FORCE FIELD FOR IN-PLANE VIBRATIONS OF TEREPHTHALONITRILE

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The general quadratic force field for the in-plane vibrations of terephthalonitrile was calculated by the semi-empirical MINDO/3 method. This force field was refined to the frequencies observed experimentally for terephthalonitrile and isotopic shifts of terephthalonitrile-$[^{15}N_2]$. The refined frequencies reproduce the experimental data with errors less than 0·5%. The normal coordinates and the force field in internal coordinates were also calculated from the refined field.

The IR and Raman spectra of the terephthalonitrile molecule were first studied by Barraclough et al.[1]. More recently, Castro-Pedrozo et al.[2] carried out an assignment of the vibrational spectra of terephthalonitrile and terephthalonitrile-$[^2H_4]$. In addition, several recent publications[3-6] deal with the molecular structure of terephthalonitrile in the crystalline or gaseous state. These studies demonstrate that in the gaseous phase the molecule belongs to the D_{2h} group. In the solid phase, some distortions of the molecule are produced by intermolecular interactions, although these are of small magnitude and so, in this phase, the molecular symmetry is also D_{2h}.

A previous study in this laboratory[7] recorded the IR and Raman spectra of the terephthalonitrile and terephthalonitrile-$[^{15}N_2]$ molecules which facilitated a new assignment of their normal vibrations. The present work made use of these new assignments as the starting point for the calculation of a harmonic force field for the in-plane vibrations of these two molecules. The semi-empirical MINDO/3 method was used to obtain a force field from which a process of refinement adjusted to experimental data was carried out. The method had been successfully employed in previous studies[8-9].

RESULTS AND DISCUSSION

In agreement with the D_{2h} symmetry, and orientating the molecule according to the rules given in ref.[10], the in-plane vibrations of terephthalonitrile are distributed in the following way: $7A_g + 6B_{3g} + 6B_{1u} + 6B_{2u}$.

The refinement process was taken to the space of the independent symmetry coordinates and their calculation followed the algorithm described in ref.[8] which is based on the diagonalization of the **B$\tilde{B}$** matrix. All the calculations were carried out with a UNIVAC 1100/82 computer and a Perkin–Elmer 3220 minicomputer. Figure 1 shows the defined in-plane internal coordinates for terephthalonitrile from which, by applying the projection operators of the corresponding symmetry group, the following primitive symmetry coordinates were constructed (see also Table I). The elimination of redundancies by the previously mentioned method provided a set of independent symmetry coordinates for each species of symmetry, expressed as linear combinations of the primitive symmetry coordinates.

Prior to this calculation, the semiempirical force field was obtained. This required
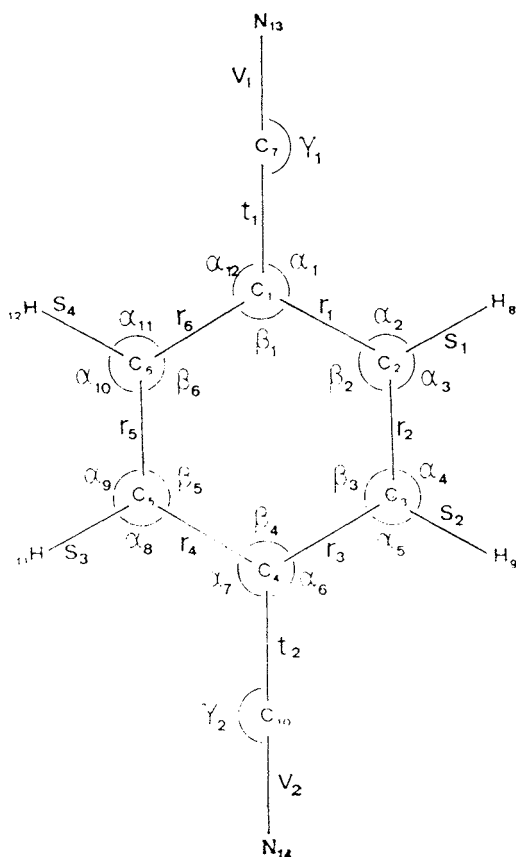

