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Infrared and Raman spectra of terephthalonitrile and terephthalonitrile-$^{15}N_2$. Force field for out-of-plane vibrations

J. F. ARENAS, J. I. MARCOS and F. J. RAMÍREZ
Department of Physical Chemistry, Faculty of Sciences, 29071 Málaga, Spain

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Abstract—A general assignment of the vibrational spectra of terephthalonitrile and terephthalonitrile-$^{15}N_2$ is proposed on the basis of their infrared and Raman spectra. The relevant symmetry is found to be D_{2h}. The force field for the out-of-plane vibrations of these molecules was calculated by refining the general quadratic force field obtained by the semi-empirical MINDO/3 method, starting with a geometry optimized by this method. The refined force field reproduces the observed frequencies of the out-of-plane vibrations to better than $\pm 0.5\ \mathrm{cm}^{-1}$.

INTRODUCTION

Terephthalonitrile (1,4-dicyanobenzene) is a molecule related to terephthalic acid and the terephthalate ion which we have studied previously as a part of a research programme on carboxylic acids and their derivatives [1]. In this particular case we have been able to synthesize the terephthalonitrile-$^{15}N_2$, which besides the deuterated derivative and the natural molecule provides an important number of experimental data to allow for a sensible refinement of the harmonic force field. The terephthalonitrile molecule has been the subject of many studies in recent years. On the one hand, there are several published papers [2–5] concerning its molecular structure in both the solid and gaseous phases; these studies confirm that the molecule has D_{2h} point group symmetry in both aggregation states, although in the condensed phase the molecule is slightly distorted because of intermolecular interactions. The first reported vibrational assignment of this molecule [6] was carried out on the basis of the i.r. and Raman spectra of the non-deuterated compound; another more recent study employed spectra of both natural and tetradeuterated terephthalonitrile [7].

On the other hand, in previous studies in this laboratory [8, 9], the MINDO/3 method was used to calculate the quadratic force field of other compounds. This field was then refined to fit the experimental frequencies with fast convergence of the process. This encouraged us to use the force field calculated by MINDO/3 as a relevant starting point to refine to the experimental data in the present case.

The first part of this work concerns a study of the i.r. and Raman spectra of the terephthalonitrile and terephthalonitrile-$^{15}N_2$ molecules to enable a more complete assignment of the observed vibrational spectra on the basis of the D_{2h} symmetry of both isotopic derivatives. Using this information and MINDO/3 results, the force field was refined for the symmetry blocks involving out-of-plane vibrations. The force constants obtained were then transformed to the space of the internal coordinates to obtain the so-called canonic force field of KUCZERA and CZERMINSKY [10] which is much more suitable to be either transferred or compared with that of related molecules.

EXPERIMENTAL

The terephthalonitrile (98% pure) was supplied by EGA-Chemie and its i.r. spectrum was recorded without further purification from KBr pellets with a Beckman 4260 i.r. spectrophotometer. The instrument was calibrated with polystyrene films as well as with indene–camphor–cyclohexanone mixtures. The Raman spectrum of microcrystalline powder was recorded with a Jobin Yvon U-1000 spectrometer. The measurements of the depolarization ratio of each Raman band were done in DMSO solution. The excitation lines employed were those at 4880 and 5145 Å from a Spectra Physics 2020 Ar$^+$ laser.

Terephthalonitrile-$^{15}N_2$ was synthesized from terephthalic acid dissolved in thionyl chloride and stirred for 15 h, after which it was boiled and refluxed for another 4 h. The solvent was then removed by distillation to leave a solid residue of terephthaloyl chloride. This residue was then reacted with ammonium chloride-^{15}N with 99% isotope content in dry pyridine to form the terephthalamide which was transformed into terephthalonitrile by dehydration with thionyl chloride. The final product was extracted by acetic acid and the resulting solution was treated several times with activated charcoal; the filtrate was allowed to cool and crystals of terephthalonitrile-$^{15}N_2$ were then formed.

Calculations involved in this work were carried out with a Perkin–Elmer 3220 minicomputer and a Univac 1100/82 computer.

