

Force Field for In-Plane Vibrations of Isophthalonitrile

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Summary. The general quadratic force field for the in-plane vibrations of isophthalonitrile was calculated by the semi-empirical MINDO/3 method. This force field was refined to the frequencies observed experimentally for isophthalonitrile and isotopic shifts of isophthalonitrile- $^{15}\text{N}_2$. The normal coordinates and the force field in internal coordinates were also calculated from the refined field.

Keywords. Isophthalonitrile; Force field.

Kräftefeld für die nichtebenen Schwingungen von Isophthalsäuredinitril

Zusammenfassung. Das allgemeine quadratische Kräftefeld für die nichtebenen Schwingungen von Isophthalsäuredinitril wurde mit der halbempirischen MINDO/3-Methode berechnet. Das Kräftefeld wurde aufgrund der experimentalen Frequenzen von Isophthalsäuredinitril und der Isotopen-Verschiebungen von Isophthalsäuredinitril- $^{15}\text{N}_2$ verfeinert. Die Normalkoordinaten und das Kräftefeld in inneren Koordinaten wurden auch vom verfeinerten Kräftefeld berechnet.

Introduction

A previous work [1] reported a vibrational analysis of the isophthalonitrile molecule and its isotopomer, isophthalonitrile- $^{15}\text{N}_2$ in which their infrared and Raman spectra were recorded and an assignment of their normal vibrations was made. Prior to this, Castro-Pedrozo et al. [2] carried out the first assignment of the vibrational spectra of isophthalonitrile and isophthalonitrile- d_3 .

The present work made use of the assignments of [1] as the starting-point for the calculation of the harmonic force field of the in-plane vibrations of isophthalonitrile and its derivative with $^{15}\text{N}_2$. The MINDO/3 method was employed to calculate a general quadratic force field which was refined to the experimental frequencies and isotopic shifts of these molecules, respectively. The refined force field was transformed to the space of the internal coordinates by the method of Kuczera et al. [3] to obtain the canonic field which will facilitate the comparison of the force constants with similar molecules and also allow for their transference.

Results and Discussion

The FORCE program [4] was used to obtain the starting force field by calculating the analytical first derivatives and the numerical second derivatives of the energy

with respect to the Cartesian coordinates. The program used a Hamiltonian MINDO/3 and prior optimization of the structure of the isophthalonitrile molecule by this semiempirical method was required so that the derivations could be carried out at the minimum energy point. The calculations were carried out using a UNIVAC 1100/82 computer and a Perkin-Elmer 3220 minicomputer. The final geometry given in Table 1 shows that, as was to be expected, the isophthalonitrile

Table 1. Calculated geometry using the MINDO/3 method for the isophthalonitrile molecule

Bond lengths in Å		Angles in degrees	
C ₁ —C ₂	1.404	C ₁ —C ₂ —C ₃	121.6
C ₂ —C ₃	1.424	C ₂ —C ₃ —C ₄	116.4
C ₃ —C ₄	1.423	C ₃ —C ₄ —C ₅	124.0
C ₁ —H ₇	1.105	C ₆ —C ₁ —C ₂	120.0
C ₂ —H ₈	1.107	C ₂ —C ₁ —H ₇	120.0
C ₃ —C ₉	1.456	C ₁ —C ₂ —H ₈	118.7
C ₄ —H ₁₀	1.108	C ₃ —C ₂ —H ₈	119.7
C ₉ —N ₁₃	1.161	C ₂ —C ₃ —C ₉	121.8
		C ₃ —C ₄ —H ₁₀	118.6

molecule is planar with a C_{2v} symmetry. As a search of the bibliography revealed no experimental data about isophthalonitrile geometry, all calculations used the optimized geometry obtained by MINDO/3. In agreement with this and with the axes orientation according to the rules of the Joint Commission for Spectroscopy [5], the in-plane vibrations of the isophthalonitrile molecule were distributed as follows: $13A_1 + 12B_2$.