FIG. 1

Out-of-plane internal coordinates for terephthalonitrile

the previous optimization of the molecular structure until a minimum potential geometry was reached according to the hamiltonian MINDO/3. In Table II this geometry is compared with the experimentally obtained geometry of the molecule in gaseous phase; the quality of fit is satisfactory, especially for the C—CN, C=N, and C—CH bonds. From this geometry, and with the FORCE program[11] an initial

TABLE I

Primitive symmetry coordinates for in-plane vibrations of terephthalonitrile

Species A_g

$s_1 - s_5 \quad : r_1 ; \quad r_2 ; \quad s_1 ; \quad t_1 ; \quad v_1$
$s_6 - s_8 \quad : 2\beta_1 - \alpha_1 - \alpha_{12} ; \quad 2\beta_2 - \alpha_2 - \alpha_3 ; \quad \alpha_2 - \alpha_3$

Species B_{3g}

$s_9 - s_{10} \quad : r_1 ; \quad s_1$
$s_{11} - s_{14} : \alpha_1 - \alpha_{12} ; \quad 2\beta_2 - \alpha_2 - \alpha_3 ; \quad \alpha_2 - \alpha_3 ; \quad \gamma_1$

Species B_{1u}

$s_{15} - s_{18} : r_1 ; \quad s_1 ; \quad t_1 ; \quad v_1$
$s_{19} - s_{21} : 2\beta_1 - \alpha_1 - \alpha_{12} ; \quad 2\beta_2 - \alpha_2 - \alpha_3 ; \quad \alpha_2 - \alpha_3$

Species B_{2u}

$s_{22} - s_{24} : r_1 ; \quad r_2 ; \quad s_1$
$s_{25} - s_{28} : \alpha_1 - \alpha_{12} ; \quad 2\beta_2 - \alpha_2 - \alpha_3 ; \quad \alpha_2 - \alpha_3 ; \quad \gamma_1$

TABLE II

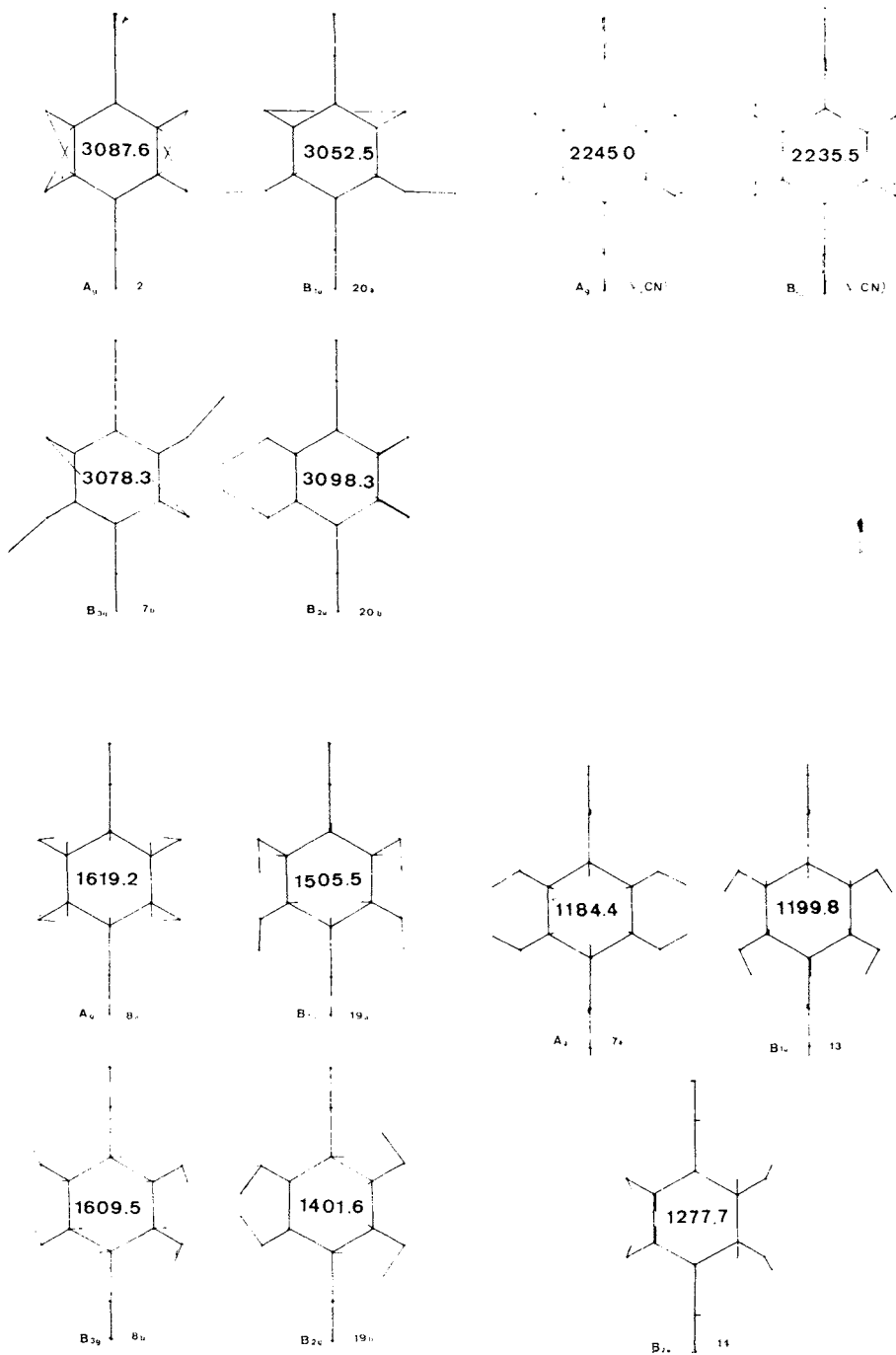Experimental and calculated geometries of the terephthalonitrile molecule