RESULTS AND DISCUSSION

The terephthalonitrile molecule has 36 normal vibrations which are distributed as follows: $7\,A_g + 6\,B_{3g} + 6\,B_{1u} + 6\,B_{2u}$ in-plane vibrations and $1\,B_{1g} + 4\,B_{2g} + 2\,A_u + 4\,B_{3u}$ out-of-plane vibrations. The coordinate axes are orientated according to the rules given in Ref. [11]. Table 1 shows the frequencies of the observed bands, the depolarization ratios where they could be measured and the proposed assignments. The vibrations were classified as: (1) ring vibrations using Wilson's notation for the vibrations of benzene; (2) ring-substituent vibrations, maintaining Wilson's not-

Table 1. Wavenumbers and assignments of the i.r. and Raman bands of terephthalonitrile and terephthalonitrile-$^{15}N_2$ (cm^{-1})

Terephthalonitrile				Terephthal.-$^{15}N_2$					
i.r.		Raman		i.r.		Raman			
ν	I	$\Delta\nu$	I	ν	I	$\Delta\nu$	I	ρ	Assignment
3432.7	vw			3401.9	vw				ν_s(CN)+13, B_{1u}
3404.1	vw			3373.4	vw				ν_{as}(CN)+7a, B_{1u}
3121.7	vw			3120.3	vw				8a+19a, B_{1u}
3098.7	m			3098.5	m				20b, ν(CH), B_{2u}
		3088.1	m			3088.1	m		2, ν(CH), A_g
		3078.2	w			3077.9	w		7b, ν(CH), B_{3g}
3053.4	m			3053.0	m				20a, ν(CH), B_{1u}
2997.7	w			2997.3	w				8b+19b, B_{1u}
2818.9	w			2818.7	w				19a+3, B_{2u}
		2242.8	vs			2214.1	vs	p	ν_s(CN), A_g
2233.9	vs			2209.3	vs				ν_{as}(CN), B_{1u}
1814.2	w			1814.0	w				10b+11, B_{1u}
1690.3	w			1689.6	w				9a+16b, B_{3u}
		1619.4	s			1619.4	s	p	8a, ν(CC), A_g
		1609.4	sh			1609.4	w		8b, ν(CC), B_{3g}
1504.4	m			1504.1	m				19a, ν(CC), B_{1u}
1401.4	m			1401.1	m				19b, ν(CC), B_{2u}
		1328.0	w			1326.6	w		3, δ(CH), B_{3u}
1277.3	m			1276.4	m				14, ν(CC), B_{2u}
1200.4	m			1194.1	m				13, ν(CX), B_{1u}
		1190.6	vw			1184.9	vw		1+9b, B_{3g}
		1183.5	m			1178.3	m	p	7a, ν(CX), A_g
		1134.5	vw			1134.3	vw		9a, δ(CH), A_g
1122.6	vw			1122.1	vw				18b, δ(CH), B_{2u}
1027.6	w			1026.6	w				18a, δ(CH), B_{1u}
		970.8	vw			970.5	vw		10b, γ(CH), B_{2g}
845.8	vs			845.7	vs				11, γ(CH), B_{3u}
		820.2	s			816.6	s	p	1, ν(CC), A_g
		794.1	vw			794.0	vw		10a, γ(CH), B_{1g}
		724.7	w			723.8	w		4, γ(CC), B_{2g}
		661.9	m			660.5	m		6b, δ(CC), B_{3g}
636.5	m			635.7	m				12, δ(CC), B_{1u}
		565.8	m			564.5	m		γ_{as}(CN), B_{2g}
562.1	s			561.2	s				16b, γ(CC), B_{3u}
530.5	vw			529.4	vw				δ_s(CN), B_{2u}
		524.3	m			522.8	m	dp	δ_{as}(CN), B_{3g}
		377.9	w			373.8	w		9b, δ(CX), B_{3g}
360.6	m			360.1	m				γ_s(CN), B_{3u}
		213.2	m			210.0	m	dp	5, γ(CX), B_{2g}

ation, but changing the character of the C–H mode to the C–X mode, and (3) vibrations of the substituent with an appropriate specific notation. The assignments were based on the relative intensities of the infrared and Raman bands which are in agreement with the principle of mutual exclusion, the isotopic shifts, the depolarization ratios measured in the Raman spectra of the solutions, the correlations with the spectra of benzene and its disubstituted derivatives and the characteristic frequencies of the substituents.

