nu(\text{C-C})$ mode 19b, confirming the assignment of 1486 cm^{-1} in the i.r. spectrum.

There is another band at 1452 cm^{-1} , appearing as a weak broad band. This is attributed to the non-totally symmetric mode 19a with frequency of 1450 cm^{-1} in the i.r. spectrum.

The data in table (4.1.7), reveal that the i.r. and Raman frequencies of these normal modes decrease upon deuteration by 40 cm^{-1} for 19b and by 60 cm^{-1} for 19a. Similar decreases are found for other ortho-hydrogenic and ortho-deuterated disubstituted benzenes (24).

The remaining $\nu(\text{C-C})$ vibration with a_1 symmetry is the mode 14. Some discussion of this vibration was given in section (3.2). The normal mode gives an infrared band with very strong intensity. The mode is totally symmetric and the observed depolarization ratio is small. The assigned frequency in the Raman spectrum for ortho-DCB- h_4 is at 1233 cm^{-1} , and at 1143 cm^{-1} in ortho-DCB- d_4 , supporting the assignment.

Varsányi (16) gave the frequency range for this vibration as 1250-1350 cm^{-1} for ortho-disubstitution.

1.2 The C-X in-plane bending vibrations

In the Raman spectrum of nitriles Herzberg (3) identified a band of medium to strong intensity for aromatic and aliphatic nitriles between 385-350 cm^{-1} . It was attributed to the in-plane deformation of the $\beta(\text{C}-\text{C}\equiv\text{N})$ group.

In each DCB, two in plane bending C-X vibrations are found. Information about these modes is given in section (3.2).

The Para-disubstituted Compounds

Wilson and Bloor (17) have observed a band at around 370 cm^{-1} in many para-substituted benzonitriles, both in the i.r. and Raman spectra. They suggested that this band is produced by the in-plane C-X vibration.

In para-DCB- h_4 the normal modes 9b and 18b are identified with the bands at 375 cm^{-1} and 360 cm^{-1} in the Raman spectra. Only weak signals could be observed in the expected narrow frequency range and no depolarization ratios could be measured. The 18b fundamental is only expected to appear weakly, if at all, since it is Raman forbidden by the selection rules. The above two fundamentals are shifted by around 20 cm^{-1} upon ring deuteration. The shifts in frequency observed for vibration 9b and 18b in para-DCB are supported by the data given by Jakobsen (28) for benzonitrile. He observed a change of 25 cm^{-1} upon deuteration in the in plane bending $\beta(\text{C}-\text{CN})$ vibration.

The Meta-disubstituted Compounds

In the Raman spectrum of meta-DCB-h₄, two bands are observed at around 380 cm⁻¹. The first band at 377 cm⁻¹ assigned to the mode 9a and the band at 343 cm⁻¹ to normal mode 15, in agreement with the assignments proposed from the infrared spectrum. Deuterium substitution results in a decrease of about 20 cm⁻¹ in both bands. This also agrees with the studies by Jakobsen upon benzonitrile-h₅ and benzonitrile-d₅.

The Ortho-disubstituted Compounds

In the Raman spectrum of ortho-DCB, two other weak bands are found at 365 cm⁻¹ for normal mode 15 and at 385 cm⁻¹ for mode 18a. The assignments for both modes are straightforward because only two bands are observed in this region. A small drop in frequency does occur for the ring deuterated isotopes also in agreement with Jakobsen (28).

1.3 The C-H in-plane bending vibrations

The Para-disubstituted Compounds

The totally symmetric Raman active β (C-H) mode 9a can be identified easily in the spectra of para-DCB-h₄ and para-DCB-d₄, by comparison with the frequency values given by Green (30), Steele, Gates and Radcliffe (18), Stojiljkovic and Whiffen (19) for this normal mode in halogenobenzenes. This vibration is found as a component of the strong band at 1184 cm⁻¹ in the Raman spectrum of para-DCB-h₄.

For para-DCB-d₄ the corresponding band is one that is polarized band at 895 cm⁻¹.

The non-totally symmetric mode 3 should be Raman active but could not be seen in the spectrum. The infrared active modes 18a and 15, which are not Raman allowed, have infrared frequencies of 1025 cm⁻¹ and 1120 cm⁻¹ respectively; these modes are discussed in section (3.2).

The β(C-H) frequencies in table (4.1.1) show a relatively large decrease of 120 cm⁻¹-280 cm⁻¹ upon deuteration. Similar decreases are also found for other para-disubstituted benzene compounds.

The Meta-disubstituted Compounds

Green (23), for halogenobenzenes, and Herz (47) in his study of Raman spectra of meta-chlorotoluene, meta-fluorotoluene and meta-methoxytoluene, each found small values for the depolarization ratio of the totally symmetric vibration 18a.

Many authors have established that this vibration falls in the frequency range of 1060-1110 cm⁻¹. In para-DCB-h₄, the normal mode 18a is assigned to a weak band in the Raman spectrum at 1104 cm⁻¹. This mode could be seen in the deuterated Raman spectrum at 820 cm⁻¹.

The vibrations 3, 9b and 18b have been assigned in the Raman spectrum to bands at 1280 cm⁻¹, 1176 cm⁻¹ and 1150 cm⁻¹ respectively. These modes have been found in the ring deuterated spectrum at 1190 cm⁻¹, 930 cm⁻¹ and 840 cm⁻¹ respectively.

The Ortho-disubstituted Compounds

In the Raman spectrum of ortho-DCB-h₄ the 9a and 18b β(C-H) modes appear as strong and medium polarized bands at 1177 cm⁻¹ and 1038 cm⁻¹ respectively.

Katritzky and Jones (48) have established the frequency for the 9a β(C-H) vibration, for donor electron ring substituents as between 1174-1181 cm⁻¹. However Varsányi does not entirely agree with this interpretation. He gives the range as from 1150 cm⁻¹ to 1168 cm⁻¹.

Green (25) and Kohlrausch (44) have assigned the frequency range for vibration 18b in the Raman spectrum as 1020 cm⁻¹ to 1051 cm⁻¹.

The non-totally symmetric fundamentals 3 and 9b are found as a weak broad and weak bands at 1295 cm⁻¹ and 1096 cm⁻¹ respectively in the Raman spectrum. The infrared spectrum of these vibrations has been discussed in Chapter III. These assignments also are supported by the corresponding β(C-D) bands which decrease in frequency by about 278-202 cm⁻¹.

2.1 The skeletal vibrations for radial motion, including the C-X stretching vibrations

Para-disubstituted Compounds

The vibration 6a, which appears only in the Raman spectrum of para-DCB-h₄, has been assigned to the strong band at 213 cm⁻¹. In the spectrum of para-DCB-d₄ it is found to be polarized, with a frequency of 204 cm⁻¹.