The refinement process was carried out in the space of the independent symmetry coordinates which were calculated following the algorithm described in [6] using the diagonalization of BB' . This B matrix describes the primitive symmetry coordinates as $s = Bx$. Figure 1 displays the in-plane internal coordinates defined for isophthalonitrile and the primitive symmetry coordinates displayed in Table 2 were constructed by applying the projection operators of the corresponding symmetry species. The elimination of redundancies by the method in [6] gave a set of independent symmetry coordinates for each species of symmetry and these were expressed as linear combinations of the primitive symmetry coordinates. The theoretical force field was related to these new coordinates by carrying out the transformation $F_{sym} = B'^{-1}F_{car}B^{-1}$ because the FORCE program calculates the force constants in Cartesian coordinates. This B describes in turn the independent symmetry coordinates. The great size of the F_{sym} matrixes, one for each species of symmetry, and also the matrixes of the independent symmetry coordinates mentioned above preclude their publication in this work, but are available for consultation on request.

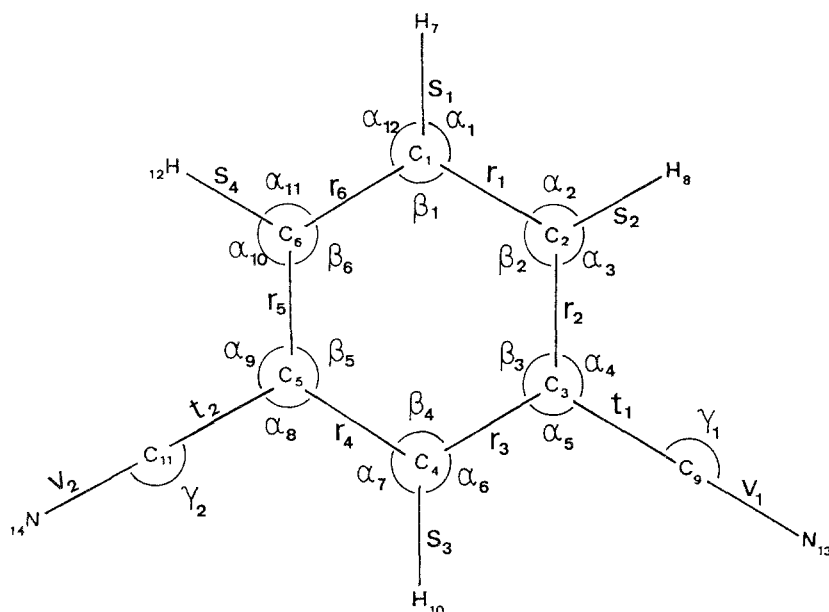


Fig. 1. In-plane internal coordinates for isophthalonitrile

Table 2. Primitive symmetry coordinates for the in-plane vibrations of isophthalonitrile; each coordinate is constructed by applying the species projection operator to each internal coordinate

Species A_1

s_1-s_8 : $r_1; r_2; r_3; s_1; s_2; s_3; t_1; v_1$

s_9-s_{15} : $2\beta_1-\alpha_1-\alpha_{12}; 2\beta_2-\alpha_2-\alpha_3; \alpha_2-\alpha_3; 2\beta_3-\alpha_4-\alpha_5; \alpha_4-\alpha_5; 2\beta_4-\alpha_6-\alpha_7; \gamma_1$

Species B_2

$s_{16}-s_{21}$: $r_1; r_2; r_3; s_2; t_1; v_1$

$s_{22}-s_{28}$: $\alpha_1-\alpha_{12}; 2\beta_2-\alpha_2-\alpha_3; \alpha_2-\alpha_3; 2\beta_3-\alpha_4-\alpha_5; \alpha_4-\alpha_5; \alpha_6-\alpha_7; \gamma_1$