Bond	Bond length, Å[a]		Bonds	Angle, deg	
	exp.[b]	MINDO/3		exp.[b]	MINDO/3
C1—C2	1·396	1·424	C1—C2—C3	119·0	122·2
C2—C3	1·392	1·403	C6—C1—C2	122·1	115·7
C1—C7	1·453	1·456	C1—C7—N13	180·0	180·0
C7—N13	1·165	1·161	C1—C2—H8	120·5	119·5
C2—H8	1·073	1·106	C7—C1—C2	119·0	122·1
			C3—C2—H8	120·5	119·5

[a] 1 Å = 10^{-10} m; [b] ref.[6]

set of force constants was calculated by an analytical first derivation and a second numerical derivation of the energy with respect to the cartesian coordinates. This gave force constants in cartesian coordinates which were transformed to the space of the independent symmetry coordinates by the conversion $F_{sym} = \widetilde{B}^{-1}F_{car}B^{-1}$, which reduced the total number of force constants to be refined. The F_{sym} matrices, one for each species of symmetry, and the matrices of the independent symmetry coordinates previously referred to, were omitted from this work they are available for consultation on request.

The refinement process was applied initially to the experimental data for tere-phthalonitrile and its $[^{15}N_2]$ derivative, and also to the frequencies published in ref.[2] for the terephthalonitrile-$[^2H_4]$ derivative. This permitted the simultaneous refine-ment of a greater number of force constants. In the case of B_{3g}, as many as 50% were refined; for the rest, it was around 40%. The final result was obtained by only refining the frequencies of the natural derivative and of that labelled with $^{15}N_2$ so that the number of force constants in simultaneous refinement was reduced because now less experimental data were available. A closer agreement between the observed and calculated frequencies was achieved by this second refinement as this may be seen in Table III. It is noteworthy to stress that the calculated frequency of 297·1 cm^{-1} for the 15, B_{2u} normal mode in terephthalonitrile is in agreement with the interval which is given in ref.[12] for this vibration, $\delta(CX)$, which was not seen in the present experiment. This is a further confirmation that the force field obtained is accurate. The isotopic shift of $-6·8$ cm^{-1} calculated for this vibration is of expected magnitude for a C—X mode with large amplitudes of vibration for the nitrogen atom, as may be seen in Fig. 2, in which the atomic displacements for each frequency are shown to give a better description of the shape and symmetry of each normal mode. In every case, the atomic displacements were in agreement with our assignments[7]. The atomic displacement matrix is available on request.