Gates, Radcliffe and Steele (18), Stojilkovic and Whiffen place this frequency near 215 cm⁻¹ for para-dibromobenzenes. This is in agreement with the assignment proposed for the DCB.

A weak band is found at 653 cm^{-1} and 644 cm^{-1} in the Raman spectra of the DCB para- h_4 and para- d_4 respectively. This signal is attributed to the non-totally symmetric Raman active $\alpha(\text{C-C-C})$ 6b mode. This band has a similar frequency in both the hydrogenic and deuterated halogenobenzenes.

The $\nu(\text{C-CN})$ stretching vibrations are numbers 7a, 1, 13 and 12 in para-disubstituted benzenes.

The Raman spectrum of para-DCB- h_4 shows two strong bands at 1184 cm^{-1} and 817 cm^{-1} . These are identified as the fundamentals (7a, 9a) and 1 respectively. The Raman spectrum of para-DCB- d_4 shows that both bands are polarized.

The coupling between these $\nu(\text{C-CN})$ modes and the $\alpha(\text{C-C-C})$ bending vibrations of the benzene ring is discussed in Chapter III.

The normal modes 13 and 12 are observed in the i.r. spectrum only, at 1278 cm^{-1} and 643 cm^{-1} respectively. These assignments were verified with the spectra of the ring deuterated of para-DCB. Different frequency changes are observed. Each vibration shows a different frequency shift on deuteration. See table (4.1.1). These bands show similar changes in frequency upon deuteration as do the diethynylbenzenes (31).

The Meta-disubstituted Compounds

As discussed in Chapter III, the 6a and 6b fundamentals in meta-DCB- h_4 should occur in the ranges $450\text{--}550\text{ cm}^{-1}$ and $220\text{--}560\text{ cm}^{-1}$ respectively. The totally symmetric Raman active mode 6a gives a medium band at 460 cm^{-1} . In the spectrum of

deuterated meta-DCB, this band is now at 457 cm^{-1} , and is polarized. The 6b normal mode for the hydrogenic compound, shows a strong band in the i.r. spectrum and a weak band in the Raman spectrum at 502 cm^{-1} . These fundamentals decrease in frequency upon deuteration by only 3 cm^{-1} for vibration 6a and 24 cm^{-1} for vibration 6b.

For mono-, meta-di and sym- trisubstitution vibration 12 corresponds to ring-breathing mode of trigonal symmetry and gives rise to a very strong Raman line in the range $1003\text{--}1005\text{ cm}^{-1}$ (16). In meta-DCB- h_4 this band falls at 1005 cm^{-1} , and is a polarized band at 970 cm^{-1} in the spectrum of meta-DCB- hd_3 . The other totally symmetric vibrations 1 and 13 fall at 709 cm^{-1} and 1246 cm^{-1} respectively, and are also polarized. The remaining $\nu(\text{C-CN})$ vibration is the non-totally symmetric mode 7b. This mode could be seen in the i.r. spectrum as a weak band at 900 cm^{-1} . Its frequency is almost unaffected upon deuteration at 898 cm^{-1} . A similarity frequency is found in meta-xylene (23).

The Ortho-disubstituted Compounds

The Raman active mode 6a for ortho-DCB- h_4 has been assigned to a band at 480 cm^{-1} , appearing also in the i.r. spectrum at 472 cm^{-1} . This band has a small depolarization ratio. The mode 6b appears as a medium intensity depolarized band at 530 cm^{-1} , at the same frequencies as in the i.r. spectrum. Both vibrations are only slightly deuterium sensitive.

The substituent-stretching vibrations in ortho-DCB benzenes are 7a, 1, 13 and 12.

Varsányi established that in ortho-disubstitution by two light substituents vibrations 7a and 13 should be found near to each other in frequency. From data by Fenske et al (49) the frequency of vibration 13 is higher than 7a for ortho-dialkylbenzenes. On the other hand, the ordering of the two frequencies in other ortho-disubstituted benzene derivatives carrying light substituents is the reverse of this.

The frequency of vibration 7a for ortho-DCB-h₄ is 1210 cm⁻¹, where a polarized band appears in the Raman spectrum. The weak band at 1197 cm⁻¹ is attributed to vibration 13. The vibrations 1 and 12 appear at lower frequency at 707 cm⁻¹ and 805 cm⁻¹ respectively in the Raman spectrum. The totally symmetric normal mode 1 is polarized as expected.

Upon deuteration, the vibration 7a appears at 1126 cm⁻¹, vibration 1 at 673 cm⁻¹, 13 at 1100 cm⁻¹ and 12 at 770 cm⁻¹, as shown in diethynylbenzenes and ortho-dichlorobenzenes (31,24).

2.2 The C-H stretching vibrations

The Para-Disubstituted Compounds

In the Raman spectrum of para-DCB-h₄, two weak bands are found at 3095 cm⁻¹ and 3027 cm⁻¹, being assigned to vibrations 2 and 7b respectively. No Raman bands are found for the vibrations 20a and 20b (16,17,18,30). The C-H stretching modes decrease in frequency by nearly 700 cm⁻¹ upon ring deuteration. This decrease commonly occurs for these vibrations in para-disubstituted compounds.

Table 4.1.1 Ground state fundamental frequencies (cm^{-1}) of the isotopes of para-DCB

				para-h ₄	para-d ₄	sym.
1	2	$\nu(\text{C-H})$	R	3090	2305	
2	A	$\nu(\text{C}\equiv\text{N})$	R	2218	2224	
3	8a	$\nu(\text{C-C})$	T	1615	1593	
4	7a	$\nu(\text{C-CN})$	R	1184	1177	a _g
5	9a	$\beta(\text{C-H})$	T	1184	895	
6	1	$\nu(\text{C-CN})$	R	817	790	
7	6a	$\alpha(\text{C-C-C})$	R	213	204	
8	10a	$\gamma(\text{C-H})$	O	794	669	b _{1g}
9	10b	$\gamma(\text{C-H})$	O	975	810	
10	4	$\phi(\text{C-C})$	O	662	()	
11	5	$\gamma(\text{C-CN})$	O	206	193	b _{2g}
12	E	$\gamma(\text{C}\equiv\text{N})$	O	165	160	
13	7b	$\nu(\text{C-H})$	R	3027		
14	8b	$\nu(\text{C-C})$	T	1610		
15	3	$\beta(\text{C-H})$	T	()	1035	b _{3g}
16	6b	$\alpha(\text{C-C-C})$	R	653	644	
17	9b	$\beta(\text{C-CN})$	T	368	365	
18	C	$\beta(\text{C}\equiv\text{N})$	T	525	506	
19	17a	$\gamma(\text{C-H})$	O	880	730	a _u
20	16a	$\phi(\text{C-C})$	O	395	375	
21	20a	$\nu(\text{C-H})$	R	3060	2268	
22	B	$\nu(\text{C-N})$	R	2220	2216	
23	19a	$\nu(\text{C-C})$	T	1502	1390	b _{1u}
24	13	$\nu(\text{C-CN})$	R	1278	1262	
25	18a	$\beta(\text{C-H})$	T	1025	845	
26	12	$\nu(\text{C-CN})$	R	643	608	
27	20b	$\nu(\text{C-H})$	R	3102	2295	
28	19b	$\nu(\text{C-C})$	T	1403	1302	
29	14	$\nu(\text{C-C})$	T	1294	1284	b _{2u}
30	15	$\beta(\text{C-H})$	T	1120	910	
31	D	$\beta(\text{C}\equiv\text{N})$	T	535	509	
32	18b	$\beta(\text{C-CN})$	T	360	335	
33	11	$\gamma(\text{C-H})$	O	840	711	
34	16b	$\phi(\text{C-C})$	O	563	482	b _{3u}
35	F	$\gamma(\text{C}\equiv\text{N})$	O	165	160	
36	17b	$\gamma(\text{C-CN})$	O	109	109	

