

- KELLERMANN, E. W. (1940). *Philos. Trans. R. Soc. London*, **238**, 513-548.
- KITTEL, C. (1966). *Introduction to Solid State Physics*. New York: Wiley.
- KROON, P. A. & VOS, A. (1978). *Acta Cryst.* **A34**, 823-824.
- KROON, P. A. & VOS, A. (1979). *Acta Cryst.* **A35**, 675-684.
- PILATI, T., BIANCHI, R. & GRAMACCIOLI, C. M. (1990). *Acta Cryst.* **B46**, 301-311.
- PRICE, G. D., PARKER, S. C. & LESLIE, M. (1987). *Mineral. Mag.* **51**, 157-170.
- REID, J. S. & SMITH, T. (1970). *J. Phys. Chem. Solids*, **31**, 2689-2697.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.

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## Lattice Dynamics and Thermal Parameters in Azahydrocarbons

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### Abstract

Lattice frequencies and crystallographic thermal parameters are calculated for some azahydrocarbons with the external Born-von Karman formalism using an atom-atom potential model which accounts explicitly for electrostatic interactions modelled as atomic point charges. Results are satisfactory, encouraging the application of this procedure to a wider range of molecular crystals. Comparison of calculated thermal parameters with experimental data obtained with different techniques increases the need for reliable experimental thermal parameters in order to make meaningful deductions.

### Introduction

Lattice dynamics of molecular crystals based on semi-empirical models for atomic forces has been a field of growing interest stemming from the basic work (Cochran & Pawley, 1964) where the complete lattice dynamics of a molecular crystal was studied for the first time, followed by a series of papers (Pawley, 1967, 1972) which established the practical formulation for these calculations. The development of optical spectroscopy probing the far-infrared lattice region and the advent of neutron spectroscopy have also increased the activity in this field.

Lattice dynamics also finds a very important application as an aid to crystallographic studies (see Willis & Pryor 1975). For instance, an adequate lattice-dynamical model can help to correct experimental Bragg intensities for thermal-diffuse-scattering (TDS) contributions. Another interesting application is the calculation of crystallographic thermal parameters using potential-energy models for comparison with the experimental values obtained in a least-squares

structure refinement process. This procedure can reveal possible bias in the experimental thermal parameters as a consequence of systematic errors; some information on the different contributions of crystal forces to thermal motion can also be obtained.

These calculations have been successful especially in connection with hydrocarbons. Here atom-atom potential models in the form  $V(r) = -A/r^6 + B \exp(-Cr)$  seem to work particularly well for both rigid and non-rigid molecules (Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974). In the latter case, the contribution of internal modes tends to increase the thermal parameters; a further increase is observed if coupling between internal and external modes is taken into account (Gramaccioli, Filippini & Simonetta, 1982; Gramaccioli & Filippini, 1983). Other studies which successfully calculate thermal parameters from lattice dynamics for hydrocarbons are: *o*-terphenyl (Gramaccioli & Filippini, 1985), tetraphenylmethane (Filippini & Gramaccioli, 1986), biphenyl (Bonadeo & Burgos, 1982) and benzene (Filippini & Gramaccioli, 1989). There are also some applications to heteroatomic crystals (Filippini, Gramaccioli, Simonetta & Suffritti, 1976; Filippini, Gramaccioli & Simonetta, 1981).

The remarkable success of calculations of thermal motion for hydrocarbons resides in the fact that the crystal force field can be modelled adequately using 6-exp potential functions. Nevertheless, if we try to extend the method to other kinds of molecular crystals where atoms very different in electronegativity are bound together, electrostatic forces arising from molecular static-multipole moments appear which must be accounted for. If these forces are small they can be absorbed into effective 6-exp models (although these turn out to be non-transferable to other molecules) but if the electrostatic interactions are

large they must be explicitly considered in the potential model. Even in the case of hydrocarbons the inclusion of electrostatic forces in the model significantly affects the lattice dynamics (Califano, Righini & Walmsley, 1979).