Finally, the transformation of the refined force constants to the space of the internal coordinates was carried out. The improved physical interpretation obtained will facilitate their future comparison with those of similar molecules. The transformation employed was $F_{int} = \widetilde{U}F_{sym}U$. The F_{int} field defined in this way is unequivocal in spite of being a function of the dependent coordinates as it was calculated from the F_{sym} force field in independent coordinates[13]. Because 34 internal coordinates were defined, the dimensions of the F_{int} matrix make its printing difficult. For this reason, Table IV only contains the diagonal force constants and those off-diagonal ones greater, in absolute values, than 30% of the related diagonal constants approximately. The complete results are available on request. The diagonal force constants can be compared with those of benzene and of molecules with the C=N bond given in Table V, although, these cases were deduced by employing methods different of that of Kuczera[13]. As can be seen, the value obtained in this present work for the $v(C-N)$ force constant is very similar to that obtained for other molecules like

3087.6   A$_g$ 2

3052.5   B$_{1u}$ 20$_a$

2245 0   A$_g$ \ CN

2235 5   B$_{2u}$ \ CN)

3078.3   B$_{3u}$ 7$_b$

3098.3   B$_{2u}$ 20$_b$

1619.2   A$_g$ 8$_a$

1505.5   B$_{1u}$ 19$_a$

1184.4   A$_g$ 7$_a$

1199.8   B$_{1u}$ 13

1609.5   B$_{3g}$ 8$_b$

1401.6   B$_{2u}$ 19$_b$
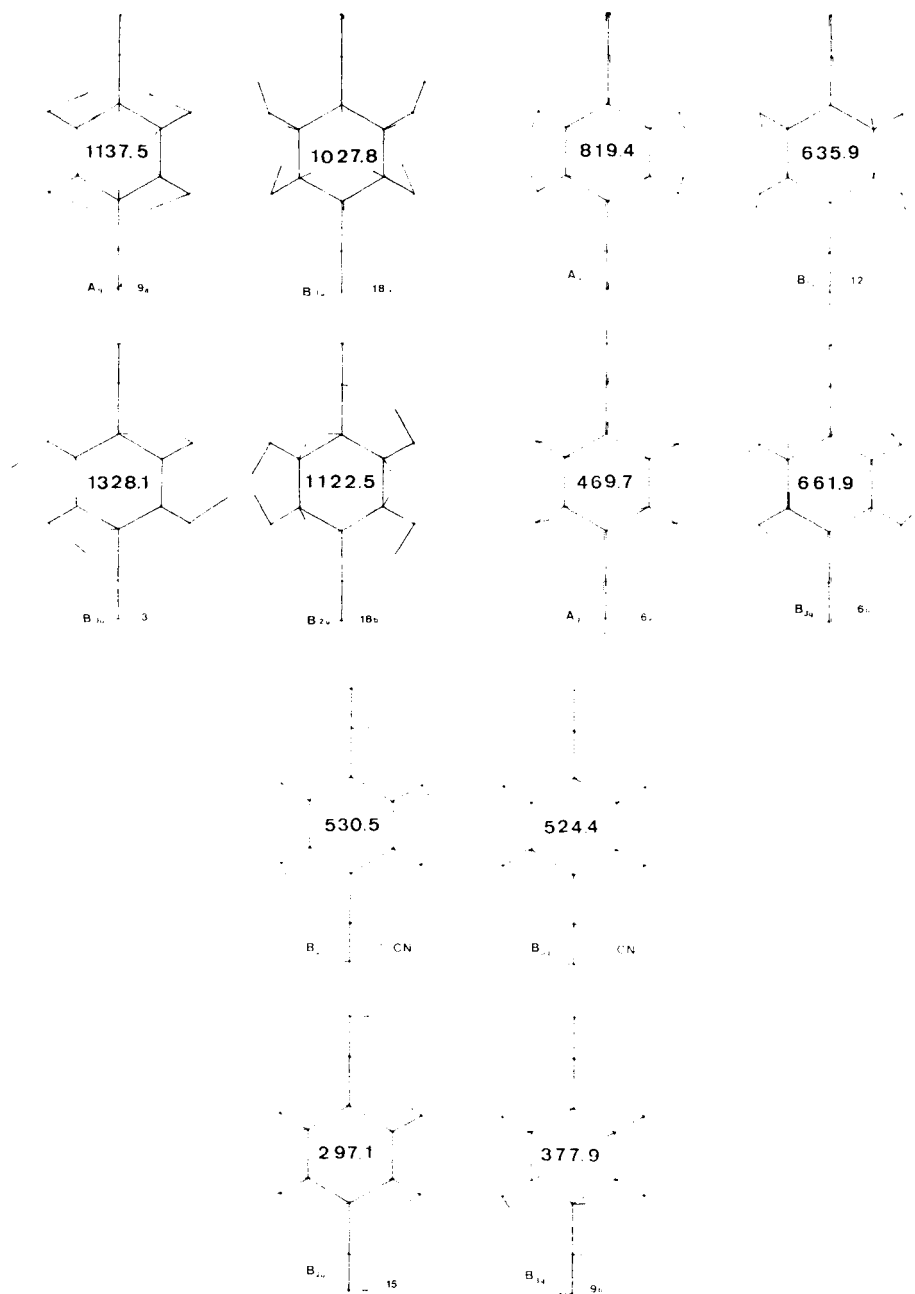
1277.7   B$_{1g}$ 14

FIG. 2

Calculated Cartesian displacements for the out-of-plane vibrations for terephthalonitrile