Table 4.1.2 Ground state fundamental frequencies (cm^{-1}) of the isotopes of meta-DCB

				meta-h ₄	meta-h-d ₃	sym.
1	20a	$\nu(\text{C-H})$	R	3089	2300	
2	2	$\nu(\text{C-H})$	R	3089	2297	
3	7a	$\nu(\text{C-H})$	R	3056	2252	
4	A	$\nu(\text{C}\equiv\text{N})$	R	2232	2232	
5	8a	$\nu(\text{C-C})$	T	1580	1550	
6	19a	$\nu(\text{C-C})$	T	1430	1361	
7	13	$\nu(\text{C-CN})$	R	1246	1226	
8	18a	$\beta(\text{C-H})$	T	1104	820	a ₁
9	12	$\nu(\text{C-CN})$	R	1005	967	
10	1	$\nu(\text{C-CN})$	R	709	690	
11	C	$\beta(\text{C}\equiv\text{N})$	T	524	520	
12	6a	$\alpha(\text{C-C-C})$	R	460	457	
13	9a	$\beta(\text{C-CN})$	T	377	361	
14	10a	$\gamma(\text{C-H})$	O	905	790	
15	16a	$\phi(\text{C-C})$	O	620	602	a ₂
16	17a	$\gamma(\text{C-CN})$	O	211	196	
17	E	$\gamma(\text{C}\equiv\text{N})$	O	148	145	
18	5	$\gamma(\text{C-H})$	O	990	863	
19	10b	$\gamma(\text{C-H})$	O	870	749	
20	11	$\gamma(\text{C-H})$	O	793	690	b ₁
21	4	$\phi(\text{C-C})$	O	672	550	
22	16b	$\phi(\text{C-C})$	O	460	448	
23	F	$\gamma(\text{C N})$	O	160	152	
24	17b	$\gamma(\text{C-CN})$	O	65	40	
25	20b	$\nu(\text{C-H})$	R	3119	2292	
26	B	$\nu(\text{C N})$	R	2220	2220	
27	8b	$\nu(\text{C-C})$	T	1600	1590	
28	19b	$\nu(\text{C-C})$	T	1475	1420	
29	3	$\beta(\text{C-H})$	T	1271	1190	
30	14	$\nu(\text{C-C})$	T	1329	1284	
31	9b	$\beta(\text{C-H})$	T	1170	930	b ₂
32	18b	$\beta(\text{C-H})$	T	1148	840	
33	7b	$\nu(\text{C N})$	R	900	898	
34	D	$\beta(\text{C N})$	T	580	550	
35	6b	$\alpha(\text{C-C-C})$	R	502	478	
36	15	$\beta(\text{C-CN})$	T	343	320	

Table 4.1.3 Ground state fundamental frequencies (cm^{-1}) of the isotopes of ortho-DCB

				ortho-h ₄	ortho-d ₄	sym.
1	2	$\nu(\text{C-H})$	R	3095	2302	
2	20b	$\nu(\text{C-H})$	R	3095	2297	
3	A	$\nu(\text{C}\equiv\text{N})$	R	2230	2233	
4	8a	$\nu(\text{C-H})$	T	1575	1552	
5	19b	$\nu(\text{C-C})$	T	1485	1442	
6	14	$\nu(\text{C-C})$	T	1233	1143	
7	7a	$\nu(\text{C-CN})$	R	1210	1126	
8	9a	$\beta(\text{C-H})$	T	1177	917	a ₁
9	18b	$\beta(\text{C-H})$	T	1038	836	
10	1	$\nu(\text{C-CN})$	R	707	673	
11	C	$\beta(\text{C}\equiv\text{N})$	T	565	545	
12	6a	$\alpha(\text{C-C-C})$	R	480	470	
13	15	$\beta(\text{C-CN})$	T	365	336	
14	17a	$\gamma(\text{C-H})$	O	970	750	
15	10b	$\gamma(\text{C-H})$	O	846	650	
16	4	$\phi(\text{C-C})$	O	735	()	a ₂
17	16a	$\phi(\text{C-C})$	O	()	()	
18	E	$\gamma(\text{C}\equiv\text{N})$	O	174	174	
19	5	$\gamma(\text{C-CN})$	O	144	144	
20	10a	$\gamma(\text{C-H})$	O	922	669	
21	11	$\gamma(\text{C-H})$	O	770	620	
22	16b	$\phi(\text{C-C})$	O	410	400	b ₁
23	17b	$\gamma(\text{C-CN})$	O	206	200	
24	F	$\gamma(\text{C}\equiv\text{N})$	O	180	180	
25	20a	$\nu(\text{C-H})$	R	3040	2250	
26	7b	$\nu(\text{C-H})$	R	3040	2250	
27	B	$\nu(\text{C}\equiv\text{N})$	R	2228	2224	
28	8b	$\nu(\text{C-C})$	T	1589	1552	
29	19a	$\nu(\text{C-C})$	T	1450	1390	
30	3	$\beta(\text{C-H})$	T	1295	1130	
31	13	$\gamma(\text{C-CN})$	R	1190	1100	b ₂
32	9b	$\beta(\text{C-H})$	T	1092	853	
33	12	$\nu(\text{C-CN})$	R	804	770	
34	D	$\beta(\text{C}\equiv\text{N})$	T	565	540	
35	6b	$\alpha(\text{C-C-C})$	R	530	494	
36	18a	$\beta(\text{C-CN})$	T	380	370	

The Meta-disubstituted Compounds

A very intense line is found in the Raman spectrum of meta-DCB-h₄ at 3089 cm⁻¹. This is assigned as a superposition of vibrations 20a and 2. As is discussed in Chapter III the aromatic C-H stretches are overlapped in both the i.r. and Raman spectra of meta-disubstituted compounds. The other $\nu(\text{C-H})$ a₁ mode 7a is found at 3056 cm⁻¹ (23,24). The deuterated spectra reveal that the above totally symmetric vibrations are polarized, with frequency shifts of about 750 cm⁻¹.

