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Lattice-Dynamical Evaluation of Temperature Factors for Aromatic Hydrocarbons, Including Internal Molecular Motion: A Straightforward Systematic Procedure

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Abstract

As a part of a systematic project of evaluating temperature factors for molecular crystals in a harmonic approximation, following the Born–von Kàrmàn procedure, application to essentially 'rigid' aromatic hydrocarbons has been reconsidered. In this approximation, where 'rigidity' just implies non-mixing between internal vibrational modes and external ('lattice') modes, contributions of the former to the temperature factors of the various atoms have been added to the corresponding contributions of the latter modes. Following Gwinn's method for normal coordinate analysis in the molecule, and Pawley's method for calculating the lattice modes, it is possible to write highly efficient routines, so that practical application to the various molecules becomes easy and straightforward, the final result being reached in a quite reasonable computing time, with a 'usual' crystallographic input. For intermolecular interactions, Williams IV*a* potentials have been used, and a Califano–Neto harmonic force field has been adopted for calculating in-plane internal vibration modes; a suitable value for torsional force constants has been assigned for calculating the out-of-plane modes. For these calculations, which have been carried out on benzene, naphthalene (h_8 and d_8), anthracene, phenanthrene and pyrene as examples, the relative importance of intramolecular contribution can be seen in all these compounds, with respect, for instance, to the ring members (here only carbon atoms), or to the peripheral members (here only hydrogen atoms). Because of TDS influence upon the experimental results, the agreement with the observed **B**'s is generally less good than for simpler models, where the internal modes are neglected. For H atoms, the calculated internal contributions to the **B**'s are too high in the case of benzene and naphthalene, and about right for pyrene. The situation is discussed in terms of the effect of packing upon internal modes, and relative non-rigidity of pyrene with respect to smaller molecules.

Introduction

In recent years, an ever-growing interest is being given to temperature factors of molecular crystals. Whereas fitting to rigid-body or similar models and possible evaluation of bond-length corrections has been considered for a long time (see, for instance, Cruickshank, 1956*a*,*b*,*c*, 1961; Busing & Levy, 1957, 1964; Schomaker & Trueblood, 1968; Johnson, 1969, 1970*a*,*b*, 1980; Willis & Pawley, 1970; Pawley & Willis, 1970; Pawley, 1970; Prince & Finger, 1973), until quite recently comparatively little effort was made in deducing further useful information. Similarly, little comparison of these experimental data with theoretical estimates had been published, until the appearance of the 'classical' works by Cochran & Pawley (1964) and Pawley (1967, 1968, 1972). Here, the rigid-body vibration tensors were calculated starting from semi-empirical atom–atom potentials, through a Born–von Kàrmàn lattice-dynamical procedure, and practical application to compounds such as hexamethylenetetramine, naphthalene, and anthracene were given as examples. Similarly, theoretical derivation of these quantities from lattice dynamics, including an approximative method for evaluating internal-mode contributions, has been thoroughly examined by Scheringer (1972*a*,*b*,*c*); a series of systematic calculations on several 'rigid' molecular substances, and comparison with experimental results has been reported by various authors (Gramaccioli, Simonetta & Suffritti, 1973; Cerrini & Pawley, 1973; Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974*a*,*b*, 1976*a*,*b*, 1978; Willis & Howard, 1975; Kroon & Vos, 1979; Filippini, Gramaccioli & Simonetta, 1981). These systematic calculations showed the possibility of simplifying the computing routines considerably, *e.g.* by scanning the

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Brillouin zone at uneven intervals. Moreover, the agreement between observed and calculated values was substantially good; this supported not only the validity of such theoretical estimates, but also the essential 'rightness' of the experimental data, which up to then were often disregarded by most crystallographers.