Therefore, the extension of lattice dynamical studies and calculations of thermal parameters to a greater variety of crystals depends upon the possibility of obtaining suitable models to describe electrostatic interaction. Unfortunately, very few measurements of phonon dispersion curves in heteroatomic molecules have been carried out so far, some of them quite recently (e.g. Link, Grimm, Dörner, Zimmermann, Stiller & Bleckmann, 1985; Dove, Powell, Pawley, Chaplot & Mierzejewski, 1989) and it is desirable that this number is increased. Indirect evidence for 'goodness' of force-field models and potentials over the whole Brillouin zone comes from comparison between theoretical and experimental atomic thermal parameters; considering this problem, we have initiated a series of systematic calculations on different groups of substances.

In a previous paper (Criado, 1989) we studied the influence of Coulombic interactions on thermal parameters for naphthalene and anthracene and we now present a study dealing with azahydrocarbons. An important difference from the former study is that in this case Coulombic interactions are crucial, in fact some of the compounds considered present unstable patterns when only 6-exp models are adopted.

### Potential parameters

The number of potential-parameter sets for nitrogen-nitrogen interactions available in the literature is much more limited than in the case of carbon-carbon potentials and not all of them have been obtained from fits to a wide number of nitrogen compounds. A brief account of some of these sets is given below. A set proposed by Mirskaya & Nauchitel (1972) was derived from a fit to equilibrium structures and sublimation energies of  $\text{NO}_2$ ,  $\alpha$ -nitrogen and hexamethylenetetramine and is of interest since Coulombic interactions were explicitly considered. Govers (1975) uses a much wider database of crystal structures and sublimation energies but electrostatic interactions are absorbed into the resulting 6-exp parameters. Another parameter set was derived by Reynolds (1973) from the elastic constants and phonon frequencies of pyrazine. In this case Coulombic interactions were included in the fit as distributed dipoles and they turned out to be necessary in order to achieve a good fit. Another attempt which combines adjusted 6-exp potential parameters with a distributed-dipole Coulombic model obtained from *ab initio* data for the multipole moments of several azabenzene compounds is the parameter set which has been proposed by Gamba & Bonadeo (1981). In

Table 1. *Potential parameters*

$$V(r) = -A/r^6 + B \exp(-Cr).$$

	$A$ ( $\text{kJ mol}^{-1} \text{ \AA}^6$ )	$B$ ( $\text{kJ mol}^{-1}$ )	$C$ ( $\text{\AA}^{-1}$ )
C—C <sup>(a)</sup>	2377.6	350 075.2	3.60
C—H	521.24	36 694.5	3.67
H—H	114.28	11 109.6	3.74
N—N <sup>(b)</sup>	1384.7	255 710.2	3.78
N—C	1814.6	300 002.2	3.69
N—H	397.67	30 552.8	3.76
N—N <sup>(c)</sup>	1084.17	175 812.0	3.78
N—C	1605.33	248 981.2	3.69
N—H	352.04	27 260.1	3.76

References: (a) Williams (1967); (b) Williams & Cox (1984); (c) Mirskaya & Nauchitel (1972).

this case the agreement of structural and vibrational properties with experiment is good but the resulting 6-exp nitrogen-nitrogen function does not present a defined minimum, pointing to lack of physical meaning. This work also shows how higher-order multipole contributions to the electrostatic energies are important and may even dominate in many cases.

A last important set has been derived by Williams & Cox (1984). As before, the Coulombic terms were not fitted but extracted from *ab initio* calculations. Point charges located at the atomic sites and extra charges to simulate lone-pair nitrogen atoms were adjusted in order to reproduce the calculated *ab initio* electrostatic field around the molecule. The 6-exp parameters were obtained from a fit to equilibrium structures and sublimation energies of a large number of compounds. The parameters so derived gave better agreement with the experimental data than the other potentials available in the literature. This work also confirms that the electrostatic contribution to the lattice energy is very important in the considered compounds.