The remaining $\nu(\text{C-H})$ 20b vibration is found as a weak band in both i.r. and Raman spectra, with decreases in frequency of about 800 cm⁻¹ upon deuteration.

The Ortho-disubstituted Compounds

In the spectrum of ortho-DCB-h₄, a strong polarized band is found at 3095 cm⁻¹, being assigned to the totally symmetric vibrations 2 and 20b, by analogy with the Raman frequencies given by Van Putten (31) for ortho-diethynylbenzenes. These variations also decrease by about 750 cm⁻¹ upon deuteration.

3.1 The out-of-plane skeletal vibrations, including the out-of-plane C-X vibrations

Many of these vibrations can only be identified from infra-red data. The Raman spectra are not very useful here, since they show large numbers of weak and depolarized bands at lower frequencies.

The Para-disubstituted Compounds

The Raman active vibrations 16a and 4 in para-DCB are found at 395 cm^{-1} and 662 cm^{-1} respectively, showing weak intensity. The i.r. active fundamental 16b is discussed before. Upon deuteration no bands are observed in the Raman spectrum, but in the i.r. spectrum two signals are seen at 375 and 482 cm^{-1} , being assigned to vibrations 16a and 16b respectively. The former band appears in the spectrum violating the selection rules. No band could be found for vibration 4.

The Raman active b_{2g} vibration 5 appears in the Raman spectrum at 206 cm^{-1} with weak intensity (16,17,18,19). The $\gamma(\text{C-X})$ vibrations 5 and 17b are found in the deuterated spectrum, with frequencies of 193 and 109 cm^{-1} respectively, being almost unaffected by deuteration.

The Meta-disubstituted Compounds

In the Raman spectrum of meta-DCB- h_4 three signals are found at 625 cm^{-1} , 460 cm^{-1} and 678 cm^{-1} . These values have been identified as the $\phi(\text{C-C})$ out-of-plane modes 16a, 16b and 4 respectively (23,24). These fundamentals are shifted by about 15 cm^{-1} in the deuterated spectra, except for the fundamental 4 that shows a change of 50 cm^{-1} .

The Raman active mode 17a appears in the Raman spectrum at 215 cm^{-1} . Green (23) has placed this vibration in the Raman spectrum of meta-halogenated compounds in the range of 250 - 199 cm^{-1} . In all cases the measured depolarization ratio is bigger than 0.78 . The vibration 17b is observed at 62 cm^{-1} in the infrared spectrum. Both vibrations 17a and 17b with deuterated frequencies

of 196 and 60 cm^{-1} respectively.

Ortho-disubstituted Compounds

The Raman allowed vibration 4 appears as a weak band at 735 cm^{-1} in ortho-DCB. No justification is found for this vibration since no signal is observed in the deuterated spectra. The vibration 16a is also left unassigned because no bands are seen in the spectrum. The infrared-active mode 16b at 410 cm^{-1} is correlated with a weak band at 415 cm^{-1} in the Raman spectrum. A decrease of 15 cm^{-1} is obtained upon deuteration.

3.2 The out-of-plane C-H vibrations

para-DCB. The Raman active vibrations 10a and 10b give rise to Raman bands of weak intensity at 794 cm^{-1} and 975 cm^{-1} respectively (30).

meta-DCB. In this molecule the only γ (C-H) normal mode observed in the Raman spectrum is that at 910 cm^{-1} , being assigned to the a_2 mode 10a.

ortho-DCB. The Raman active modes 17a and 10b are left unassigned because no signals are found in the limits of frequency for these.

These normal modes revealed in Table (4.1.7).
a large drop in frequency of around 150 to 320 cm^{-1} .

3.3 Vibrations localized in the substituents

A - The $\nu(\text{C}\equiv\text{N})$ stretching vibrations

Para-DCB - The Raman active mode A is assigned to a Raman band at 2218 cm^{-1} , and the other $\nu(\text{C}\equiv\text{N})$ stretching mode B(ν_{22}) assigned to a strong i.r. band at 2220 cm^{-1} . In the i.r. and Raman spectra of the deuterated para-DCB, the corresponding frequencies are observed at 2216 cm^{-1} and 2224 cm^{-1} respectively. The totally symmetric normal mode has a small value of polarization ratio as expected.

Meta-DCB - ν_4 and ν_{26} are assigned to the Raman bands observed at 2232 cm^{-1} and 2226 cm^{-1} for meta-DCB. The totally symmetric (ν_4), A vibration is found as polarized band at 2232 cm^{-1} in the deuterated spectrum, the non-totally symmetric is assigned at 2217 cm^{-1} .

Ortho-DCB - A very strong polarized band at 2230 cm^{-1} observed in the Raman spectrum of this molecule is assigned to the superposed A and B fundamentals. This assignment is confirmed from the deuterated molecule spectra which shows a very strong polarized band at 2233 cm^{-1} .

B - The $\beta(\text{C}\equiv\text{N})$ in-plane vibrations

Para-DCB - A weak Raman band is observed at 525 cm^{-1} , and is proposed for the Raman active mode C, while the i.r. active mode D, is assigned at 535 cm^{-1} . A shift of about 20 cm^{-1} is observed upon ring deuteration.

Meta-DCB - The totally symmetric Raman active $\beta(\text{C}\equiv\text{N})$ mode C is found as a weak Raman band at 524 cm^{-1} . The nontotally symmetric infrared active fundamental D is assigned also as a weak band at 580 cm^{-1} . A decrease of around 30 cm^{-1} is found in the deuterated spectrum for both frequencies.

Ortho-DCB - The fundamental C appears as a polarized Raman band with medium intensity at 565 cm^{-1} . The infrared-active mode D has been assigned to a weak band at 565 cm^{-1} .

C - The $\gamma(\text{C}\equiv\text{N})$ out-of-plane vibrations

Para-DCB - The Raman active fundamental E has been assigned to a weak band at 165 cm^{-1} , and the infrared active mode F to 165 cm^{-1} , being shifted by only 5 cm^{-1} upon deuteration.

Meta-DCB - For this molecule, the frequencies at 148 cm^{-1} and 160 cm^{-1} are shown in the Raman and i.r. spectra respectively. The former frequency is assigned to the fundamental E while the latter to F. They are almost unaffected by deuteration.

Ortho-DCB - In the case of this compound the normal modes E and F are assigned at 174 cm^{-1} in the Raman spectrum and at 180 cm^{-1} in the i.r. spectrum respectively, being unaffected upon deuteration.