At the same time, determination of mean-square displacement amplitudes in several molecules was being developed by spectroscopists. A good review of this is given especially in books by Cyvin (1968, 1972); Cyvin himself is co-author of several papers dealing with this subject (*e.g.* Whitmer, Cyvin & Cyvin, 1978; Bakke, Cyvin, Whitmer, Cyvin, Gustavsen & Klaeboe, 1979; Cyvin, Cyvin, Brunvoll, Whitmer, Klaeboe & Gustavsen, 1979). Application of these spectroscopic routines in crystals, especially concerning the **FG** method, was considered by Scheringer and his group (Scheringer & Fadini, 1979; Ishii & Scheringer, 1979). Quite recently, the importance of determining temperature factors as a probe for structural dynamics of biologically important molecules like proteins has been illustrated (Frauenfelder, Petsko & Tsernoglou, 1979; Artymiuk, Blake, Grace, Oatley, Phillips & Sternberg, 1979). Besides biological application, an accurate evaluation of thermal vibration tensors becomes essential for accurate electron-density determination, bond-length correction, and also for checking the 'goodness' of semi-empirical potentials, or of a certain structural model, over the entire Brillouin zone.

Method of calculation

For essentially 'rigid' molecules, *i.e.* where separation is assumed between internal (molecular) and external (lattice) modes, the calculated **B**'s can be considered to be the sum of internal and external contributions. For the latter, the method here used is essentially the same as we adopted in our former works, *i.e.* evaluation of temperature factors *via* the rigid-body tensors **T**, **L**, **S**, as they derive from a Born–von Kàrmàn lattice-dynamical treatment (Pawley 1967, 1968; Filippini, Gramaccioli, Simonetta & Suffritti, 1973). Apart from a different evaluation of self–self terms, the essential difference between Pawley's original procedure and ours is a different sampling of the Brillouin zone, which in our case is made at uneven intervals (Filippini, Gramaccioli, Simonetta & Suffritti, 1976*a*; from this paper, the sequence reported as '*C*' has been adopted, with a net comprising four points per reciprocal axis).

For the internal modes, we followed the normal coordinate analysis, according to Gwinn's (1971) method. This method has been used and recommended also by Stølevik, Seip & Cyvin (1972) for evaluating mean-square amplitudes. It has the advantage over the traditional **FG** method of avoiding construction of symmetry coordinates and search for redundancy relationships. Moreover, the treatment is essentially similar to the usual lattice-dynamical one, thereby providing a parallel procedure, which is quite useful when the same set of programs is used for both kinds of calculations. Moreover, this way affords comparatively easy extension to cases where mixed internal–external modes are present (*i.e.* non-rigid molecules), and such a possibility is being actively considered by us.

In this procedure, we first build the **F** matrix, where $F_{ij} = \partial^2 V/\partial\xi_i\,\partial\xi_j$. Here, ξ_i and ξ_j are internal coordinates in terms of variation of all bond lengths, angles, torsion angles, *etc.* in the molecule, regardless of their number, which is usually redundant with respect to the vibrational degrees of freedom. Then **F** is referred to mass-weighted atomic coordinates through the transformation: $\mathbf{M} = \mathbf{S}^T\mathbf{F}\mathbf{S}$. Here, **S** is a rectangular matrix, where $S_{ij} = \partial\xi_i/\partial x'_j$, where x'_j is the mass-weighted coordinate of a certain atom. Owing to the considerable dimensions of the involved matrices, this multiplication implies a non-negligible computing time, and also necessary space in the memory. Since most elements of **F** and **S** are zero, we find that a satisfactory procedure is to consider only the relatively few non-zero terms in one array, and a parallel array contains the row and column indices. After these arrays have been filled, a preliminary sorting based on indices allows a subsequent very fast multiplication.

Diagonalization of **M** (*via* a Householder routine) affords squares of the normal mode frequencies, since $\omega^2\mathbf{q} = \mathbf{M}\mathbf{q}$, and the six lowest modes (five for a linear molecule) have zero frequency, and correspond to the degrees of freedom of the free isolated molecule: they can consequently be omitted from our consideration.

The contribution of each internal mode to the U_{ij}'s of every atom p are evaluated as: $U_{ij(p)} = q_{i'}\, q_{j'}\, \varepsilon(\omega)/m\omega^2$, where $q_{i'}$ and $q_{j'}$ are the components of the eigenvector corresponding to the ith and jth coordinate of the atom p, and the average energy of the mode $\varepsilon(\omega) = \hbar\omega[\frac{1}{2} + 1/\exp(\hbar\omega/kT - 1)]$.

From these expressions, the analogy between this treatment and the lattice-dynamical procedure is evident.