Ring vibrations

These vibrational modes are almost insensitive to substitution with ^{15}N, the isotopic shifts being between 0 and 2 cm^{-1}, since the vibrational amplitudes of the nitrogen atoms are quite small. Two i.r.-active and two Raman-active C–H stretching fundamental bands were recorded at about 3000 cm^{-1}. To assign them, the data given in Ref. [12] for disubstituted benzenes were taken into account. The C–C stretching bands appeared at frequencies above 1250 cm^{-1}, except that of vibration 1; A_g which usually appears in the spectra of this kind of derivative at frequencies lower than 1000 cm^{-1} and was in fact recorded at 820.2 cm^{-1} in the natural molecule. This fundamental mode is usually coupled with mode 7a; A_g and the respective band was found at 816.6 cm^{-1} in the spectrum of the isotopic molecule. All the in-plane C–H bending vibrations were recorded between 1000 and 1150 cm^{-1} and show isotopic shifts smaller than 1 cm^{-1}; however, the mode 3; B_g has been assigned to the bands recorded at 1328.0 and 1326.6 cm^{-1} in the spectra of the natural and isotopic molecule respectively.

The highest frequency out-of-plane fundamentals are γ(CH) and in the infrared the most intense of these is the mode 11; B_{3u} assigned at 845.8 and 845.7 cm^{-1} for natural and labelled molecules respectively. Vibrations 10a and 10b, both active in the Raman, were recorded at 794.0 and 970.8 cm^{-1} respectively, with negligible isotopic shifts. The fundamental 17a; A_u was not seen because it is a silent mode in D_{2h} symmetry. Finally the out-of-plane vibration 16a; A_u could not be observed either because of the same symmetry restriction. The remaining two out-of-plane fundamentals were assigned to frequencies lower than 750 cm^{-1} and both bands were very weak.

Ring-substituent vibrations

These are the stretching modes of the C–CN bonds as well as both the in-plane and out-of-plane bendings of C–C–N with respect to the aromatic ring. They are very sensitive to substitution with ^{15}N which facilitates their assignment. The two C–CN stretching modes are notated here as 13; B_{3u} and 7a; A_g and were found above 1200 cm^{-1}, the former being active in i.r. and the latter in Raman; their isotopic shifts were greater than 6 cm^{-1}. Of the four ring-substituent deformation vibrations, we could only assign those active in Raman, 9b; B_{3g} and 5; B_{2g}, because the others are low frequency modes and could not be observed in our i.r. spectra. The isotopic shifts measured for these bands were 4.1 and 3.2 cm^{-1} respectively.

Vibrations of the substituents

The symmetric and asymmetric C–N stretching vibrations show the highest isotopic shifts, more than 20 cm^{-1}. They are recorded as sharp and intense bands between 2200 and 2300 cm^{-1} in both i.r. and Raman spectra. Furthermore, the symmetric Raman active mode is observed to be very polarized. The assignments of the bending vibrations of the nitrile group were made on the basis of their isotopic shifts which are smaller than those of the ring-substituent deformation vibrations due to the smaller vibrational amplitudes of the nitrogen atoms. The in-plane bends were assigned to 524.3 and 522.8 cm^{-1} for the symmetric, and to 530.5 and 529.4 cm^{-1} for the asymmetric mode; the former bands were seen to be depolarized. The bands at 565.8 and 360.6 cm^{-1} were chosen for the out-of-plane deformations. They show isotopic shifts of 1.3 and 0.5 cm^{-1} respectively.

Overtones and combinations

In addition to the fundamental vibrations we have assigned several overtone and combination bands to weak intensity frequencies which could not be assigned to a fundamental mode. The isotopic shifts were very helpful when looking for the corresponding combination or overtone, as were also their symmetries calculated as the direct product of the symmetry species of the fundamentals involved in each case. The differences between calculated and observed frequencies varied between 2 and 13 cm^{-1} and were due essentially to the anharmonicity.

