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The Thermal Vibrations in Diketopiperazine

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An analysis of the anisotropic atomic thermal parameters obtained by Degeilh & Marsh for diketopiperazine has shown that the principal rigid-body translations of the molecules are along the directions towards neighbouring parallel chains of molecules and are of the order of amplitude 0·13–0·14 Å. The translational amplitude within the chain is a little less. The rigid-body libration about the normal to the molecule is very small (semi-amplitude 1·8°), and results in tangential movements of C_1, C_2 and N of the order of 0·04 Å, and of O of 0·08 Å. There are very large out-of-plane librational movements about in-plane axes (semi-amplitudes 7·0° and 4·7°) the larger being about an axis making an angle of about 45° with [101] and about 10° with the C=O bond. The O and C_1 atoms appear to have vibrational movements approximately along [101] which are independent of the rigid-body vibrations. The coefficient of expansion should be minimum along [101] and maximum normal to (10$\bar{1}$).

In a recent paper by Degeilh & Marsh (1959), to which we shall refer as DM, the crystal structure of diketopiperazine has been refined. This study shows that Corey's original (1938) X-ray determination was remarkably accurate. Vainshtein (1955) later gave hydrogen positions, based on an electron-diffraction study. The latest refinement (DM) gives individual anisotropic temperature factors, but does not attempt more than a qualitative interpretation of these data in terms of rigid-body translations and librations.

Since their R-factor (for 1144 observed reflexions with non-zero weight) is 0·072, it does seem possible to analyze the DM thermal-vibration data with some confidence (Lonsdale & Milledge, 1959).
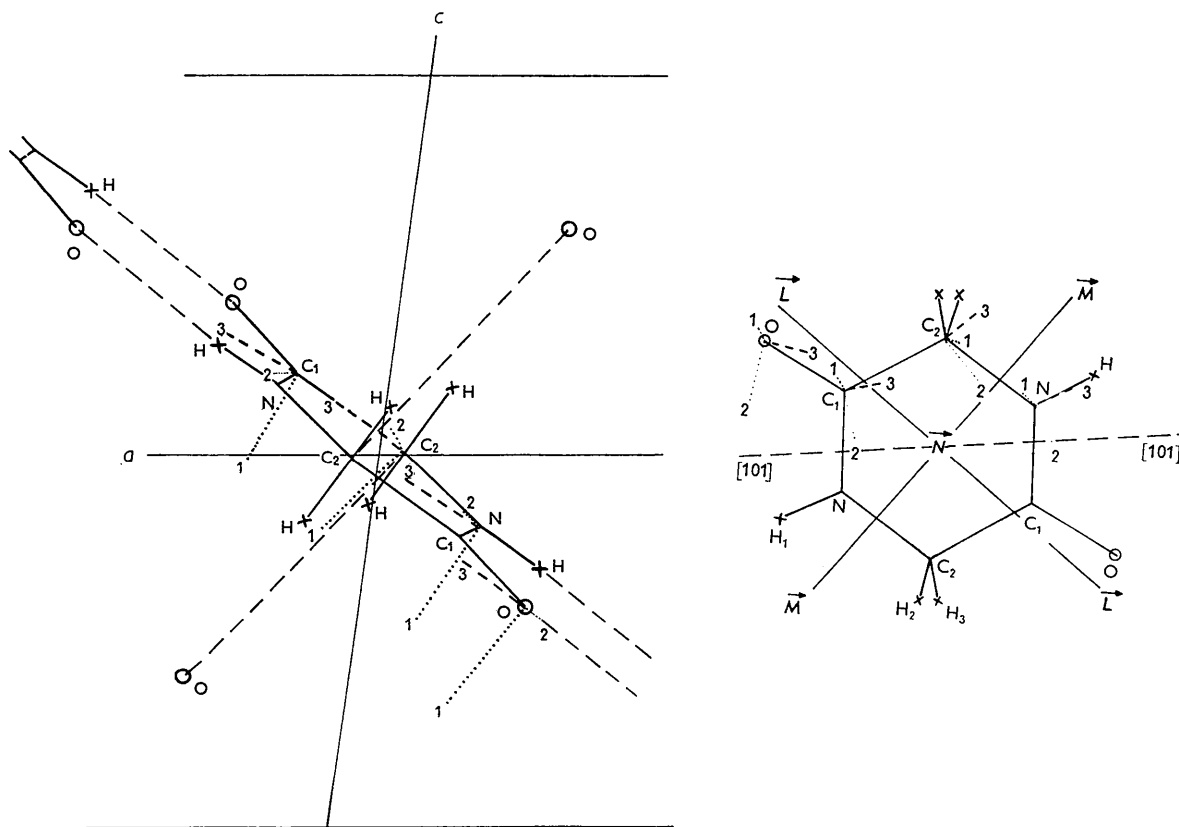
Fig. 1. (a) Directions of major axes of thermal vibration for individual atoms as seen in projection (010). (b) Directions of major axes of thermal vibration for individual atoms as seen in projection on the molecular plane. The directions shown for L, M, N are those finally selected as preferred libration axes.