For our present study we have chosen the sets proposed by Williams & Cox and Mirskaya & Nauchitel (*b* and *c* in Table 1): these models consider Coulombic interactions separately, present minima at physically meaningful distances, 3.60 and 3.66  $\text{\AA}$ , respectively, and have been found to be transferable to other compounds not included in the fit. For carbon-carbon interactions we have adopted the so-called Williams IVb set (Williams, 1967) (*a* in Table 1). These potentials have proved to be among the best in relation to lattice-dynamical models applied to crystallography (Criado & Marquez, 1988). Mixed interactions are dealt with by adopting the geometric mean for parameter *A*, the arithmetic mean for *C*; the value of *B* is calculated so that the mixed interaction-potential minimum fulfils the arithmetic-mean rule.

### Compounds and method of calculation

Seven different azahydrocarbon structures have been chosen for this study (Table 2). (I) and (II) are the

Table 2. *Compound data*

	Formula	Space group	Z
(I)	C <sub>6</sub> N <sub>4</sub>	<i>Im3</i>	6
(II)	C <sub>6</sub> N <sub>4</sub>	<i>P2<sub>1</sub>/n</i>	2
(III)	C <sub>7</sub> H <sub>2</sub> N <sub>4</sub>	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	4
(IV)	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	<i>I43m</i>	2
(V)	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	<i>Pna2<sub>1</sub></i>	4
(VI)	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	<i>Pmnn</i>	2
(VII)	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub>	<i>R3c</i>	6

(I) and (II) cubic and monoclinic ethylenetetracarboxitrile, (III) 1,1,2,2-cyclopropanetetracarboxitrile, (IV) hexamethylenetetramine, (V) pyrimidine, (VI) pyrazine and (VII) *s*-triazine.

cubic and monoclinic phases of ethylenetetracarboxitrile (Becker, Coppens & Ross, 1973; Bekoe & Trueblood, 1960), (III) is 1,1,2,2-cyclopropanetetracarboxitrile (Lemley, Skarstad & Hughes, 1976), (IV) is hexamethylenetetramine (Stevens & Hope, 1975), (V) is pyrimidine (Wheatley, 1960), (VI) is pyrazine (Wheatley, 1957) and (VII) is *s*-triazine (Wheatley, 1955).

For all these compounds, a reliable Coulombic model exists in the form of point charges located at the atomic sites and extra charges in the case of azabenzene (V, VI and VII) located at a distance of 0.25 Å from the lone-pair nitrogen atoms off the molecule centre (Fig. 1). This model has been

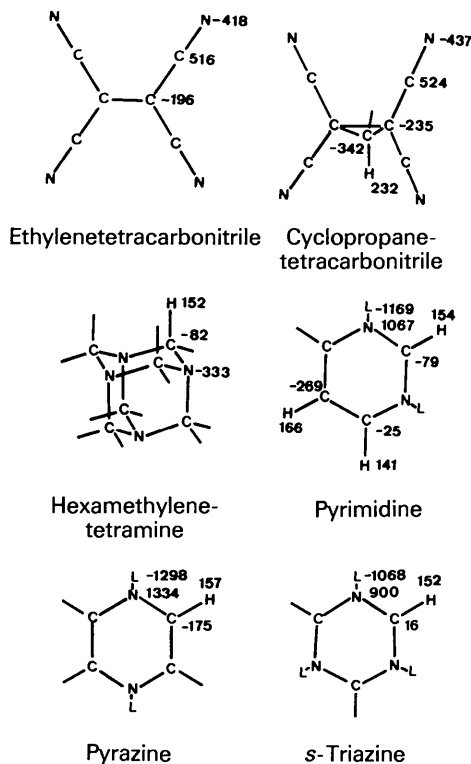


Fig. 1. Molecular charge distributions for the molecules considered in this work. The numbers are the values of the point charges (electronic units  $\times 10^3$ ) associated with the nearest atom in the drawing belonging to the molecular asymmetric unit. *L* stands for an extra charge to model lone-pair interactions of nitrogen atoms.

adjusted in order to reproduce the electrostatic field obtained from *ab initio* calculations with MO wavefunctions formed from an STO-3G basis set (Williams & Cox, 1984).