Up to 25% of the total numbers of force constants of each species of symmetry were simultaneously refined and in each case the selection was limited to those which had the largest weights in the P.E.D. matrix. To increase the number of experimental data, an initial phase of the refinement process employed the observed frequencies for isophthalonitrile- d_3 derivative published in [2] in addition to our data and this considerably reduced the weighted quadratic errors. In a second phase, only the frequencies of the normal derivatives and those labelled with ^{15}N were considered. This limitation reduced the number of experimental data and consequently the number of force constants in simultaneous refinement. The fact that the differences between the calculated and observed frequencies for both molecules were smaller was thought to be due to a greater consistency of the experimentally data obtained by us. Table 3 shows the selected frequencies for isophthalonitrile and also the isotopic shifts for isophthalonitrile- $^{15}\text{N}_2$, together with their assignments. It can be

Table 3. Observed and calculated frequencies (cm^{-1}) for in-plane vibrations of isophthalonitrile and isophthalonitrile- $^{15}\text{N}_2$ (isotopic shifts)

	Isophthalonitrile			Isophthalonitrile- $^{15}\text{N}_2$			Assignments
	Obs.	Calc.	Dif.	Obs.	Calc.	Dif.	
Species A_1	3 079.9	3 109.6	- 29.7	- 0.5	- 0.2	- 0.3	$\nu(\text{CH})$, 20a
	3 073.6	3 075.4	- 1.8	- 0.3	0.0	- 0.3	$\nu(\text{CH})$, 2
	3 047.9	2 992.4	55.5	- 0.7	- 0.9	0.2	$\nu(\text{CH})$, 7a
	2 236.7	2 241.8	- 5.1	- 26.7	- 26.4	- 0.3	$\nu(\text{CN})$
	1 577.1	1 606.8	- 29.7	- 0.1	- 0.5	0.4	$\nu(\text{CC})$, 8a
	1 424.5	1 424.0	0.5	- 1.6	- 0.5	- 1.1	$\nu(\text{CC})$, 19a
	1 235.8	1 241.1	- 5.3	- 5.8	- 4.5	- 1.3	$\nu(\text{CX})$, 13
	999.8	1 000.8	- 1.0	0.0	- 1.9	1.9	$\delta(\text{CC})$, 12
	981.6	978.8	2.8	- 1.3	- 2.9	1.6	$\delta(\text{CH})$, 18a
	701.0	695.3	5.8	- 0.8	- 3.2	2.4	$\nu(\text{CC})$, 1
	518.3	513.5	4.8	- 1.5	- 3.6	2.1	$\delta(\text{CN})$
	458.5	462.6	- 4.1	- 5.2	- 7.8	2.6	$\delta(\text{CX})$, 9a
	368.8	369.4	- 0.6	0.0	- 4.1	4.1	$\delta(\text{CC})$, 6a
Species B_2	3 109.8	3 153.4	- 43.6	- 0.8	- 0.2	- 0.6	$\nu(\text{CH})$, 20b
	2 235.9	2 293.4	- 57.5	- 26.2	- 27.1	0.9	$\nu(\text{CN})$
	1 598.3	1 612.9	- 14.6	- 1.6	- 0.3	- 1.3	$\nu(\text{CC})$, 8b
	1 481.5	1 524.1	- 42.6	- 0.7	- 1.9	- 1.2	$\nu(\text{CC})$, 19b
	1 334.0	1 330.8	3.2	- 0.9	- 1.4	0.5	$\nu(\text{CC})$, 14
	1 271.8	1 271.5	0.3	- 0.4	- 0.9	0.5	$\delta(\text{CH})$, 3
	1 148.0	1 144.1	3.9	- 0.6	- 1.2	- 0.6	$\delta(\text{CH})$, 9b
	1 104.3	1 101.8	2.5	0.0	- 0.7	0.7	$\delta(\text{CH})$, 18b
	894.1	895.3	1.2	- 4.1	- 6.1	2.0	$\nu(\text{CX})$, 7b
	504.1	504.6	0.5	- 1.8	- 1.2	- 0.6	$\delta(\text{CN})$
	-	290.7	-	-	- 1.4	-	$\delta(\text{CC})$, 6b
	202.9	202.9	0.0	- 4.3	- 2.6	- 1.7	$\delta(\text{CX})$, 15

seen that the greatest differences are seen in the higher frequencies. The errors displayed by 80% of these values are less than 1%; in the other cases the errors were always below 3%. The best results for the isotopic shifts were found for the $\nu(\text{CN})$, $\nu(\text{CH})$, and $\nu(\text{CX})$ stretching vibrations, while the calculated shifts for the stretching and in-plane bending vibrations of the benzene ring were, in general, overestimated by an amount between 1 and 2 cm^{-1} .