H—CN or Cl_3C—CN. This suggests that they are affected little by the presence of the benzene ring. The force constant relevant to the stretching $v(C$—CN) was calculated greater than that for the $v(C$—C) stretching which would indicate the participation of substituent groups in the aromaticity of the ring with the result that the (C—CN) bond is strengthened in comparison with those of the benzene ring in which the greatest force constants correspond with C_2—C_3 and C_5—C_6 bonds which could be interpreted as a significant involvement of resonant forms of the quinone

TABLE III

Observed and calculated frequencies (cm⁻¹) for in-plane vibrations of terephthalonitrile and terephthalonitrile-[¹⁵N₂] (isotopic shifts)

Species	Terephthalonitrile			Terephthalonitrile-[¹⁵N₂]			Assignments
	obs.	calc.	dif.	obs.	calc.	dif.	
A_g	3 088·1	3 087·6	0·5	0·0	−0·1	0·1	$v(CH)$, 2
	2 242·8	2 245·0	−2·2	−28·7	−28·8	0·1	$v(CN)$
	1 619·4	1 619·2	0·2	0·0	0·0	0·0	$v(CC)$, 8a
	1 183·5	1 184·4	−0·9	−5·2	−5·2	0·0	$v(CX)$, 7a
	1 134·4	1 137·5	−2·9	−0·2	−0·3	0·1	$\delta(CH)$, 9a
	820·2	819·4	0·8	−3·6	−3·7	0·1	$v(CC)$, 1
	470·0ᵃ	469·7	0·3	− −	—	−−	$\delta(CC)$, 6a
B_{3g}	3 078·2	3 078·3	−0·1	−0·3	−0·2	−0·1	$v(CH)$, 7b
	1 609·4	1 609·5	−0·1	0·0	0·0	0·0	$v(CC)$, 8b
	1 328·0	1 328·1	−0·1	−1·4	−1·2	−0·2	$\delta(CH)$, 3
	661·9	661·9	0·0	−1·4	−1·2	−0·2	$\delta(CC)$, 6b
	524·3	524·4	−0·1	−1·5	−0·3	−0·2	$\delta(CN)$
	377·9	377·9	0·0	−4·1	−3·8	−0·3	$\delta(CX)$, 9b
B_{1u}	3 053·4	3 052·3	0·9	−0·4	−0·5	0·1	$v(CH)$, 20a
	2 233·9	2 235·5	−1·6	24·6	−24·2	−0·4	$v(CN)$
	1 504·4	1 505·5	−1·1	0·3	−0·3	0·0	$v(CC)$, 19a
	1 200·4	1 199·8	0·6	−6·3	−6·0	−0·3	$v(CX)$, 13
	1 027·6	1 027·8	−0·2	−1·0	−0·8	−0·2	$\delta(CH)$, 18a
	636·5	635·9	0·6	−0·8	−0·9	0·1	$\delta(CC)$, 12
B_{2u}	3 098·7	3 098·3	0·4	0·2	−0·3	0·1	$v(CH)$, 20b
	1 404·4	1 404·6	−0·2	−0·3	−0·3	0·0	$v(CC)$, 19b
	1 277·3	1 277·7	−0·4	−0·9	−0·8	−0·1	$v(CC)$, 14
	1 122·6	1 122·5	0·1	−0·5	−0·6	0·1	$\delta(CH)$, 18b
	530·5	530·5	0·0	−1·1	−1·1	0·0	$\delta(CN)$
	− −	297·1	− −		−6·8	− −	$\delta(CX)$, 15