The internal mode contribution to the coupling tensors $\mathbf{U}_{pp'}$, where p and p' are different atoms, can be obtained as for the **U**'s, provided $q_{i'}$ and $q_{j'}$ are referred to p and p', respectively. These tensors can be useful for correcting bond lengths for thermal motion (Scheringer, 1972*c*), albeit in practice their explicit use becomes useful in non-rigid bodies only. As for lattice vibrations, a check of the calculated frequencies with experimental data (if available) may be quite useful. For this purpose, the Raman- or infrared-active frequencies are always calculated. An appropriate labelling countersigns the symmetry of each mode: this labelling is automatically given by a proper routine (Filippini & Gramaccioli, 1982).

On the whole, the complete process involving calculation of internal and external modes is reasonably fast, employing about one minute of computing time on a UNIVAC 1100/80.

Application to hydrocarbons

For aromatic hydrocarbons, some harmonic force fields of general application are reported in the literature. Such force fields are especially reliable for calculating vibration modes in the molecular plane, where the assignment of fundamental frequencies is nowadays clear. The classical work by Neto, Scrocco & Califano (1966: here onwards NSC) gives an excellent agreement with the experimental data (see also Schettino, 1967; Schettino, Neto & Califano, 1966; Neto & Di Lauro, 1970); this force field has been used in all our calculations, with minor modifications (see below). More recently, Cyvin and his collaborators (Whitmer, Cyvin & Cyvin, 1978; Bakke, Cyvin, Whitmer, Cyvin, Gustavsen & Klaeboe, 1979; Cyvin *et al.*, 1979) give another in-plane force field involving a diagonal **F** matrix, and this approximation requires five independent parameters only. Although the agreement with experimental frequencies is somewhat less good than for the NSC field, these authors show that the mean amplitudes are nearly identical for the two fields. This is not surprising, in view of the extensive averaging over the various modes; moreover, considering the relatively limited accuracy of the experimental **B**'s, where the contribution of lattice modes predominates over that of internal modes, this emphasizes the relatively little importance of fitting the internal-mode frequencies exactly, an approximate agreement being more than sufficient for most purposes involving temperature factors.

In the NSC force field, bending and stretching force constants are assigned taking account of the nature and the π order of the bond. The π order can be derived either from the experimental bond length, or, better, from considering the various Kekulé structures; a detailed analysis of these structures permits assignment of stretching–stretching force constants. In order to extend the NSC force field to all possible aromatic hydrocarbons, a separate polynomial interpolation for the reported constants relative to bonds in *ortho*, *meta*, and *para* positions with respect to each other has been made. Similarly, a rather elaborate way for reproducing the NSC bending–bending force constants correctly, based on bond geometry, has been introduced in the program. It can be noticed, however, that not all the reported values in Table 9 of NSC's work can be exactly reproduced on this basis (see, for instance, the corresponding stretching–stretching force constants for C—H bonds, which are 0·17 nN Å^{-1} for benzene, and 0·68 nN Å^{-1} for naphthalene and anthracene, or some apparently 'equivalent' bending–bending force constants – at least from the geometric point of view – which are –0·45 and 1·11 nN Å^{-1} for naphthalene and anthracene, respectively). In these cases, although the program can provide for separate assignment of any (or any kind) of force constant, we have followed the 'automatic' assignment made by the program, which just considers the most common value.

For out-of-plane vibrations, the situation is more complex, since no force field which is as reliable as for in-plane vibrations has been reported in the literature. We first tried the Evans–Scully (1964) force field, which uses seven different constants, including out-of-plane bendings and twistings and mixed terms (bending–bending, bending–twisting, twisting–twisting). This field gives a remarkably good agreement with the experimental data, at least if the reported assignment of the fundamental frequencies is correct. However, this force field did not meet our requirements: firstly, because of the considerable complexity in assigning the off-diagonal elements of the **F** matrix by a computer routine, and, secondly, there seems to be an incompatibility between the Evans–Scully treatment and Gwinn's procedure. This can be explained in view of the approximations involved in considering derivatives of twisting around the various π bonds.