Force field for the out-of-plane vibrations

The calculation of the semi-empirical force field required the previous optimization of the molecular geometry to reach a MINDO/3 potential energy minimum. The resulting geometry is compared in Table 2 with the experimental one given in Ref. [5] for this molecule in the gaseous state, and a very satisfactory agreement can be realized, especially for the

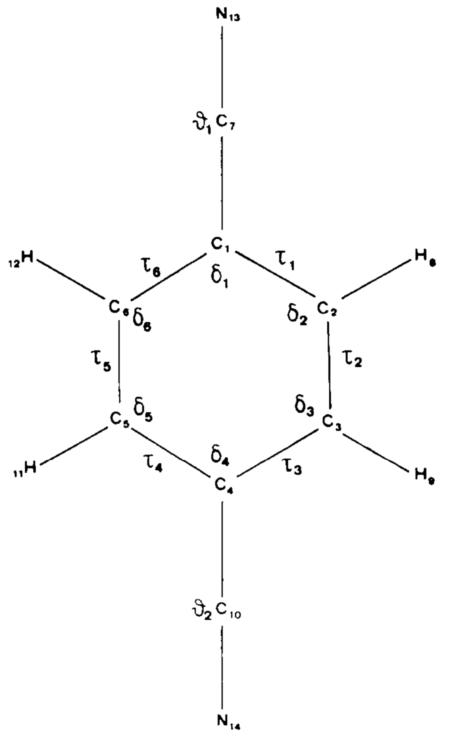

Fig. 1. Out-of-plane internal coordinates for terephthalonitrile.

Table 2. Experimental and calculated geometries of the terephthalonitrile molecule

Bond lengths	Exp.*(Å)	MINDO/3(Å)	Angles	Exp.*(°)	MINDO/3(°)
C_1–C_2	1.396	1.424	C_1–C_2–C_3	119.0	122.2
C_2–C_3	1.392	1.403	C_6–C_1–C_2	122.1	115.7
C_1–C_7	1.453	1.456	C_1–C_7–N_{13}	180.0	180.0
C_7–N_{13}	1.165	1.161	C_1–C_2–H_8	120.5	119.5
C_2–H_8	1.073	1.106	C_7–C_1–C_2	119.0	122.1
			C_3–C_2–H_8	120.5	119.5

*Ref. [4].

Table 3. Primitive symmetry coordinates for out-of-plane vibrations of terephthalonitrile

Species B_{1g}	
s_1	$1/2(\delta_2+\delta_3-\delta_5-\delta_6)$
s_2	$1/2(\tau_1-\tau_3-\tau_4+\tau_6)$
Species B_{2g}	
s_3	$1/\sqrt{2}(\delta_1-\delta_4)$
s_4	$1/2(\delta_2-\delta_3-\delta_5+\delta_6)$
s_5	$1/\sqrt{2}(\theta_1-\theta_2)$
s_6	$1/2(\tau_1+\tau_3-\tau_4-\tau_6)$
s_7	$1/\sqrt{2}(\tau_2-\tau_5)$
Species A_u	
s_8	$1/2(\delta_2-\delta_3+\delta_5-\delta_6)$
s_9	$1/2(\tau_1+\tau_3+\tau_4+\tau_6)$
s_{10}	$1/\sqrt{2}(\tau_2+\tau_5)$
Species B_{3u}	
s_{11}	$1/\sqrt{2}(\delta_1+\delta_4)$
s_{12}	$1/2(\delta_2+\delta_3+\delta_5+\delta_6)$
s_{13}	$1/\sqrt{2}(\theta_1+\theta_2)$
s_{14}	$1/2(\tau_1-\tau_3+\tau_4-\tau_6)$

Table 4. Independent symmetry coordinates for out-of-plane vibrations

Species B_{1g}

$S_1=0.8666s_1-0.4990s_2$

Species B_{2g}

$S_2=0.5139s_3-0.8398s_4+0.1493s_5+0.0914s_6+0.0030s_7$
$S_3=0.5200s_3+0.4116s_4+0.6404s_5-0.1765s_6-0.3450s_7$
$S_4=0.3459s_3+0.1577s_4-0.5677s_5+0.4505s_6-0.5746s_7$
$S_5=0.4307s_3+0.0982s_4-0.4953s_5-0.7169s_6+0.2136s_7$