We have adopted in this work the rigid-ion approximation assuming that the isolated-molecule electronic distribution is not perturbed when forming the crystal. The atoms become polarized in the crystal for two reasons. First, the long-range Coulombic interaction can induce an atomic polarization and, second, dipole moments may be induced on the atoms by the displacement of near neighbours through short-range forces. This fact can be accounted for with the shell model (Woods, Cochran & Brockhouse, 1960) in which the atom is assumed to be composed of a core and an electronic shell held together by a spring constant. In this model, the additional parameters introduced are not calculated *ab initio* but adjusted in order to reproduce the experimental frequencies. A second simplified approach (Gamba & Bonadeo, 1981) to deal with polarization assumes the rigid-ion model but it uses an effective electronic distribution in order to reproduce the Coulombic field created by the polarized atoms. This model must also be adjusted in order to reproduce the experimental frequencies.

The inclusion of polarization in molecular crystals affects generally the fine details of the dispersion curves (Luty & Pawley, 1975) and it can be neglected if we are using universal potential parameters which are just an approximation to the crystal force field.

Fig. 1 shows the molecular structures and electrostatic models of the chosen compounds. Experimental sublimation energies and lattice frequencies are available for the majority of these compounds and constitute another source for comparison with experiment. Also, some of these compounds have been subjected to several crystallographic studies with different techniques and this allows the comparison of reliable experimental thermal parameters with those obtained from lattice dynamics, using different models and potentials.

The method of calculation has been described in detail in previous papers (Criado, Conde & Marquez, 1984; Criado, 1989) and we will only give a brief account. Lattice dynamics is considered in the harmonic approximation using the external Born-von Karman formalism (Born & Huang, 1954) in terms of molecular rotations and translations. The quasi-harmonic approximation is adopted in which the experimental lattice constants are taken as a basis for the calculations. A cut-off radius of 8 Å is taken when constructing the dynamical matrix for 6-exp interactions whereas the convergence of Coulombic sums is accelerated using the Ewald technique (Ewald, 1921). The rigid-body T, L and S thermal motion tensors (Schomaker & Trueblood, 1968) and hence the individual thermal parameters are calculated as a sum of the contributions of all phonons to the atomic

Table 3. *Newton-Raphson translation ( $\text{\AA}$ ) and rotation ( $^\circ$ ) shifts, calculated Coulombic, total and experimental energies ( $\text{kJ mol}^{-1}$ )*

The experimental values are taken from Williams & Cox (1984) and Gamba (1985).

	$\Delta t$	$\Delta\theta$	$E_C$	$E_T$	$E_{\text{exp}}$
(I)	—	—	49.8	90.8	86.1
(II)	—	2.9	43.1	84.5	—
(III)	0.07	2.1	63.6	110.5	—
(IV)	—	—	10.5	83.7	74.9
(V)	0.04	0.9	21.3	62.8	48.8
(VI)	—	2.2	19.2	60.3	60.7
(VII)	—	—	19.7	60.7	47.7

displacements at a given temperature. For this calculation, the Brillouin zone is divided into a mesh with 13 divisions along each reciprocal basic vector and the contribution of the acoustic phonons with small wave vectors is calculated analytically following Kroon & Vos (1978). Crystal and time-reversal symmetry are effective for reducing the portion of the Brillouin zone to be sampled.

Prior to the calculation of the lattice dynamics a Newton-Raphson energy-minimization process must be carried out shifting the molecules from their experimental position in order to get the equilibrium structure corresponding to the chosen parameter set. The program *WMIN* (Busing, 1972) has been used for this process whereas our program *DYN* has been used in the lattice-dynamical calculations. As usual, C—H bond distances have been normalized to 1.09  $\text{\AA}$  in order to obtain consistency with the model and a better agreement with the experimental data.