In Table 2 of DM the temperature parameters are given in the form

$$T_i = \exp \left(- \alpha_i h^2 - \beta_i k^2 - \gamma_i l^2 - \delta_i hk - \varepsilon_i hl - \eta_i kl \right).$$

In their Table 7 the $\alpha_i \ldots \eta_i$ are transformed by the method of Rollett & Davies (1955) into magnitudes and direction cosines of principal axes of the B-ellipsoids.* It is stated that for all atoms except C_1 the

* Dr Marsh writes to say:

'It has been pointed out by Dr Allen Larson that the transformed direction cosines in Table 7 of DM are in error. The correct values of the principal temperature factors and their direction cosines relative to the real crystallographic axes are as follows:

Atom	Axis i	B_i	g_{i1}	g_{i2}	g_{i3}
C_1	1	2·356	−0·552	0·096	0·897
	2	1·604	0·188	0·982	−0·015
	3	1·252	0·812	−0·162	0·442
C_2	1	3·248	−0·724	−0·133	0·771
	2	1·520	0·341	0·784	0·467
	3	1·224	0·600	−0·606	0·434
N	1	3·444	−0·563	−0·062	0·894
	2	1·668	0·235	0·944	0·197
	3	1·080	0·792	−0·324	0·402
O	1	4·856	−0·617	−0·018	0·865
	2	1·920	−0·241	0·956	−0·132
	3	1·304	0·749	0·293	0·484'

B_1 axis is within 8° of the normal N to the molecular plane, while for C_1 it is within 16° (cf. our Table 2); and the authors add 'Probably none of these deviations is greater than the experimental error', the implication being that B_1 may really lie along N for all the heavy atoms. But if this were so, one would expect to find the directions of B_1 scattered randomly about N in space, whereas in fact they all lie much more closely *in* (010) and *normal to* (10$\bar{1}$). This may be seen from Table 1, where the angle of B_1 with [010] is always greater than the angle of N with [010], whereas B_1 lies at $-5 \cdot 5°$, $+7 \cdot 7°$, $+3 \cdot 6°$, $+1 \cdot 0°$ to (010); and the scatter of B_1 about the normal to (10$\bar{1}$) is random.

The molecular plane is about 9° away from (10$\bar{1}$) but B_2 and B_3 are rather nearer to (10$\bar{1}$) than to the molecular plane, although if we except B_2 for C_1 there is not a great deal to choose between them (Fig. 1(a)).

Fig. 1(b) shows that *in* the molecular plane there is considerable dispersion of the directions of B_2 and B_3, although on the whole they can be described as being along the normal to [101] and along [101], respectively.

Using the molecular dimensions given in DM, it is possible to write down equations (Lonsdale & Milledge, 1959; Lonsdale, Milledge & Rao, 1960) which express the mean-square amplitudes in terms of independent

Table 1. *Values of B_i, $\overline{u_i^2}$ and $(\overline{u_i^2})^{\frac{1}{2}}$, with corresponding angles, direction cosines and (direction cosines)^2, relative to [101], [010] and the normal ($\perp$) to (10$\bar{1}$), deduced from Table 2 of DM*