Species A_u

$S_6=-0.9799s_8-0.1127s_9+0.1762s_{10}$
$S_7=0.2089s_8-0.5709s_9+0.7940s_{10}$

Species B_{3u}

$S_8=0.7268s_{11}-0.5857s_{12}+0.3401s_{13}-0.1144s_{14}$
$S_9=0.0863s_{11}+0.5868s_{12}+0.0820s_{13}-0.0713s_{14}$
$S_{10}=0.6050s_{11}+0.4431s_{12}-0.3387s_{13}+0.5682s_{14}$
$S_{11}=-0.3135s_{11}-0.3411s_{12}+0.3555s_{13}+0.8118s_{14}$

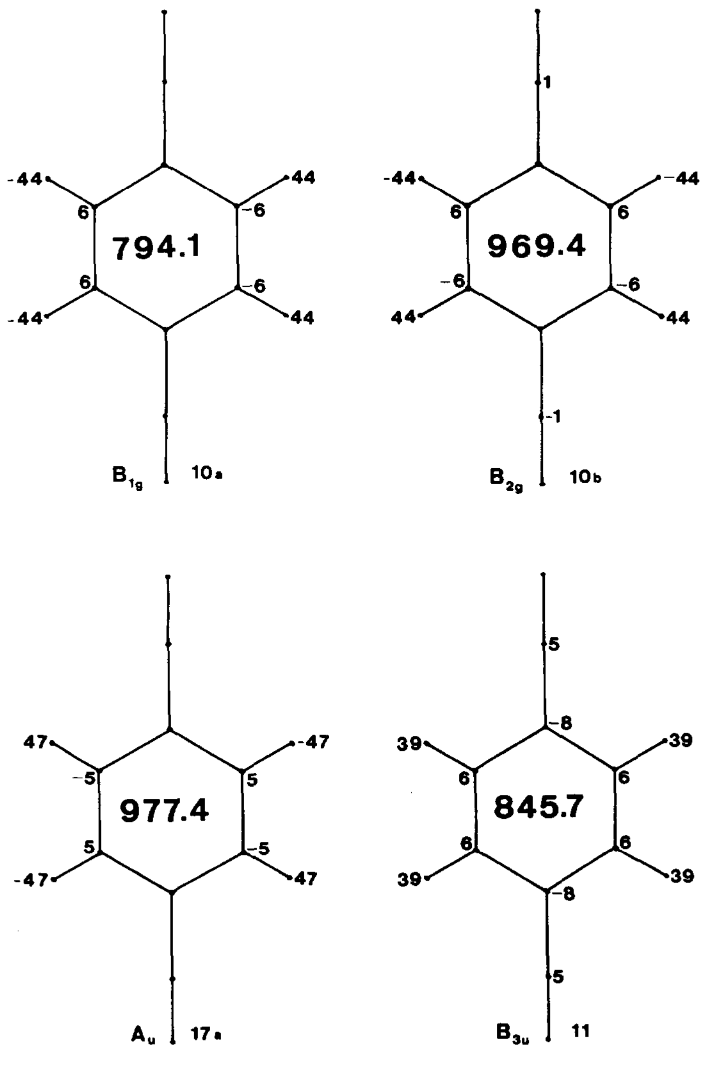

Fig. 2a.