### Equilibrium structures and lattice frequencies

The best agreement between calculated and observed crystallographic thermal parameters is obtained using the Williams & Cox set; therefore, in order to save space, only the results for this set are reported, concerning lattice frequencies and equilibrium configurations. The results for the other set are quite similar. Table 3 shows the calculated lattice energy (at infinite cut-off radius) and the shifts obtained in the energy-minimization process; the latter are comparable to the commonly accepted threshold values 0.1  $\text{\AA}$  and  $2^\circ$  (Hsu & Williams, 1980) and the energy values show that the Coulombic contribution amounts to a large part of the total, except for hexamethylenetetramine. This is in agreement with former lattice-dynamical studies of this compound using 6-exp potential functions only (Dolling, Pawley & Powell, 1973). Table 4 shows the experimental and calculated lattice frequencies. The agreement is acceptable and similar to other calculations with potentials which have not been explicitly adjusted to fit the lattice frequencies. The poorer agreement for pyrazine (especially for some frequencies) might be due to the possible pres-

Table 4. *Calculated and experimental lattice frequencies in THz (1 THz =  $33.356 \text{ cm}^{-1}$ )*

(I)	cal.	exp. <sup>(a)</sup>	cal.	exp.	
$F_g$	3.59	3.93	$F_u$	3.46	
	2.63	2.40		2.22	—
	1.78	2.10		—	—
(II)	cal.	exp. <sup>(b)</sup>	cal.	exp.	
$A_g$	1.92	2.24	$A_u$	1.18	
	2.38	2.57		3.30	3.22
	3.69	3.21		—	—
$B_g$	1.07	1.09	$B_u$	2.01	
	2.27	2.90		2.77	—
	3.47	3.70		—	—
(IV)	cal.	exp. <sup>(c)</sup>			
$F_1$	1.57	1.75			
(V)	cal.	exp. <sup>(d)</sup>	cal.	exp.	
$A_1$	3.10	2.82	$B_1$	3.16	
	2.49	2.64		2.16	2.58
	2.21	2.01		2.04	1.89
	1.95	—		1.64	1.50
	1.35	—		1.04	1.02
$A_2$	3.04	—	$B_2$	2.75	
	2.68	—		2.11	1.98
	2.04	—		2.01	—
	1.81	1.74		1.69	—
	1.27	1.29		1.04	—
(VI)	cal.	exp. <sup>(d)</sup>	cal.	exp.	
	$A_{1u}$	2.66	—	$B_{3g}$	3.36
	$A_{2g}$	3.05	2.82	$B_{1g}$	1.59
				1.33	1.26
	$B_{1u}$	1.32	2.04	$B_{2g}$	2.68
$B_{2u}$	1.66	1.44		1.23	
(VII)	cal.	exp. <sup>(d)</sup>	cal.	exp.	
	$A_{2g}$	2.20	—	$A_{2u}$	0.97
		3.50	—		—
	$E_g$	2.46	2.74	$E_u$	2.52
		2.68	2.02		2.52

References: (a) Chaplot, Mierzejewski & Pawley (1985); (b) Chaplot, Mierzejewski, Pawley, Lefebvre & Luty (1983); (c) Dolling & Powell (1970); (d) Gamba & Bonadeo (1981).

ence of a weak hydrogen bond (Reynolds, 1973). Considering that these potentials have been obtained by a fit to only equilibrium properties, we can say that the vibrational results are similar to those found in hydrocarbons with potentials derived in the same way. An important fact in favour of the electrostatic model is that phonon curves are stable everywhere inside the Brillouin zone and that omitting Coulombic interactions produces instabilities in some of the compounds. This gives support to the feasibility of calculating thermal parameters in azahydrocarbons using this potential model.

### Thermal parameters

Results obtained with the two parameter sets are very alike, although as a rule the Williams & Cox parameters tend to give a slightly better agreement in nearly all cases; therefore, we decided to show these results only in Table 5, together with the experimental values obtained from different techniques and the

Table 5. Calculated and experimental thermal parameters ( $\times 10^4 \text{ \AA}^2$ )
$$T(\mathbf{H}) = \exp\left(-2\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* H_i H_j\right); \mathbf{H} = (hkl).$$