The description of the calculated normal modes was done by calculating the Cartesian atomic displacements matrix. Figure 2 presents the results for the in-plane vibrations which are in complete agreement with the assignments reported in [1] for this molecule except those for the $\delta(\text{CX})$ and $\delta(\text{CN})$ deformation modes whose descriptions suggest to permute our previous assignments. This, nevertheless, does not contradict the experimental data because they are two vibrations of the same species with very close vibrational frequencies; both appear polarized in the solution Raman spectra and, in addition, they have high isotopic shifts which makes their

Table 4. Canonic force field; only the diagonal force constants and the most important off-diagonal ones are shown (all units mdyn/Å)

Type	Force const.	Type	Force const.
r_1	5.8017	$\alpha_4\alpha_5$	-1.6339
r_2	5.2781	$\alpha_4\alpha_8$	-1.6051
r_3	6.2428	$\alpha_4\alpha_9$	1.0990
s_1	5.0980	$\alpha_5\alpha_8$	1.8406
s_2	5.0642	$\beta_1\beta_4$	-0.6813
s_3	5.1799	$\beta_4\gamma_1$	-0.6088
t_1	6.2818	$\gamma_1\gamma_2$	-1.1954
v_1	18.7266	$r_3\alpha_4$	-1.1730
α_1	0.9571	$r_4\alpha_4$	-1.1805
α_2	0.6839	$r_3\alpha_5$	1.8333
α_3	0.3869	$r_4\alpha_5$	1.4203
α_4	1.7353	$r_3\beta_1$	0.9406
α_5	2.3645	$r_1\beta_2$	-0.9492
α_6	0.5257	$r_3\beta_4$	-1.2963
β_1	0.9756	$r_3\beta_6$	0.9906
β_2	0.9482	$r_3\gamma_1$	1.1477
β_3	0.8320	$r_3\gamma_2$	-0.9312
β_4	1.1693	$\alpha_4\gamma_1$	-1.1938
r_1r_4	2.0269	$\alpha_4\gamma_2$	1.0978
r_2r_5	2.3189	$\alpha_5\beta_4$	-1.0213
r_3r_4	1.1746	$\alpha_5\gamma_1$	1.4643
t_1v_1	1.4402	$\alpha_5\gamma_2$	-1.4207

Table 5. Force constants calculated by methods different to that of Kuczera et al. [3] for benzene and the CN group

	$\nu(\text{CC})$	$\nu(\text{CH})$	$\beta(\text{CCC})$	$\alpha(\text{CCH})$
Benzene [10]	7.015	5.125	0.881	0.563
Benzene [11]	7.006	5.022	1.461	0.946
	$\text{H}_3\text{C}-\text{CN}$ [12]	$\text{H}-\text{CN}$ [13]	$\text{Cl}_3\text{C}-\text{CN}$ [14]	
$\nu(\text{CN})$	18.11	17.88	17.71	

assignment difficult. It is also noteworthy the coupling of vibration 1; $\nu(\text{CC})$ with $\nu_s(\text{CX})$ as predicted in [7] which confirms the assignment proposed by us [1]. Likewise, the coupling between the 7b; $\nu(\text{CX})$ and 6b; $\delta(\text{CC})$ becomes evident and gives account of the low frequency of the former as well as the isotopic shift of the latter.