Atom	B_i (Å²)	$\overline{u_i^2}$ (Å²)	$(\overline{u_i^2})^{\frac{1}{2}}$ (Å)	Angles relative to [101]	[010]	$\perp$ (10$\bar{1}$)	Direction cosines [101]	[010]	$\perp$ (10$\bar{1}$)	(Direction cosines)² [101]	[010]	$\perp$ (10$\bar{1}$)
C₁ (1)	2·356	0·0298	0·173	96·4	95·5	8·6	−0·111	−0·096	0·989	0·012	0·009	0·978
(2)	1·604	0·0203	0·143	81·6	10·8	83·5	0·151	0·982	0·113	0·023	0·964	0·013
(3)	1·252	0·0158	0·126	10·9	99·3	84·6	0·982	−0·161	0·094	0·964	0·026	0·009
C₂ (1)	3·248	0·0411	0·203	83·3	82·3	10·2	0·117	0·133	0·984	0·014	0·018	0·968
(2)	1·520	0·0192	0·139	53·5	38·3	100·2	0·594	0·784	−0·177	0·353	0·615	0·031
(3)	1·224	0·0155	0·124	37·3	127·3	90·7	0·795	−0·606	−0·013	0·632	0·367	0·000
N (1)	3·444	0·0436	0·209	95·7	86·4	6·8	−0·100	0·062	0·993	0·010	0·004	0·986
(2)	1·668	0·0211	0·145	70·7	19·3	91·5	0·330	0·943	−0·026	0·109	0·889	0·001
(3)	1·080	0·0137	0·117	20·2	109·0	83·4	0·938	−0·326	0·115	0·880	0·106	0·013
O (1)	4·856	0·0616	0·248	92·0	89·0	2·3	−0·035	0·018	0·999	0·001	0·000	0·998
(2)	1·920	0·0243	0·156	106·9	17·0	91·6	−0·291	0·956	−0·028	0·085	0·914	0·001
(3)	1·304	0·0165	0·128	17·1	73·0	88·4	0·956	0·292	0·029	0·914	0·085	0·001
Directions of molecular normal N, relative to these axes				90·3	80·7	9·2	−0·006	0·161	0·987	0·000	0·026	0·974

Note 1. E.s.d. for thermal parameters are not given by DM but in a private communication Dr Marsh says that they average to about 0·05 in units of B (0·0006 in units of $\overline{u^2}$).

Note 2. The directions [101], [010] and $\perp$ (10$\bar{1}$) are referred to in later discussion as E, F, G.

rigid-body and non-rigid-body vibrations, as follows:

$$\overline{u_i^2} = \sum_k t_k^2 \alpha_{ik}^2 + \sum_j R_{ij}^2 \varphi_j^2 \alpha_{ij}^2 + \overline{u_{id}^2}, \qquad (\mathrm{I})$$

where the t_k are the rigid-body translational amplitudes (Å) along specified directions k, and α_{ik} are the direction cosines for the individual atomic vibration amplitudes relative to those directions; φ_j are the rigid-body librational amplitudes (in radians) and $R_{ij}\varphi_j$ are the actual librational atomic amplitudes (Å) assumed tangential to the radius vectors to axes j, which may but need not be identical with k. The non-rigid-body (distortional) atomic vibration u_{id} is assumed to be along the direction of the resultant vibration u_i and will be taken as near to zero unless there is a clear indication to the contrary.

The translational vibrations, which include long thermal waves of large amplitude in which neigh-bouring molecules move together, may be expected to predominate, and thus largely to control the directions of the resultant individual atomic principal vibration directions (thermal axes). Figures 1(*a*) and (*b*) both imply that the average directions k are [101], [010] and the perpendicular to (10$\bar{1}$) which we have named E, F, G directions. Table 1 lists the corresponding values of α_{ik}.