		$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
(I)							
N1	(cal.)	284	421	256	0	-73	0
	$R = 21.4$ (a)	451	453	300		-139	
	31.6 (b)	507	479	403		-94	
C2	29.0 (c)	469	465	324		135	
		232	254	220	0	-29	0
		311	306	239		-39	
C1		346	319	299		9	
		331	306	247		-32	
		207	160	193	0	0	0
C1		277	254	195			
		355	253	257			
		272	267	225			
(II)							
C1	(cal.)	294	340	496	-6	-20	31
	$R = 23.6$ (d)	368	277	626	12	105	59
C2		477	461	535	-56	55	54
		489	369	586	-152	338	-74
C3		411	360	573	-30	-43	-6
		456	303	606	0	121	6
N2		774	650	624	-152	174	100
		942	525	831	-176	752	48
N3		605	393	719	-87	-75	-51
		717	397	853	-220	50	-81
(III)							
C1	(cal.)	316	352	272	-20	-31	5
	$R = 21.5$ (e)	277	281	252	-8	-25	-13
C2		282	238	310	4	-66	-5
		225	216	265	4	-25	-2
C3		359	400	406	-113	-84	104
		305	311	453	-80	-27	63
C4		427	422	338	-37	-129	-19
		399	338	361	-18	-130	2
C5		396	462	359	93	7	-104
		332	384	324	39	6	-72
C6		322	289	471	62	-81	-82
		280	262	390	39	-20	-48
C7		310	286	286	44	-57	-8
		296	266	280	32	-20	1
N1		561	564	482	-37	-273	-58
		608	550	681	-91	-387	30
N2		561	589	574	246	-16	-224
		488	401	576	151	18	-123
N3		372	462	734	154	-95	-190
		319	457	681	99	-10	-137
N4		574	472	324	145	-140	3
		480	431	366	109	-90	58
(IV)							
C	(cal.)	387	677	677	0	0	0
	$R = 14.9$ (f)	262	652	652			5
	16.6 (g)	320	684	684			34
N	16.0 (h)	267	638	638			5
		541	541	541	-77	-77	-77
		485	485	485	-101	-101	-101
H		523	523	523	-100	-100	-100
		486	486	486	-105	-105	-105
		972	972	469	-41	149	149
		1106	1106	513	-55	235	235
		932	932	433	-83	512	512
		1110	1110	515	-53	238	238

corresponding  $R$  factors. A look at this table shows that the agreement between calculated and experimental crystallographic thermal parameters is similar to that displayed for such calculations in hydrocarbons and can be regarded as good in view of the

Table 5 (cont.)

		$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
(V)							
N1	(cal.)	420	985	682	-84	-49	-27
	$R = 19.9$ (i)	371	794	512	-47	-22	-63
		540	934	550	-55	-86	13
C1		449	847	456	-62	-66	-31
		507	916	576	-86	27	3
C2		466	727	500	-102	57	-34
		545	884	563	-78	-110	-5
C3		499	807	487	-72	-66	-21
		548	795	548	-130	14	-42
C4		464	643	449	-113	54	-57
		428	836	623	-83	-47	-67
C1		372	754	539	-108	30	-61
(VI)							
C	(cal.)	250	412	268	-27	-34	47
	$R = 17.2$ (j)	292	381	285	-28	-30	19
	17.0 (k)	308	375	295	-33	-39	30
N	28.2 (l)	278	346	265	-33	-39	30
		182	480	426	0	0	73
		225	452	335			61
C1		238	435	358			68
		208	403	327			65
(VII)							
C1	(cal.)	517	609	866	—	13	—
	$R = 16.8$ (m)	520	520	1050		20	
	20.1 (n)	540	760	1130		40	
N1	27.4 (o)	520	790	1080		-30	
		521	623	903	—	-14	—
		490	550	1150		-30	
H1		560	560	1290		-30	
		580	510	1340		10	
		591	904	1656	—	24	—
		700	750	1990		-40	
		750	550	1730		-20	
		670	450	1870		490	

References: (a) Neutron data, 293K (Becker, Coppens & Ross, 1973); (b), (c) FA and HO X-ray data, 293K (Little, Pautler & Coppens, 1971); (d) X-ray data, 293K (Bekoe & Trueblood, 1960); (e) X-ray data, 293K (Lemley, Skarstad & Hughes, 1976); (f) Neutron data, 293K, TDS (Duckworth, Willis & Pawley, 1970); (g), (h) LO and HO, 293K, TDS (Stevens & Hope, 1975); (i) X-ray data, 271K (Wheatley, 1960); (j), (k), (l) HO TDS, FA TDS, FA no TDS, X-ray data 184K (de With, Harkema & Feil, 1976); (m), (n), (o) Neutron data, Cu and Mo X-ray data, 297K (Coppens, 1967).