A sufficiently approximate force field for out-of-plane vibrations can be obtained by considering all twistings, involving any possible set of four atoms around any C(sp^2)—C(sp^2) bond. Force constants of 0·9 nN Å^{-1} were assigned to each twisting, and no off-diagonal term involving twisting was introduced in the **F** matrix. From Table 1, it can be seen that the agreement with the experimental frequencies (at least considering the most accepted assignment) is satisfactory, and comparable with the results afforded by harmonic force fields, which have recently been developed by other authors, such as Whitmer, Cyvin & Cyvin (1978).

For lattice vibrations, we used the Williams IV*a* functions (Williams, 1967). As we had noticed in our previous works, these functions are among the best for reproducing Raman- and infrared-active vibration frequencies, and temperature factors. Quite recently, these functions have been shown to be particularly valuable in reproducing the experimental dispersion curves of naphthalene (Natkaniec *et al.*, 1980; Pawley *et al.*, 1980). Some comments about the maximum packing distance $D_{\max}$ are necessary: in Pawley's works and in our first applications a value of 5·5 Å was considered; the same distance is apparently assumed in the work by Natkaniec *et al.*, concerning dispersion curves, which probably gives the most convincing evidence about the practical validity of these potential functions in reproducing lattice vibrations. Whereas for evaluation of several physical-chemical properties such a distance does not correspond to convergence to infinity, if a larger value for the maximum packing distance is assumed, the calculated values for the frequencies are somewhat too low with respect to experiment, and the corresponding **B**'s become too large, beyond a reasonable expectation due to some thermal diffuse scattering (TDS) contribution in lowering the observed values. For phenanthrene, if this larger value for $D_{\max}$ is assumed, imaginary frequencies result for a certain range of the wave vector **q**, a phenomenon which does not happen if $D_{\max}$ is shorter. In a previous work (Filippini & Gramaccioli, 1981), we had already considered the possibility of including $D_{\max}$ as a parameter in empirical calculations involving atom–atom potentials. For all these reasons, and considering the arguments for this purpose given by Williams himself (Williams, 1967), we have chosen a value of 5·5 Å for the maximum packing distance. When extrapolation to infinity has to be considered, other potentials appropriate to the case should be derived.

Discussion

Results of our calculations for benzene (Bacon, Curry & Wilson, 1964), d_8-naphthalene (Pawley & Yeats, 1969), anthracene (Lonsdale & Milledge, 1961; Mason, 1964), phenanthrene (Kay, Okaya & Cox, 1971) and pyrene (Hazell, Larsen & Lehman, 1972) are shown in Table 2. In this table, the results including contribution of internal modes are compared with the corresponding ones involving contribution of lattice modes only, *i.e.* the usual rigid-body motion. For each compound, the disagreement indices are given as: $R = 100\sum|B_{ij(\text{obs})} - B_{ij(\text{calc})}|/\sum|B_{ij(\text{obs})}|$, and $\Delta B = 100\sum(B_{ij(\text{obs})} - B_{ij(\text{calc})})/\sum B_{ij(\text{obs})}$. R gives the percentage disagreement between observed and calculated temperature factors, similar to that currently used for structure factors; ΔB shows a systematic excess (or deficiency) relative to the observed values with respect to the corresponding calculated data.

The agreement between the experimental **B**'s and the lattice dynamical results is, on the whole, satisfactory. In all these cases the effect of internal motion upon the **B**'s is relatively limited, at least if the peripheral H atoms are not considered. The observed values of the **B**'s are smaller than the corresponding calculated data: this is presumably due to the effect of thermal diffuse scattering (TDS) upon the experimental data, which were not corrected for this purpose (Willis & Pryor, 1975).

It might be tempting to scale the observed and calculated **B**'s; the agreement obviously becomes much better (R_t = 20·7% for benzene, 14·2% for naphthalene and 20·2% for pyrene). However, the assumption of TDS to be isotropic is questionable, and anyway it does not seem wise to estimate a possible correction for such an effect in this manner.