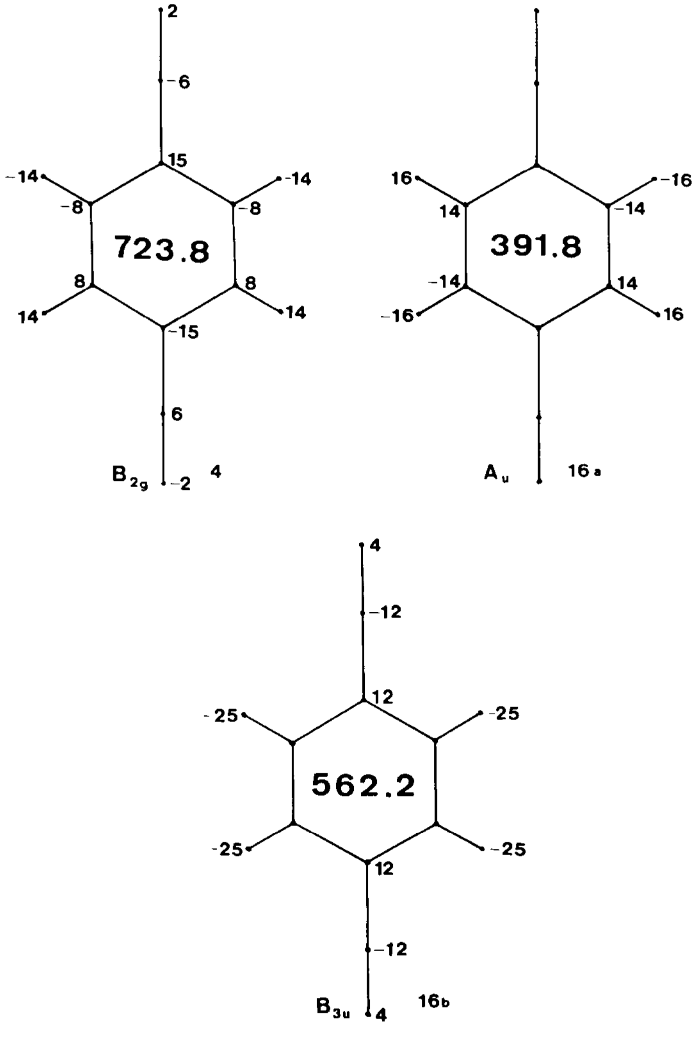

Fig. 2b.

C–CN, C–N and C–H bonds. Using this geometry the initial set of force constants was determined with the FORCE program [13] by calculating analytical first derivatives and numerical second derivatives of the energy with respect to Cartesian coordinates. According to the method previously described in Ref. [8], we obtained a set of independent symmetry coordinates by diagonalization of the $B{\cdot}B'$ matrix, where B defines the primitive symmetry coordinates as $s = B{\cdot}x$; the primitive symmetry coordinates were set up from the internal coordinates by means of the projection operators. In this way, the initial set of force constants was transformed from Cartesian coordinates to independent symmetry coordinates by the transformation $F_{\mathrm{sym}} = B'^{-1}\cdot F_{\mathrm{cart}}\cdot B^{-1}$, where now B defines the independent symmetry coordinates. Figure 1 shows the internal coordinates defined for the out-of-plane vibrations. Table 3 shows the primitive symmetry coordinates as linear combinations of the internal ones and Table 4 shows the independent symmetry coordinates for the out-of-plane species as linear combinations of the primitive ones. Table 5 shows in turn the force constants belonging to each symmetry block; it can be seen that the refined constants do not differ much from the values calculated by MINDO/3. This confirms the suitability of this semi-empirical method in providing a good starting point for the refinement of force fields in molecules which, as in this case, are rather larger for *ab initio* calculations even with bases of moderate size.

It was possible to simultaneously refine all the force constants in the blocks of symmetry B_{1g} and A_u. However, for the blocks B_{2g} and B_{3u}, where the number of force constants far exceeded the number of available experimental data, only 70% of the force constants could be refined simultaneously in any case because in an early phase of the process, the data given in Ref. [7] for the terephthalonitrile-d_4 derivative, and also some frequency of the natural compound, were employed in addition to ours; this allowed a consider-