TELLER-REDLICH PRODUCT RATIOS

Teller and Redlich have shown that the following relationship holds within each symmetry species.

$$\pi_j \left(\frac{\omega_j^i}{\omega_j} \right) = \left[\left(\frac{m_1}{m_1^i} \right)^\alpha \left(\frac{m_2}{m_2^i} \right)^\beta \dots \left(\frac{M}{M^i} \right)^t \left(\frac{I_x}{I_x^i} \right)^{\delta_x} \left(\frac{I_y}{I_y^i} \right)^{\delta_y} \left(\frac{I_z}{I_z^i} \right)^{\delta_z} \right]^{1/2}$$

where ω_j = zero order frequencies

m_1, m_2, \dots - masses of the representative atoms in the symmetry related sets

α, β, \dots - the number of degrees of freedom each set contributes to the symmetry type being considered.

M - total mass of the molecule

t - the number of translational coordinates that belong to the symmetry species being considered.

$\delta_x, \delta_y, \delta_z$ - this is 1 if R_x, R_y or R_z transforms as the given symmetry species. It is 0 otherwise.

I_x, I_y, I_z - the moments of inertia about the axis used to obtain the point group

(i) denotes the isotopically substituted molecule.

Applying this formula to the three dicyanobenzenes and their deuterated species the theoretical and experimental Teller-Redlich Product Ratios are calculated. It should be noted that there is always a slight anharmonic character in the vibrations and precise product values cannot be obtained.

Table 4.1.4

Experimental and theoretical R-T ratios for the isotopes of ortho-, meta- and para-DCB.

Sym. class	para-d ₄		Sym. class	meta-hd ₃		ortho-d ₄	
	para-h ₄ th.	exp.		meta-h ₄ th.	exp.	ortho-h ₄ th.	exp.
A _g	.50	.59	a ₁	.36	.26	.25	.24
b _{1g}	.73	.84	a ₂	.79	.73	.53	.57
b _{2g}	.72	.74	b ₁	.55	.51	.55	.55
b _{3g}	.61	.67	b ₂	.39	.33	.28	.25
a _u	.71	.78					
b _{1u}	.51	.52					
b _{2u}	.51	.50					
b _{3u}	.72	.70					

Table 4.1.5 Frequencies (cm^{-1}) and assignments for para-DCB

Para-h ₄		Para-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
3825 vw				$\nu_{14} + \nu_2$
		3800 ww		$\nu_2^D + \nu_{14}$
3750 vvw				$\nu_{13} + 2\nu_{32}$
3720 vvw				$\nu_2 + \nu_{23}$
		3125 vvw		$\nu_2^D + \nu_{30}^D$
3102 m				ν_{27}
3085 w	3090 w	3080 vvw		$\nu_1, \nu_5^D + \nu_{30}^D + \nu_{23}^D + \nu_{36}^D$
3060 m		3060 vvw		$\nu_{21}, \nu_2^D + \nu_{31}^D + \nu_{32}$
3029 w	3027 w	3025 w		$\nu_{13}, \nu_{32}^D, \nu_{28}^D + \nu_{23}^D$
		3000 vvw		$\nu_{13}^D + \nu_{19}^D$
2822 w				$\nu_{20} + \nu_{25} + \nu_{28}$
2760 vvw				$\nu_2 + \nu_{31}$
2700 w				$\nu_{28} + \nu_{29}$
		2673 vvw		$\nu_{23}^D + \nu_{29}^D$
2618 vvw				$\nu_2 + \nu_{20}$
2604 w				$\nu_5 + \nu_{26} + \nu_{32}$
		2570 vvw		$\nu_{23}^D + \nu_4$
2522 vw				$\nu_{28} + \nu_{30}$
		2480 vw		$\nu_5^D + \nu_{14}^D$
2444 vw				$\nu_{14} + \nu_{33}$
2389 w				$\nu_2 + \nu_{35}$
2320 w				$\nu_{29} + \nu_{25}$

(continued next page)

Table 4.1.5 (continued)

Para-h ₄		Para-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
		2295 m	2305 m P(.46)	ν_1^D, ν_{27}^D
		2268 m	2260 w	ν_{13}^D, ν_{21}^D
2222 w	2218 vs		2224 vs P(.08)	ν_2, ν_2^D
2220 vvs				ν_{22}
		2216 vvs	2213 w	ν_{22}^D, ν_2^D
1943 m				$2\nu_9$
1814 w				$\nu_9 + \nu_{33}$
1690 w				$\nu_9 + \nu_8$
1623 sh	1615 s			ν_3
1602 w	1610 s			ν_{14}
		1598 vw	1393 s P(.41)	ν_3
1583 vw		1588 vw	1585 m P(.35)	ν_{14}^D
		1540 vvw		$\nu_9^D + \nu_{19}^D$
1532 w				$\nu_9 + \nu_{20} + \nu_{35}$
1502 vs				ν_{23}
1403 vs				ν_{28}
		1390 s		ν_{23}^D
1365 vvw				$\nu_{35} + \nu_{32} + \nu_{33}$
1345 vvw				$\nu_{35} + \nu_{20} + \nu_{36}$
		1302 vs		ν_{28}^D
1294 w				ν_{29}
1278 s		1284 w		ν_{24}, ν_{29}^D
		1262 s		ν_{24}^D

(continued next page)

Table 4.1.5 (continued)

Para-h ₄		Para-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
1240 w				$\nu_{19} + \nu_{32}$
1188 s	1184 s			ν_4, ν_5
		1180 vw	1177 m P(.18)	ν_4^D
1149 w				$\nu_{32} + 2\nu_{20}$
		1139 w		$\nu_{26}^D + \nu_{17}^D + \nu_{35}^D$
1120 w				ν_{30}
1102 vw				$\nu_{34} + \nu_{31}$
1080 vvw		1080 w		$\nu_9 + \nu_{36}, \nu_{33}^D + \nu_{17}^D$
1062 vvw				$\nu_{31} + \nu_{32} + \nu_{35}$
		1035 w		ν_{15}^D
1025 m				ν_{25}
		1012 vw		$\nu_{35}^D + \nu_{17}^D + \nu_{34}^D$
		990 vvw		$\nu_{31}^D + \nu_{34}^D$
975 w	975 w			ν_9
		910 w		ν_{30}^D
902 vw				$\nu_{35} + \nu_{32} + \nu_{17}$
		892 vw	895 s P(.21)	ν_5^D
880 w				ν_{19}
		845 m		ν_{25}^D
840 vs				ν_{33}
	817 s			ν_6
		810 w	810 w	ν_9^D
	794 w			ν_8
			790 s. P(.03)	ν_6
643 s				ν_{26}

Table 4.1.5 (continued)