Reliable experimental values for temperature factors of hydrogen atoms are obtained by neutron diffraction only; among the substances here treated, three (benzene, d_8-naphthalene and pyrene) have been examined so far by neutron diffraction. For benzene and naphthalene, there is a systematic disagreement between the observed and calculated **B**'s of hydrogen (deuterium) atoms: this disagreement can hardly be ascribed to TDS, since it is considerably larger than for all the other cases here treated and for the carbon atoms in the same compounds. It seems that the

Table 1. *Observed and calculated out-of-plane internal frequencies* (cm^{-1})

	Benzene				h_8-Naphthalene			d_8-Naphthalene			Anthracene			Pyrene				Phenanthrene		
	obs[a]	calc[b]	calc[a]		obs[c]	calc[b]	calc[d]	obs[e]	calc[b]	calc[f]	obs[g]	calc[b]	calc[h]	obs[i]	calc[b]	calc[i]		obs[j]	calc[b]	calc[j]
B_{2g}	995	1067	996	B_{1g}	943	962	934	761	748	751	915	979	936	–	927	899	B	951	1045	962
	703	607	703		717	676	702	547	504	528	–	696	739	–	793	811		874	978	923
E_{1g}	849	801	850		386	371	312	348	338	316	–	455	466	–	523	512		819	856	837
											243	248	235	263	268	251		735	797	810
				B_{2g}	980	1048	1305	–	846	812	978	1044	960	–	1034	963		713	692	733
					876	882	952	–	759	754	904	931	909	971?	996	947		494†	674	702
					846	735	679	649	626	665	–	838	871	780?	856	764		441†	479	498
					461	451	379	410	417	429	765	748	754	–	731	755		427	397	407
											622	535	617	530?	534	579		233	241	226
											290	288	321	–	464	469		–	116	103
														227	282	272				
E_{2u}	975	1010	977	B_{3u}	958	995	999	791	800	798	954	992	952	963	1031	957	A	–	1046	966
	405	371	402		782	721	714	628	579	594	883	910	892	845	827	816		–	1010	946
					476	446	429	402	387	382	730	692	732	748	726	753		928	979	922
					176	190	139	166	174	163	469	451	504	710	688	717		880	877	834
											166*	363	383	484	460	483		761	774	752
											110	99	96	219	222	195		594	711	726
														126	121	113		513	538	601
A_{2u}	675	607	676	A_u	970	1041	1150	–	814	829	–	1042	966	–	1005	942		–	503	502
					841	827	776	–	638	648	–	853	876	–	915	897		352	401	384
					581	558	417	–	506	511	–	704	826	–	637	660		–	256	258
					195	206	185	193	190	185	–	482	552	319?	406	391		123	146	138
											–	144	137	164	173	179				

References: (*a*) Harada & Shimanouchi (1966); see also Taddei *et al.* (1973); (*b*) Present work; (*c*) Hagen & Cyvin (1968); (*d*) Whitmer *et al.* (1978); (*e*) Bree & Kydd (1970); (*f*) Scully & Whiffen (1960); (*g*) Raman frequencies–Suzuki, Yokoyama & Ito (1968), infrared frequencies–Bree & Kydd (1968); (*h*) Evans & Scully (1964); (*i*) Bree, Kydd, Misra & Vilkos (1971); (*j*) Schettino *et al.* (1966).

* Other values, either observed or calculated, in closer agreement with our calculated ones, are reported by Bree & Kydd (1970).

† Values of 495 and 715 cm^{-1}, which fit better with our calculations, have been observed by Bree, Solven & Vilkos (1972).

internal contribution to these **B**'s is too large; on the other hand, the calculated values for the frequencies are plausible, and this disagreement does not occur for pyrene.

A possible explanation can be given if the effect of crystal packing forces upon the molecule is considered. This effect has been calculated for naphthalene by Pawley & Cyvin (1970). As is shown in Table 1 of their work, these authors report a considerable increase of the lowest (out-of-plane) vibrational frequencies (up to 40 cm^{-1}) on passing from the free state to the molecule packed in the crystal. Since the lowest modes are the most effective in contributing to the **B**'s, this might explain the observed disagreement. For pyrene, instead, the internal (molecular) modes can be considerably lower than for smaller molecules (see Table 1): in such a case, some mixing between the lowest internal modes and the highest lattice modes might occur, and no reason for having substantially higher frequencies than for the free molecule should result.