LO, HO, FA and TDS mean low-order, high-order, full-angle Bragg data and TDS correction, respectively.

many limitations of the lattice-dynamical model (harmonic approximation, molecular rigidity, approximate character of the potential functions *etc.*). Another fact which shows up in Table 5 is the different value of the agreement factor

$$R = 100 \sum_i \sum_j |U_{ij}(\text{exp.}) - U_{ij}(\text{cal.})| / \sum_i \sum_j |U_{ij}(\text{exp.})|,$$

obtained for experimental thermal parameters from different sources, including neutron data or high-order and low-order X-ray data separately; in some cases a TDS correction is also performed, otherwise the experimental parameters are smaller than their true values (Criado, Conde & Marquez, 1985). On the other hand, thermal parameters obtained from neutron data are in general more reliable than those from X-ray data because asphericity in the electrical cloud due to bonding induces bias in thermal parameters calculated from spherical-atom models. This

deviation can be minimized if we use high-order X-ray data because valence electrons contribute less compared with core electrons for high-angle Bragg reflections. We can see that experimental parameters from neutron data show a better agreement with our calculations and the same applies to TDS-corrected thermal parameters. As for high-order and low-order parameters, the differences are not very important.

The agreement factor with the experimental thermal parameters taken from the earlier X-ray photographic study for pyrazine (Wheatley, 1957) (36%) is notably poorer than that obtained with the more accurate data of de With, Harkema & Feil (1976) and this shows the essential accuracy of our model.

### Concluding remarks

Calculations of crystallographic thermal parameters using atom-atom potential functions can be performed successfully for azahydrocarbons and hopefully for other heteroatomic systems provided that a reliable molecular electrostatic model is available and the results are comparable with those obtained for hydrocarbons. In order to make meaningful comparisons, reliable experimental parameters must be used, preferably those obtained from neutron data and corrected for TDS.