ᵃ Ref.[2].

type in the structure of the terephthalonitrile molecule according to the theory of localized bonds.

TABLE IV

Canonic force field. Only the diagonal force constants and the most important off-diagonal ones are shown (all units N m^{-1} . 10^2; M multiplicity)

Type	Force constant	M	Type	Force constant	M
r_1	6·8565	4	$r_2 s_1$	1·5309	4
r_2	8·1112	2	$t_1 v_1$	1·7933	2
s_1	4·5715	4	$\alpha_1 \alpha_{12}$	−1·2962	2
t_1	8·3662	2	$\beta_1 \beta_4$	0·5396	1
v_1	17·9784	2	$\alpha_1 r_1$	1·9828	4
α_1	1·9163	4	$\alpha_1 r_3$	−1·4640	2
α_2	0·6755	4	$\alpha_2 r_1$	1·1344	4
α_3	0·6364	4	$\beta_1 r_1$	−1·0675	4
β_1	1·2402	2	$\beta_2 r_4$	1·0386	4
β_2	1·1194	4	$\gamma_1 r_3$	−1·1373	2
γ_1	1·7177	2	$\gamma_1 r_4$	1·1373	2
$r_1 r_4$	2·4607	2	$\gamma_1 \alpha_1$	1·1237	2
$r_2 r_5$	4·6260	1	$\gamma_1 \alpha_{12}$	−1·1237	2
$r_1 s_3$	−1·8629	4			

TABLE V

Force constants calculated by different methods (all units N m^{-1} . 10^2). a For benzene molecule

Literature	$v(CC)$	$v(CH)$	$\beta(CCC)$	$\alpha(CCH)$
Ref.[15]	7·015	5·125	0·881	0·563
Ref.[16]	7·006	5·022	1·461	0·946

b For the CN group

Vibration	H_3C—CN^a	H—CN^b	Cl_3C—CN^c
$v(CN)$	18·11	17·88	17·71

^{a} Ref.[17]; ^{b} ref.[18]; ^{c} ref.[19].

TABLE VI

The results of the application of the equation proposed by Byler et al.[14] for different terephthalo-nitriles geometries (bond lengths in Å $= 10^{-10}$ m; force constants in N m^{-1} . 10^2)

Geometry	$r(C\equiv N)$	F(calc.)	F(exp.)$-F$(calc.)	Error, %
Exp.(gas.)^a	1·165	16·477	1·501	8·35
Exp.(sol.)^a	1·145	18·076	−0·098	0·55
MINDO/3	1·161	16·782	1·196	6·65

^{a} Ref.[6].

The value of 1 797·8 N m^{-1} for the $\nu(C\equiv N)$ force constant could be theoretically calculated from the bond length using the equation:

$$F = a \cdot r^{-b}, \qquad (1)$$

where F is the force constant, r is the bond length, and a and b are empirical parameters calculated by Byler et al.[14] from a series of compounds with C$\equiv$N bonds which take the following values: $a = 37·3$; $b = 5·35$. The results are given in Table VI in which it can be seen that the best agreement is obtained for the solid-state geometry; this is consistent with the fact that the force constants have been refined to the experimental frequencies of the solid molecule and it also provides further confirmation of Eq. (1). For the other two geometries the results are similar as the MINDO/3 method calculates the geometry of the isolated molecule in the gaseous state.

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