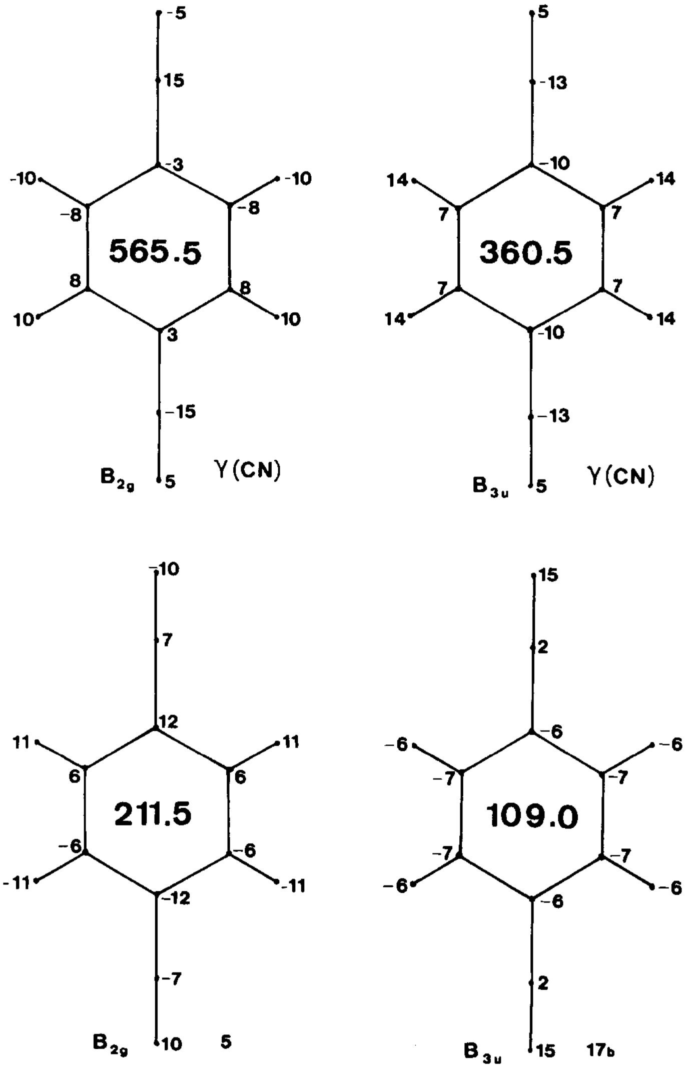

Fig. 2. Calculated Cartesian displacements for the out-of-plane vibrations for terephthalonitrile.

able reduction of the sum of the weighted squares of the errors. The final result was obtained by refining only our frequencies and isotopic shifts, which reduced the total number of force constants in the simultaneous refinement down to 40% because fewer experimental data were entered. This process considerably improved the agreement between the experimental and calculated values. Table 6 lists the observed frequencies as well as those finally calculated for the out-of-plane species and also the values of the P.E.D. greater than 10%. To better describe the form of each normal mode, the atomic displacement matrix was calculated and this gave the results shown in Fig. 2. This confirms our hypothesis that the out-of-plane ring-substituent vibrations 5 and 17b show greater vibrational amplitudes for the nitrogen atoms than do the γ(CN) substituent vibrations, and that the γ(CH) and γ(CC) ring vibrations are the least sensitive ones to labelling with ^{15}N.

The last part of this work was to calculate the force field in the space of the internal coordinates, i.e. the canonic field, to allow for the transferring and comparing of the force constants of similar molecules and therefore to construct model force fields. For this purpose, the transformation $F_{\text{int}} = U' \cdot F_{\text{sym}} \cdot U$ was carried out, where U defines the independent symmetry coordinates as $S = U \cdot R$. The results can be seen in Table 7 from which it is evident how the substituent groups affect the force constant values. For instance, upon substitution the values of the diagonal deformation force constants increase relative to those of the benzene molecule; that increase affects the C–X bonds more than the C–H ones. The same occurs with the torsions of the C–C bonds in the aromatic ring. As was to be expected the highest force constant is that involving the bending of the substituent because of the existence of a triple bond C≡N. The off-diagonal force constants are generally smaller than the diagonal

Table 5. MINDO/3 and refined force constants (mdin/Å) for out-of-plane vibrations of terephthalonitrile

		MINDO/3	Refined
Species B_{1g}	F_{11}	0.2354	0.2070
Species B_{2g}	F_{22}	0.2174	0.2172
	F_{23}	0.0354	0.0354
	F_{24}	0.0376	0.0376
	F_{25}	−0.0406	−0.0720
	F_{33}	0.3355	0.5536
	F_{34}	−0.0459	−0.0830
	F_{35}	0.0147	0.0147
	F_{44}	0.2755	0.3549
	F_{45}	0.0270	0.0270
	F_{55}	0.2417	0.3510
Species A_u	F_{66}	0.2246	0.1541
	F_{67}	−0.1043	−0.0059
	F_{77}	0.2757	0.4465
Species B_{3u}	F_{88}	0.2882	0.2871
	F_{89}	0.0461	0.0809
	$F_{8\,10}$	0.0614	−0.0133
	$F_{8\,11}$	0.0356	0.0361
	F_{99}	0.3181	0.3683
	$F_{9\,10}$	−0.0369	−0.0556
	$F_{9\,11}$	−0.0217	−0.1300
	$F_{10\,10}$	0.2736	0.2651
	$F_{10\,11}$	−0.0308	0.0371
	$F_{11\,11}$	0.2349	0.6138