As we can see by comparing the lowest internal mode frequencies reported in Table 1 with the highest lattice mode frequencies reported in the literature [see, for instance, Table V in Filippini, Gramaccioli, Simonetta & Suffritti (1973), or Taddei, Bonadeo, Marzocchi & Califano (1973)], for benzene and naphthalene only no mixing between internal and external modes is strictly true; for all the other cases, owing to the larger size of the molecules, the lowest internal modes (generally out-of-plane) are of the same magnitude as

Table 2. *Experimental and calculated crystallographic temperature factors* (Å^2 × 10^4)

First calculated values include internal mode contribution, second ones involve contribution of lattice modes only. They are in the form:

$$T_i = \exp|-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)|$$

	B_{11}			B_{22}			B_{33}			B_{12}			B_{13}			B_{23}		
	obs	calc$_t$	calc$_e$	obs	calc$_t$	calc$_e$	obs	calc$_t$	calc$_e$	obs	calc$_t$	calc$_e$	obs	calc$_t$	calc$_e$	obs	calc$_t$	calc$_e$
Benzene																		
C(1)	83	157	154	49	68	65	111	190	183	3	−3	−4	−12	−9	−9	0	−3	−3
C(2)	83	156	152	56	83	80	119	186	179	−3	−3	−2	20	14	14	−3	−5	−5
C(3)	94	158	154	51	76	74	128	179	172	0	−15	−15	0	1	1	3	8	8
H(1)	184	266	219	69	85	69	204	349	264	0	7	12	20	−1	−1	6	6	1
H(2)	174	245	210	134	141	118	243	338	253	40	27	18	114	71	73	31	−1	−6
H(3)	177	241	216	98	128	99	221	314	229	−11	−28	−23	55	34	32	46	38	35
D_8-Naphthalene																		
C(*A*)	262	352	346	357	500	491	181	217	205	−12	34	34	115	148	145	3	−2	−5
C(*B*)	202	285	278	250	367	358	187	225	213	−50	−11	−11	87	115	112	−31	−47	−51
C(*C*)	116	201	195	163	278	268	174	211	199	−10	7	6	69	99	97	0	−3	−7
C(*D*)	190	273	268	200	321	310	235	283	271	15	−4	−4	118	153	151	−18	32	28
C(*E*)	251	342	337	311	457	446	228	273	261	52	41	42	145	186	183	16	76	73
D(*A*)	432	542	520	561	792	724	197	288	221	−42	48	44	163	201	193	−17	−12	−33
D(*B*)	328	434	397	314	463	415	235	353	290	−119	−92	−78	126	167	146	−110	−117	−126
D(*D*)	307	412	379	232	383	329	338	454	391	−6	−81	−66	182	233	214	−89	21	14
D(*E*)	402	537	495	448	651	607	311	430	360	113	66	60	238	305	287	14	186	158
Pyrene																		
C(1)	91	90	85	177	215	201	234	280	274	10	21	15	23	−16	−18	−38	−62	−65
C(2)	65	75	70	149	173	162	287	326	320	−13	−2	−7	36	7	5	−59	−53	−55
C(3)	63	64	61	104	128	121	228	265	260	−4	2	0	57	25	24	−16	−19	−20
C(4)	86	85	81	123	145	135	283	308	302	−8	−4	−8	89	55	53	26	9	7
C(5)	98	98	94	151	154	144	242	254	248	15	14	10	93	55	54	47	26	24
C(6)	72	79	76	132	135	127	164	204	200	27	22	20	47	26	25	20	3	2
C(7)	86	103	98	210	184	173	176	207	202	45	36	32	22	8	6	−1	−10	−12
C(8)	75	95	90	223	198	183	244	258	253	24	27	22	18	−17	−19	−43	−45	−48
C(9)	58	74	70	171	162	151	318	301	295	−9	4	0	37	−2	−4	−57	−36	−38
C(10)	56	62	59	106	124	117	252	248	243	−1	6	3	54	18	16	−5	−8	−9
C(11)	81	77	73	132	147	137	318	286	280	−13	−1	−5	90	40	38	26	21	18
C(12)	97	89	85	142	164	153	243	240	235	13	15	11	86	42	40	54	32	30
C(13)	74	73	70	115	144	137	172	203	199	17	21	18	53	19	18	17	1	0
C(14)	102	95	91	181	201	190	153	214	209	34	33	29	29	1	0	−6	−19	−21
C(15)	55	58	54	83	116	107	170	207	203	5	15	11	46	20	19	0	−7	−9
C(16)	53	59	55	90	112	103	170	203	199	8	16	13	43	20	18	1	−4	−6
H(1)	119	134	109	279	335	269	343	367	325	9	47	19	−1	−40	−46	−86	−86	−104
H(2)	100	108	82	226	255	193	437	459	436	−60	−15	−30	63	18	10	−77	−63	−74
H(4)	121	127	103	202	225	168	462	435	412	−53	−18	−31	122	84	77	31	24	13
H(5)	155	155	134	259	246	193	302	319	279	15	30	13	119	93	80	114	57	55
H(7)	154	161	139	335	288	230	212	238	199	74	67	48	56	29	14	58	6	4
H(8)	98	140	114	375	312	246	334	340	298	17	55	27	−12	−41	−48	−84	−65	−82
H(9)	90	105	79	273	243	181	519	423	401	−51	−7	−22	87	5	−4	−75	−40	−51
H(11)	120	116	92	236	226	169	512	402	379	−52	−12	−25	133	64	56	57	41	31
H(12)	154	142	121	247	260	207	347	300	261	6	32	15	127	73	60	100	63	61
H(14)	158	150	127	287	310	251	217	242	202	36	64	45	56	17	3	49	−2	−4