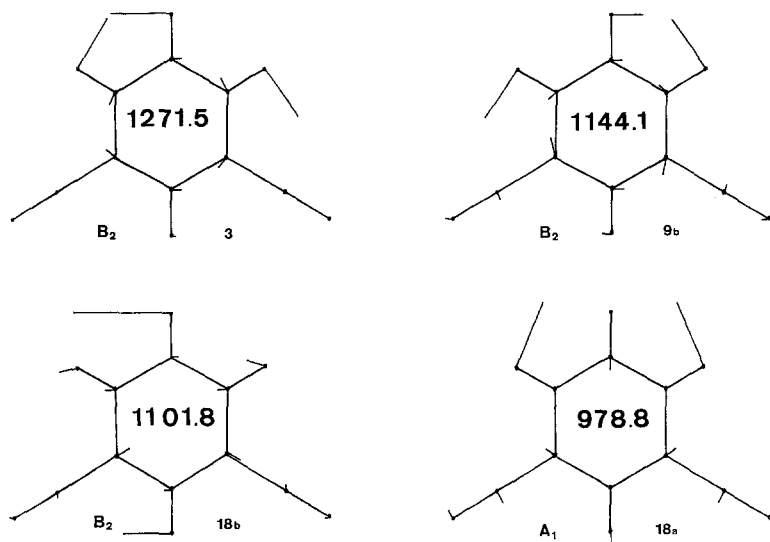


Fig. 2A

Fig. 2A-G. Calculated Cartesian displacements for the in-plane vibrations for isophthalonitrile

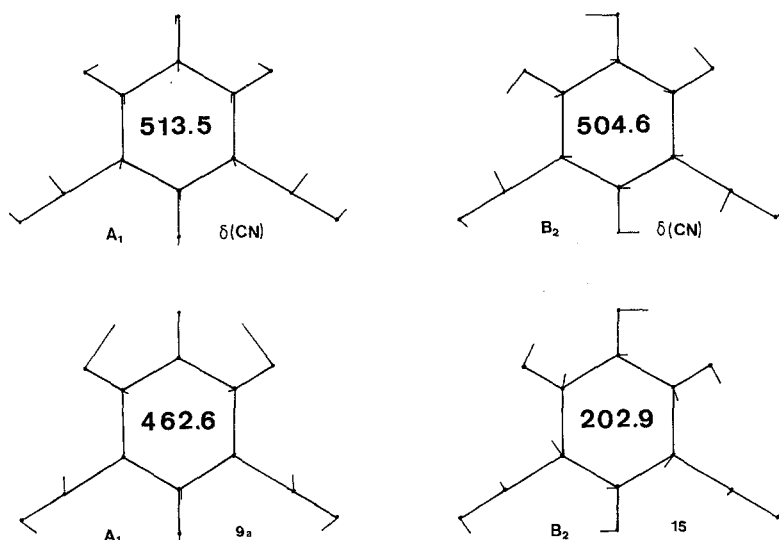


Fig. 2B

Finally, the refined force constants were transformed to the space of the internal coordinates using the matrix product $F_{int} = U' F_{sym} U$ where U defines the independent symmetry coordinates as $S = UR$. In this way, the unequivocal F_{int} field was defined because it was derived from the F_{sym} in independent coordinates [3]. Because the F_{int} matrix comprises 34 internal coordinates, Table 4 only contains the diagonal force constants and those out-of-diagonal force constants greater than 30%, approx., in absolute values of the related diagonal constants. The complete results are available on request. The data in Table 5 allow for the comparison between the diagonal force constants of the benzene molecule and those molecules with the $C \equiv N$ bond, although it should be mentioned that they were obtained by methods