Para-h ₄		Para-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
		730 w		^D v ₁₉
		711 vs		^D v ₃₃
			669 w	^D v ₈
	662 w			v ₁₀
	653 w		644 w	v ₁₆ , ^D v ₁₆
		608 m		^D v ₂₆
563 s				v ₃₄
535 w				v ₃₁
	525 w	525 vv		v ₁₈
			608 m	^D v ₂₆
		509 w	506 w	^D v ₃₁
		482 vs		^D v ₃₄
395 w	395 w			v ₂₀
375 w	368 w	375 w -		v ₁₇ , ^D v ₂₀
		369 w	365 w	^D v ₁₇
360 m	360 w			v ₃₂
		335 w		^D v ₃₂
	213 s			v ₇
	206 w			v ₁₂
			204 s P(.30)	^D v ₇
			193 w	^D v ₁₂
165 s	165 w			v ₁₁ , v ₃₅

(continued next page)

Table 4.1.5 (continued)

Para-h ₄		Para-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
		160 m	160 w	^D ν ₃₅
109 m		109 m		ν ₃₆ , ^D ν ₃₆
	93 w		100 w	ν ₁₀ -ν ₃₄
	86 w			ν ₂₆ -ν ₃₄
63 vw				ν ₃₅ -ν ₃₆
	56 w			ν ₃₅ -ν ₃₆

Table 4.1.6 Frequencies (cm^{-1}) and assignments for meta-DCB

meta-h ₄		meta-hd ₃		Assignment		
I.R.	Raman	I.R.	Raman			
3823	vvw			$\nu_4 + \nu_{27}$		
		3809	vvw	$\nu_5 + \nu_3$ ^D ^D		
3722	vvw			$\nu_{20} + \nu_{30} + \nu_{27}$		
3709	vvw			$\nu_{23} + \nu_{22} + \nu_2$		
3408	vvw			$\nu_5 + \nu_7 + \nu_{34}$		
3160	vvw			$2\nu_5$		
			3156	vvw	$2\nu_5$	
3119	w	3108	w	ν_{25}		
			3092	m	$\nu_{27} + \nu_6 + \nu_{24}$	
3090	m	3089	vs	3090	vw	$\nu_1, \nu_2, \nu_3 + \nu_{32}$ ^D ^D
				3060	vw	$\nu_{32} + \nu_{26}$ ^D ^D
3058	w	3056	m			ν_3
			3027	w		$\nu_{23} + \nu_{30} + \nu_{27}$ ^D ^D ^D
				2995	vw	$\nu_3 - \nu_{24}$
2822	vvw					$\nu_{35} + \nu_{33} + \nu_6$
2810	vw					$\nu_4 + \nu_{11} + \nu_{24}$
2760	vw					$\nu_{21} + \nu_{18} + \nu_8$
2700	w					$\nu_{27} + \nu_8$
			2690	vw		$2\nu_{21} + \nu_{27}$ ^D ^D
			2623	vvw		$\nu_{27} + \nu_9 + \nu_{24}$ ^D ^D ^D
2604	ww					$\nu_4 + \nu_{13}$
2560	vvw					$\nu_{27} + \nu_{34} + \nu_{13}$
2497	vw					$2\nu_7$
			2480	vw		$\nu_{23} + \nu_{19} + \nu_5$ ^D ^D ^D

(continued next page)

Table 4.1.6 (continued)

meta-h ₄		meta-hd ₃		Assignment
I.R.	Raman	I.R.	Raman	
		2402 w		$\nu_{23}^D + \nu_3^D$
2398 w				$\nu_7 + \nu_{32}$
2389 ww				$\nu_{27} + \nu_{20}$
2300 w	2302 vw	2292 s	2300 s P(.16)	$\nu_1^D, \nu_2^D, \nu_{25}^D$
			2297 s P(.16)	$\nu_1^D, \nu_2^D, \nu_{25}^D$
		2250 w	2252 w	ν_3^D
2225 vvw	2232 vs	2220 vvs	2232 vs P(.21)	$\nu_{26}^D, \nu_{26}^D, \nu_4^D, \nu_4^D$
2209 vvw				$\nu_{24} + \nu_{21} + \nu_{28}$
			2205 vw	$2\nu_8$
		2200 vw		$\nu_9^D + \nu_7^D$
2196 w	2190 vw		2193 vw	$\nu_{30} + \nu_{19}$
		1950 vw		$\nu_{32}^D + \nu_8^D + \nu_{13}^D - \nu_{24}^D$
1937 w				$2\nu_{19} + \nu_5 - \nu_{20}$
1886 w				$\nu_{18} + \nu_{19}$
		1870 w		$\nu_{22}^D + \nu_{28}^D$
1810 w		1800 w		$\nu_3^D - \nu_{22}^D$
		1628 w		$\nu_{18}^D + \nu_9^D + \nu_{24}^D$
	1612 vw			$\nu_{32} + \nu_{22}$
1600 m	1605 s			ν_{27}
		1590	1584 m DP(.78)	ν_{27}^D
1580 m	1580 s			ν_5
			1577 vw	ν_{14}^D
		1560 m	1550 m P(.50)	ν_5^D
		1540 vw		$2\nu_{19}^D$
1525 vw				$\nu_{32} + \nu_{13}$

(continued next page)

Table 4.1.6 (continued)

meta-h ₄		meta-hd ₃		Assignment
I.R.	Raman	I.R.	Raman	
1490	vw			$\nu_{18} + \nu_{35}$
1475	s			ν_{28}
		1420	s	ν_{28}^D
1421	m	1430	m	ν_6
1409	vw			$\nu_7 + \nu_{23}$
		1380	vw	$\nu_4^D - \nu_{32}^D, \nu_{20}^D$
1370	vw	1369	m	$\nu_{18} + \nu_{13}, \nu_6$
1329	vw	1328	w	ν_{30}
		1284	w	ν_{14}^D
1271	m	1280	w	ν_{29}
		1270	vw	$\nu_{12}^D + \nu_8^D$
1248	m	1246	s	ν_7
		1236	m	?
1222	vw	1230	w	ν_7^D
		1226	s P(.30)	?
		1213	m	?
		1190	w	ν_{29}^D
1170	m	1176	w	ν_{31}
1148	m	1150	w	ν_{32}
		1140	w	$\nu_{36} + \nu_8$
1100	w	1104	w	ν_8
1060	vw	1060	vw	$\nu_{33} + \nu_{23}, \nu_3^D - \nu_{29}^D$
		1020	w	$\nu_3^D - \nu_7^D$
1012	vw	1005	vs	ν_9

(continued next Page)