Table 7. Canonic force constants for out-of-plane vibrations (all units mdin/Å)

Type	Force constant	Type	Force constant
δ_1	0.2903	$\theta_1\theta_2$	−0.0642
δ_2	0.2197	$\delta_1\tau_1$	−0.0576
τ_1	0.2566	$\delta_1\tau_2$	−0.0665
τ_2	0.2208	$\delta_1\tau_3$	−0.0018
θ_1	0.4454	$\delta_2\tau_1$	−0.0662
$\delta_1\delta_2$	0.0381	$\delta_2\tau_2$	0.0048
$\delta_1\delta_3$	0.0006	$\delta_2\tau_3$	−0.0170
$\delta_1\delta_4$	−0.0094	$\delta_2\tau_4$	−0.0474
$\delta_2\delta_3$	0.0212	$\delta_2\tau_5$	−0.0319
$\delta_2\delta_5$	0.0281	$\delta_2\tau_6$	0.0912
$\delta_2\delta_6$	0.0574	$\delta_1\theta_1$	0.0576
$\tau_1\tau_2$	−0.1058	$\delta_1\theta_2$	−0.0131
$\tau_1\tau_3$	−0.0421	$\delta_2\theta_1$	0.0070
$\tau_1\tau_4$	0.0897	$\tau_2\theta_2$	−0.0256
$\tau_1\tau_5$	−0.0387	$\tau_1\theta_1$	−0.0236
$\tau_1\tau_6$	−0.1575	$\tau_1\theta_2$	−0.0088
$\tau_2\tau_5$	0.0638	$\tau_2\theta_1$	−0.0138

Table 6. Observed and calculated frequencies (cm^{-1}) and P.E.D. for out-of-plane vibrations of terephthalonitrile and terephthalonitrile-$^{15}N_2$ (isotopic shifts)

	Terephthalonitrile			Terephthal.-$^{15}N_2$			P.E.D. (%)
	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	
Species B_{1g}	794.1	794.1	0.0	−0.1	0.0	−0.1	$100(F_{11})$
Species B_{2g}	970.7	970.6	0.1	0.2	−0.1	−0.1	$36(F_{22}), 64(F_{33}), 44(F_{44}), -20(F_{34})$
	724.7	724.6	0.1	−0.9	−0.6	−0.3	$70(F_{22}), 22(F_{33}), 8(F_{23})$
	565.8	565.9	−0.1	−1.3	−1.1	−0.2	$18(F_{33}), 55(F_{44}), 11(F_{34})$
	213.1	213.1	0.0	−2.1	−2.1	0.0	$9(F_{44}), 90(F_{55}), -8(F_{25})$
Species A_u	977.0*	977.5	−0.5	-	0.0	—	$73(F_{66}), 29(F_{77})$
	392.0*	391.8	0.2	—	0.0	-	$27(F_{66}), 71(F_{77})$
Species B_{3u}	845.8	845.7	0.1	−0.1	−0.2	0.1	$83(F_{88}), 15(F_{99}), 24(F_{10\,10}), -18(F_{89})$
	562.1	562.2	−0.1	−0.9	−0.9	0.0	$11(F_{88}), 68(F_{99}), 25(F_{10\,10}), -15(F_{9\,10})$
	360.6	360.5	0.1	−0.6	−0.7	0.1	$13(F_{88}), 28(F_{99}), 47(F_{10\,10}), 13(F_{9\,10})$
	109.0	109.0	0.0		−2.5		$106(F_{11\,11}), -15(F_{10\,11})$

*Ref. [6].

ones, but those which interrelate the torsions of the C–C bonds in the aromatic ring are the greatest ones.

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