	R_t	ΔB_t	R_e	ΔB_e
Benzene	48·6	−34·4	33·0	−16·2
D_8-Naphthalene	43·5	−39·6	34·5	−30·0
Pyrene	19·8	2·1	21·8	12·8

the highest lattice vibration modes. The situation is somewhat contradictory with respect to our assumption of molecular rigidity, and although these effects are probably minor for carbon atoms, they are rather important for peripheral atoms, as we have seen. Especially if extension to larger molecules is claimed, a complete treatment involving mixing of internal and lattice modes is desirable, and effort is presently being made towards reaching a practical solution of this general case. Similarly, since thermal diffuse scattering is one of the most important sources of disagreement with experimental data, a practical way for correcting the collected intensities for this effect is being actively considered; from Table 2 it seems, in fact, that even a rough correction for TDS might lead to excellent agreement between theoretical and observed temperature factors. This seems to be especially important, if one considers that the necessary elastic coefficients can be easily obtained through these same lattice-dynamical calculations.

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The Observation of Molecular Orientations in Crystal Defects and the Growth Mechanism of Thin Phthalocyanine Films

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Abstract

The crystal imperfections in very thin films of metal-phthalocyanines were observed by means of high-resolution electron microscopy. It was revealed that the anisotropic molecular shape played an important role in the formation of the defect and grain boundaries. The quasi-amorphous state of phthalocyanine was found in which the existence of a linear crystal, a molecular column, was confirmed in the early stages of the formation of the three-dimensional crystal.

Introduction

The energy structure as well as the electrical and photo-conductive properties of molecular crystals cannot fully be interpreted without considering the local structures of the crystal, because the local lattice irregularities have the possibility to act as traps for electrons. Therefore, information about the local structure having certain irregularities, such as point, line, planar and bulk defects, is required for organic crystals by those who intend to develop organic materials for practical use. The properties of such defects in molecular crystals fundamentally differ from those in covalent or metallic crystals because of the anisotropy of intermolecular forces and of the shapes of the molecules. The differences also cause various peculiarities in growth mechanisms of the crystal. Investigations of defects in organic crystals have been carried out by Williams, Thomas, Williams & Hobbs (1975) on the basis of diffraction contrast in electron micrographs and by Fryer (1977) by the use of molecular imaging. In the present investigation, not only the defect structures but also the growth mechanisms of phthalocyanine crystals have been revealed through a direct observation of molecular images by means of high-resolution electron microscopy with the aid of an automatic minimum-dose system, which has been developed by the present authors (Fujiyoshi, Kobayashi, Ishizuka, Uyeda, Ishida & Harada, 1980) in order to avoid the deterioration of the images due to the radiation damage of the crystal. In the section discussing the growth mechanism, a quasi-amorphous or precrystalline state will be shown as the early stage of the crystal growth.

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