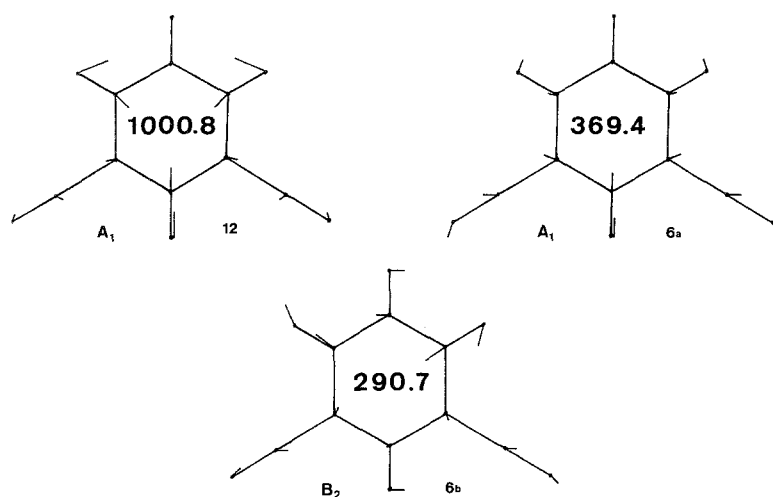


Fig. 2C

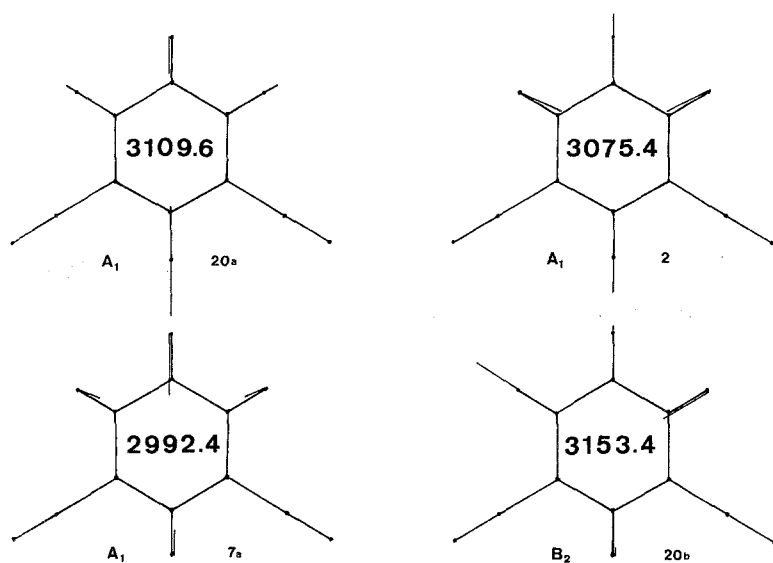
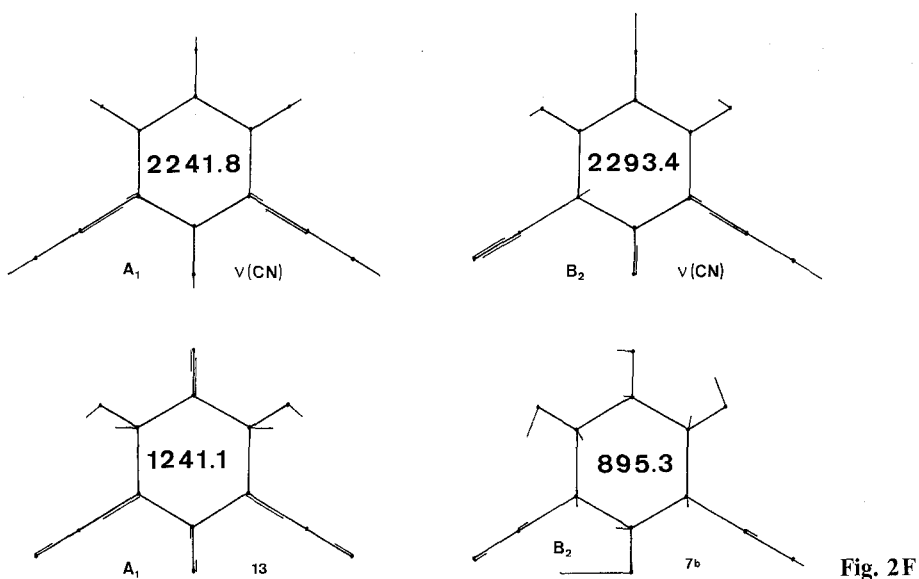
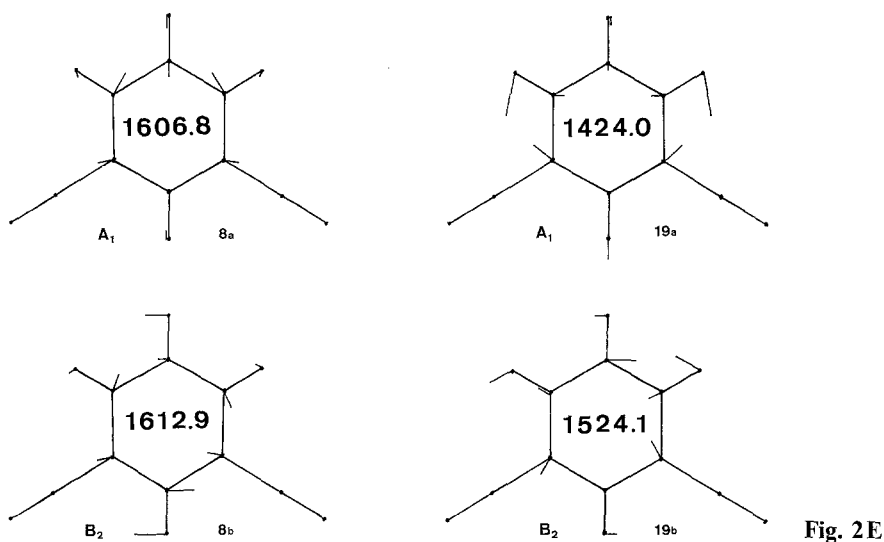