### References

- BECKER, P., COPPENS, P. & ROSS, F. K. (1973). *J. Am. Chem. Soc.* **95**, 7604-7609.
- BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1-22.
- BONADEO, H. & BURGOS, E. (1982). *Acta Cryst.* **A38**, 29-33.
- BORN, M. & HUANG, K. (1954). *Dynamical Theory of Crystal Lattices*. Oxford: Clarendon Press.
- BUSING, W. R. (1972). *Acta Cryst.* **A28**, S252-S253.
- CALIFANO, S., RIGHINI, R. & WALMSLEY, S. H. (1979). *Chem. Phys. Lett.* **64**, 491-494.
- CHAPLOT, S. L., MIERZEJEWSKI, A. & PAWLEY, G. S. (1985). *Mol. Phys.* **56**, 115-128.
- CHAPLOT, S. L., MIERZEJEWSKI, A., PAWLEY, G. S., LEFEBVRE, J. & LUTY, T. (1983). *J. Phys. C*, **16**, 625-644.
- COCHRAN, W. & PAWLEY, G. S. (1964). *Proc. R. Soc. London Ser. A*, **280**, 1-22.
- COPPENS, P. (1967). *Science*, **158**, 1577-1578.
- CRiado, A. (1989). *Acta Cryst.* **A45**, 409-415.
- CRiado, A., CONDE, A. & MARQUEZ, R. (1984). *Acta Cryst.* **A40**, 696-701.
- CRiado, A., CONDE, A. & MARQUEZ, R. (1985). *Acta Cryst.* **A41**, 158-163.
- CRiado, A. & MARQUEZ, R. (1988). *Acta Cryst.* **A44**, 76-78.
- DOLLING, G., PAWLEY, G. S. & POWELL, B. M. (1973). *Proc. R. Soc. London Ser. A*, **333**, 363-384.
- DOLLING, G. & POWELL, B. M. (1970). *Proc. R. Soc. London Ser. A*, **319**, 209-235.
- DOVE, M. T., POWELL, B. M., PAWLEY, G. S., CHAPLOT, S. L. & MIERZEJEWSKI, A. (1989). *J. Chem. Phys.* **90**, 1918-1923.
- DUCKWORTH, J. A. K., WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 263-271.
- EWALD, P. P. (1921). *Ann. Phys. (Leipzig)*, **64**, 253-287.
- FILIPPINI, G. & GRAMACCIOLI, C. (1986). *Acta Cryst.* **B42**, 605-609.
- FILIPPINI, G. & GRAMACCIOLI, C. (1989). *Acta Cryst.* **A45**, 261-263.
- FILIPPINI, G., GRAMACCIOLI, C. & SIMONETTA, M. (1981). *Chem. Phys. Lett.* **79**, 470-475.
- FILIPPINI, G., GRAMACCIOLI, C., SIMONETTA, M. & SUFFRITTI, G. B. (1973). *J. Chem. Phys.* **59**, 5088-5101.
- FILIPPINI, G., GRAMACCIOLI, C., SIMONETTA, M. & SUFFRITTI, G. B. (1974). *Acta Cryst.* **A30**, 189-196.
- FILIPPINI, G., GRAMACCIOLI, C., SIMONETTA, M. & SUFFRITTI, G. B. (1976). *Chem. Phys. Lett.* **39**, 14-18.
- GAMBA, Z. (1985). *J. Chem. Phys.* **83**, 5892-5896.
- GAMBA, Z. & BONADEO, H. (1981). *J. Chem. Phys.* **75**, 5059-5066.
- GOVERS, H. A. J. (1975). *Acta Cryst.* **A31**, 380-385.
- GRAMACCIOLI, C. & FILIPPINI, G. (1983). *Acta Cryst.* **A39**, 784-791.
- GRAMACCIOLI, C. & FILIPPINI, G. (1985). *Acta Cryst.* **A41**, 361-365.
- GRAMACCIOLI, C., FILIPPINI, G. & SIMONETTA, M. (1982). *Acta Cryst.* **A38**, 350-356.
- HSU, L. Y. & WILLIAMS, D. E. (1980). *Acta Cryst.* **A36**, 277-281.
- KROON, P. & VOS, A. (1978). *Acta Cryst.* **A34**, 823-824.
- LEMLEY, J. T., SKARSTAD, P. M. & HUGHES, R. E. (1976). *Acta Cryst.* **B32**, 35-40.
- LINK, K. H., GRIMM, H., DORNER, B., ZIMMERMANN, H., STILLER, H. & BLECKMANN, P. (1985). *J. Phys. Chem. Solids*, **46**, 135-142.
- LITTLE, R. G., PAUTLER, D. & COPPENS, P. (1971). *Acta Cryst.* **B27**, 1493-1499.
- LUTY, T. & PAWLEY, G. S. (1975). *Phys. Status Solidi B*, **69**, 551-555.
- MIRSKAYA, K. V. & NAUCHITEL, V. V. (1972). *Sov. Phys. Crystallogr.* **17**, 56-59.
- PAWLEY, G. S. (1967). *Phys. Status Solidi B*, **20**, 347-360.
- PAWLEY, G. S. (1972). *Phys. Status Solidi B*, **49**, 475-487.
- REYNOLDS, P. A. (1973). *J. Chem. Phys.* **59**, 2777-2786.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.
- STEVENS, E. D. & HOPE, H. (1975). *Acta Cryst.* **A31**, 494-498.
- WHEATLEY, P. J. (1955). *Acta Cryst.* **8**, 224-226.
- WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 182-187.
- WHEATLEY, P. J. (1960). *Acta Cryst.* **13**, 80-85.
- WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680-4684.
- WILLIAMS, D. E. & COX, S. R. (1984). *Acta Cryst.* **B40**, 404-417.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
- WITH, G. DE, HARKEMA, S. & FEIL, D. (1976). *Acta Cryst.* **B32**, 3178-3184.
- WOODS, A. D. B., COCHRAN, W. & BROCKHOUSE, B. N. (1960). *Phys. Rev.* **119**, 980-999.