Table 4.1.6 (continued)

meta-h ₄		meta-hd ₃		Assignment
I.R.	Raman	I.R.	Raman	
988 w			991 vw	v ₁₈
940 vw				3v ₂₄ +v ₈ -v ₃₆
		970 w	967 vs P(.12)	D v ₉
	910 w			v ₁₄
900 w				v ₃₃
890 w				v ₂₃ +v ₂₁ +v ₂₄
865 w				v ₁₉
873 w				D v ₁₈
		853 vw	854 w	D v ₄ -v ₆
		840 m	840 w	D v ₃₂
		820 m	820 w	D v ₈
793 vs				v ₂₀
			785 vw	D v ₁₄
		770 m		D v ₁₉
701 m	709 s		690 s P(.23)	D v ₁₀
		690 vs	685 w	D v ₂₀
672 vs	678 w			v ₂₁
		640 vw		2v ₃₆ ^D , v ₂₉ ^D -v ₂₁ ^D
	625 m		600 m DP(.95)	v ₁₅
590 w				v ₁₁ +v ₂₄
		584 w	581 vw	D v ₂₈ -v ₃₂
580 w				v ₃₄
		550 vs		D v ₂₁ , v ₃₄
524 vw	524 w		520 w	v ₁₁

(continued next page)

Table 4.1.6 (continued)

meta-h ₄		meta-hd ₃		Assignment
I.R.	Raman	I.R.	Raman	
502 vs	502 w			v ₃₅ D
		490 s	520 w	v ₁₁ D
		478 m	475 w	v ₃₅ D
460 vs	460 w			v ₂₂ D
		457 vw	457 m P(.30)	v ₁₂ D
		448 m	441 w	v ₂₂
398 vw				v ₂₂ ⁻ v ₂₄
380 m	377 m			v ₁₃ D
		355 w	361 w	v ₁₃
343 m	343 vw			v ₃₆ D
		320 m		v ₃₆
		182 w		v ₃₅ ⁺ v ₂₃ ⁺ v ₄ ⁻ v ₂₂ D
203 w				v ₂₅ ⁻ v ₂₀ ⁻ v ₂₈ D
	215 m		196 m DP(.76)	v ₁₇ , v ₁₇ ^D
	180 w		170 w	v ₁₄ ⁺ v ₁₅
	148 vs			v ₁₆
158 sb				v ₂₄ D
		152 m	145 s DP(.80)	v ₁₆ , v ₂₃ ^D
		137 w		v ₂₈ ⁻ v ₃₀ ^D
		96 b		v ₉ ⁻ v ₁₈ ^D
62 m				v ₂₄ D
		60 m		v ₂₄

Table 4.1.7 Frequencies (cm^{-1}) and assignments for ortho-DCB

ortho-h ₄		ortho-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
3985	v _w			$\nu_{22} + \nu_{11} + \nu_{11}$
3925	v _w			$\nu_{13} + \nu_{11} + \nu_{22}$
3890	w			$\nu_{15} + \nu_{26}$
3823	w			$\nu_{36} + \nu_{22} + \nu_{25}$
		3789	v _w	$\nu_{26}^D + \nu_4^D$
3720	v _w			$\nu_{10} + \nu_{29} + \nu_4$
			3206	$\nu_{31}^D + \nu_{28}^D + \nu_{12}^D$
3184	w			$\nu_{26} + \nu_{19}$
			3185	$\nu_7^D + \nu_6^D + \nu_8$
3166	v _w			$\nu_4 + \nu_9 + \nu_{34}$
3150	v _w			$\nu_3 + \nu_{20}$
3116	w		3110	$\nu_{10}, \nu_{15}, \nu_4, \nu_{23}^D, \nu_{10}^D, \nu_{26}^D$
3103	m			ν_1
3094	m	3095	vs P(.32)	ν_1, ν_2
		3090	w	$2\nu_4^D$
		3080	w	$\nu_3^D + \nu_{32}^D$
3040	m	3041	w	ν_{25}, ν_{26}
3000	v _w			$\nu_3 + \nu_{21}$
2799	v _w			$\nu_6 + \nu_4$
		2790	v _w	$\nu_{26}^D + \nu_{34}^D$
2762	w			$\nu_4 + \nu_{31}$
2702	w		2704	$\nu_3 + \nu_{11}, \nu_{22}^D + \nu_{32}^D + \nu_5^D$
2685	v _w		2680	$\nu_{32} + \nu_{28}, \nu_{19}^D + \nu_6^D + \nu_{29}^D$

(continued next page)

Table 4.1.7 (continued)

ortho-h ₄		ortho-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
		2660 vw		$\nu_{19}^D + \nu_{29}^D + \nu_7^D$
2643 w		2640 w		$\nu_{31} + \nu_{29}, \nu_{34}^D + \nu_{15}^D + \nu_5^D$
2635 vw				$\nu_3 + \nu_{22}$
2600 w				$\nu_9 + \nu_4$
		2580 w		$\nu_{34}^D + \nu_{15}^D + \nu_{29}^D$
2550 vvw				$\nu_{22} + \nu_{15} + \nu_{30}$
2518 vw				$\nu_9 + \nu_5$
		2510 vvw		$\nu_{29}^D + \nu_7^D$
2494 w				$\nu_4 + \nu_{20}$
2462 w		2462 vvw		$2\nu_6, \nu_8^D + \nu_4^D$
2430 vvw				$\nu_{24} + \nu_3$
2320 w				$\nu_{32} + \nu_6$
		2308 vw		$\nu_8^D + \nu_{29}^D$
2300 w				$\nu_{32} + \nu_7$
		2297 s	2302 m P(.33)	ν_1^D, ν_2^D
2280 w			2297 m P(.33)	ν_2^D
		2250 m	2258 w	ν_{25}^D, ν_{26}^D
2228 vvs	2230 vs P(<.1)			ν_{27}, ν_3
		2224 vvw	2233 s P(<.1)	ν_{27}^D, ν_3^D
2203 vw				ν_{14}, ν_6
2180 w		2180 w		$2\nu_{32}, \nu_{36}^D + \nu_{20}^D + \nu_6^D$
2150 vvw				$\nu_{10} + \nu_{29}$
2137 vvw				$\nu_{34} + \nu_4$
2090 vvw				$\nu_{13} + \nu_{10} + \nu_9$
		2040 vvw		$\nu_{29}^D + \nu_{15}^D$
2000 m				$3\nu_{20} - \nu_{21}$
		1950 vw		$\nu_{22}^D + \nu_{28}^D$