Fig. 2D

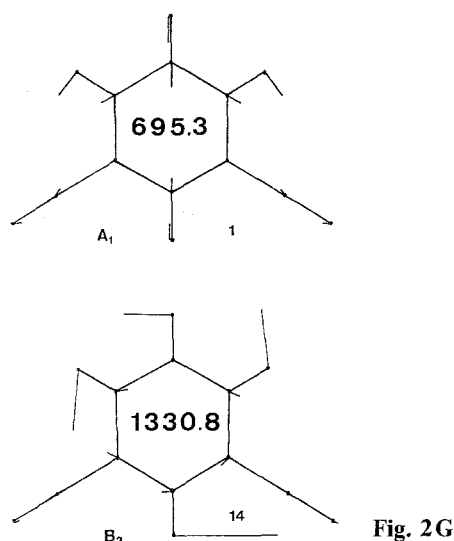
different of Kuczera's one. The greatest similarity is shown by the $\nu(\text{CN})$ force constants; of the rest, those of $\text{C}-\text{X}$ bond stretching have the largest value and this is an indication of the strength conferred by their participation in the ring aromaticity. For the in-plane deformations, the greatest force constants are concentrated in the carbon atoms which support the substituent groups, as could be expected.

The value of $18.727 \text{ mdyne}/\text{\AA}$ obtained for the $\nu(\text{CN})$ force constants can also be deduced theoretically from the bond length by the following equation:

$$F = ar^{-b}, \quad (1)$$



where F is the force constant, r is the bond length, and a and b are the empirical parameters calculated by Byler et al. [8] from a series of compounds with $C\equiv N$ bonds and which take the values of: $a = 37.3$; $b = 5.35$. The value of F given by substituting the optimized bond length of 1.161 \AA obtained in this laboratory by MINDO/3 was 16.782 mdyn/\AA . Although the resulting error, is well within the order of magnitude of those expected when using Eq. (1), we think that it can be decreased if the experimentally derived solid state bond length is known, because the MINDO/3 method calculates the bond lengths for isolated molecules in the gaseous state, while the observed frequencies used in the refinement process are those of the molecule in the crystalline state. For instance, for the terephthalonitrile molecule



[9], the $\nu(\text{CN})$ force constant was calculated from the crystalline molecule bond length by Eq. (1); the error was 0.55%, in comparison with the “experimentally derived” force constant. Taking this into account, the isophthalonitrile bond length can be calculated from the value given in Table 4 for the $\nu(\text{CN})$ stretching force and, in fact, this gave a distance of 1.137 Å which should be closer to the real value of the solid state molecular bond length than that calculated by MINDO/3 1.161 Å.

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