Table 4.1.7 (continued)

ortho-h ₄		ortho-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
1970 m				$\nu_{14} + \nu_{20} + \nu_{15}$
1924 m				$\nu_{14} + \nu_{15}$
1889 m		1880 vvw		$\nu_{14} + \nu_{20}, \nu_{26}^D - \nu_{36}^D$
		1862 vw		$\nu_{29}^D + \nu_{11}^D$
1850 m				$2\nu_{20}$
1805 w		1800 w		$\nu_{19} + \nu_{32} + \nu_{34}, \nu_2^D - \nu_{35}^D$
1770 vw				$\nu_7 + \nu_{34}$
		1668 w		$\nu_8^D + \nu_{14}^D$
1655 w		1658 w		$\nu_{13} + \nu_{30}, \nu_{34}^D + \nu_7^D$
1630 w				$\nu_{23} + \nu_{29}$
		1620 w		$\nu_2^D - \nu_{10}^D$
		1600 w		$\nu_{26}^D - \nu_{15}^D$
		1580 w		$\nu_{26}^D - \nu_{20}^D$
1589 vs	1590 vs DP(.80)			ν_{28}
1570 vs	1575 m P(.28)			ν_4
		1552 vs	1559 s DP(.79)	ν_{28}^D
		1545 m	1552 m P(.16)	ν_4^D
1528 vw				$\nu_{19} + \nu_{14} + \nu_{22}$
1508 vvw				$\nu_9 + \nu_{11}$
1490 w				$\nu_4 + \nu_{20}$
1486 m	1485 m P(.12)			ν_5
1472 w				$\nu_{32} + \nu_{36}$
1450 s	1452 wb	1450 m	1442 m P(.28)	ν_{29}, ν_5^D
		1390 vs		ν_{29}^D

(continued next page)

Figure 4.1.7 (continued)

ortho-h ₄		ortho-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
1380 w		1379 w	1397 sh	$\nu_{22} + \nu_{14}, \nu_2 - \nu_8^D$
1346 w				$\nu_{14} + \nu_{36}$
		1330 vv		$\nu_9^D + \nu_{35}^D$
1295 m	1295 wb			ν_{30}
1290 w				$2\nu_{36} + \nu_{35}$
		1288 m		$\nu_6^D + \nu_{19}^D, \nu_8^D + \nu_{36}^D$
1270 vv				$\nu_{23} + \nu_{32}$
1243 w				$\nu_{11} + \nu_{21}$
		1239 w		$2\nu_{21}^D$
1230 s	1233 s (.43)			ν_6
1205 s	1210 s P(.16)			ν_7
1190 w				ν_{31}
		1188 w		$\nu_{15}^D + \nu_{34}^D, \nu_{29}^D - \nu_{24}^D$
1178 w	1177 m P (.59)			ν_8
	1157 vw			$\nu_{14} + \nu_{23}$
		1140 m	1143 m P(<.1)	ν_6^D
		1122 m	1126 s P(<.1)	ν_7^D
		1100 w	1099 w	ν_{31}^D
1092 w	1096 w			ν_{32}
1078 vv				$\nu_{36} + \nu_{10}$
1063 w		1063 w		$2\nu_{35}^D, \nu_{19}^D + \nu_8^D$
1030 m	1038 s P(<.1)			ν_9^D
		1021 w	1020 w	ν_{30}^D
		1018 w		$\nu_{29}^D - \nu_{36}^D, \nu_9^D + \nu_{23}^D$

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Table 4.1.7 (continued)

ortho-h ₄		ortho-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
997	vw			$\nu_{19} + \nu_{15}$
		980	w	$\nu_5 - \nu_{11}$ $\nu_5 - \nu_{11}$
970	s			ν_{14}
		959	vw	$\nu_6 - \nu_{23}$ $\nu_6 - \nu_{23}$
		948	vw	$\nu_{14} + \nu_{24}$ $\nu_{14} + \nu_{24}$
939	vw			$\nu_{22} + \nu_{35}$
922	w	918	m	ν_{20}, ν_8 ν_{20}, ν_8
		900	vw	$\nu_{31} - \nu_{24}$ $\nu_{31} - \nu_{24}$
		863	vw	$\nu_{35} + \nu_{36}$ $\nu_{35} + \nu_{36}$
846	w	853	w	ν_{15}, ν_{32} ν_{15}, ν_{32}
		836	m	ν_9 ν_9
804	s	805	w	$\nu_{33}, \nu_{28} - \nu_{14}$ $\nu_{33}, \nu_{28} - \nu_{14}$
		777	w	$\nu_2 - \nu_7 - \nu_{22}$ $\nu_2 - \nu_7 - \nu_{22}$
770	vs			ν_{21}, ν_{33} ν_{21}, ν_{33}
		750	s	ν_{14} ν_{14}
		735	w	ν_{16} ν_{16}
700	vs	707	s P(.13)	ν_{10} ν_{10}
		680	s	ν_{10} ν_{10}
664	vw	669	m	ν_{20} ν_{20}
		650	m	ν_{15} ν_{15}
		620	m	ν_{21} ν_{21}
		550	m P(<.1)	ν_{12} ν_{12}
565	w	565	m P(.21)	ν_{34}, ν_{12} ν_{34}, ν_{12}
		540	w	ν_{12}, ν_{34} ν_{12}, ν_{34}
540	sh			ν_{34} ν_{34}
530	s	530	m DP(.78)	ν_{35} ν_{35}

(continued next page)

Table 4.1.7 (continued)

ortho-h ₄		ortho-d ₄		Assignment
I.R.	Raman	I.R.	Raman	
		494 m	490 m DP (.82)	ν_{35}^D
472 m	480 vs P(.38)	470 m	470 m P(.33)	ν_{11}, ν_{11}^D
410 w	415 w			ν_{22}
		400 w	405 w	ν_{22}^D
392 vw				$\nu_{32} - \nu_{10}$
380 w	385 w			ν_{36}
		370 w		ν_{36}^D
360 vw	365 w			ν_{13}
	340 vw		336 w	ν_{13}^D
		292 w		$\nu_{29} - \nu_{31}^D$
206 m	202 w			ν_{24}
		200 m	200 w	ν_{24}^D
	174 w		174 w	ν_{18}, ν_{18}^D
180 m		180 m		ν_{23}, ν_{23}^D
148 w	144 m	148 w	148 m	ν_{19}, ν_{19}^D
80 m	74 m	80 m	74 m	$\left\{ \begin{array}{l} \nu_{15} - \nu_{21}, \nu_{21} - \nu_{10}, \\ \nu_{21} - \nu_{34}, \nu_{14} - \nu_{20} \end{array} \right.$
62 w		62 w		
	48 m		48 m	$\nu_5 - \nu_{29}^D, \nu_{10} - \nu_{21}^D$

CONCLUSIONS

The agreement between the observed and calculated Teller-Redlich product ratios, supports the assignments proposed for the fundamentals. The analysis is in agreement with those of other disubstituted benzenes, particularly the very few analyses that have been made for ring-deuterated compounds.

The out-of-plane vibrations were the more difficult to assign. Many of these vibrations can only be identified from infrared data, since in the Raman spectra these vibrations often give weak and depolarized bands at lower frequencies. Upon deuteration similar frequency shifts were found in this study with those of dihalogenobenzenes and diethynylbenzenes.

The vibrational study of the dicyanobenzenes has been very valuable in confirming the interpretation of the spectra of the diethynylbenzenes. The majority of the assignments for the latter are in agreement with those proposed in this thesis.

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