The libration axes may be expected to be the normal N to the molecular plane, and two orthogonal axes in that plane. For the latter, the corresponding atomic movements (assumed small) will be parallel to N, and hence α_{ij} is the direction cosine of the thermal axis relative to N(α_{iN}). For the libration about N, the corresponding atomic movements will be in the molecular plane, normal to the radius vector of the appropriate atom. The direction cosines of the thermal axes relative to these 'tangents', α_{iT}, will be indepen-

Table 2. *Angles and direction cosines of resultant thermal axes relative to the molecular normal N and the in-plane tangential direction for each atom; and (direction cosines)^2*

Atom	B_i	Angles relative to N	T_i	Direction cosines α_{iN}	α_{iT}	$(\alpha_{iN})^2$	$(\alpha_{it})^2$
C₁(1)	2·356 Å²	16·0	81·8	0·961	0·142	0·924	0·020
(2)	1·604	74·4	134·3	0·269	−0·698	0·072	0·487
(3)	1·252	86·5	45·4	0·062	0·702	0·004	0·493
C₂(1)	3·248	7·2	83·2	0·992	0·118	0·984	0·014
(2)	1·520	93·0	47·2	−0·052	0·680	0·003	0·462
(3)	1·224	96·6	43·6	−0·115	0·724	0·013	0·524
N (1)	3·444	7·8	98·3	0·991	−0·145	0·982	0·021
(2)	1·668	82·8	8·1	0·125	0·990	0·016	0·979
(3)	1·080	86·8	88·9	0·055	0·019	0·003	0·004
O (1)	4·856	8·5	84·7	0·989	0·093	0·978	0·009
(2)	1·920	82·6	161·1	0·128	−0·946	0·017	0·896
(3)	1·304	86·1	71·9	0·070	0·310	0·005	0·096

dent of the particular orientations of the in-plane libration axes; only the values of R_{ij} for the in-plane axes will vary. Table 2 gives the values of α_{iN} and α_{iT}, therefore, for all possible directions of libration axes in and normal to the molecular plane.

Table 3 shows the variation of R_{ij} with the direction of the in-plane libration axes.

The equation (I) then assumes the following form for the $C_1(1)$ thermal vibration, with similar equations for the other eleven thermal axes.

$$0\cdot0298 = 0\cdot012t_E^2 + 0\cdot009t_F^2 + 0\cdot978t_G^2 + 0\cdot924.1\cdot440^2$$
$$\times [\varphi_L^2.\sin^2(1\cdot2+\psi) + \varphi_M^2.\cos^2(1\cdot2+\psi)]$$
$$+ 0\cdot020.1\cdot440^2.\varphi_N^2 + u_{11}^2.$$

Table 3. *Values of radial distances R_{ij} from the molecular axes L, M, N, where L is an in-plane axis making an angle of ψ with O $\cdots$ –O and of $(61\cdot4° - \psi)$ with $C_2 \cdots -C_2$*

Atom	R_{iL}	R_{iM}	R_{iN}
C_1	1·440 sin (1·2+ψ)	1·440 cos (1·2+ψ)	1·440
C_2	1·454 sin (61·4−ψ)	1·454 cos (61·4−ψ)	1·454
N	1·379 sin (57·1+ψ)	1·379 cos (57·1+ψ)	1·379
O	2·677 sin ψ	2·677 cos ψ	2·677

It is reasonable to neglect all terms with coefficients of less than 0·1 and we are left with the following set of approximate equations:

C_1 (1) $0\cdot0298 = 0\cdot98t_G^2 + 1\cdot91[\varphi_L^2.\sin^2(1\cdot2+\psi)$
$+ \varphi_M^2.\cos^2(1\cdot2+\psi)] + u_{11}^2$ (1)

C_2 (1) $0\cdot0411 = 0\cdot97t_G^2 + 2\cdot08[\varphi_L^2.\sin^2(61\cdot4-\psi)$
$+ \varphi_M^2.\cos^2(61\cdot4-\psi)] + u_{21}^2$ (2)

N (1) $0\cdot0436 = 0\cdot99t_G^2 + 1\cdot87[\varphi_L^2.\sin^2(57\cdot1+\psi)$
$+ \varphi_M^2.\cos^2(57\cdot1+\psi)] + u_{31}^2$ (3)

O (1) $0\cdot0616 = 1\cdot00t_G^2 + 7\cdot01(\varphi_L^2.\sin^2\psi$
$+ \varphi_M^2.\cos^2\psi) + u_{41}^2$ (4)

C_1 (2) $0\cdot0203 = 0\cdot96t_F^2 + 0\cdot15[\varphi_L^2.\sin^2(1\cdot2+\psi)$
$+ \varphi_M^2.\cos^2(1\cdot2+\psi)] + 1\cdot01\varphi_N^2 + u_{12}^2$ (5)

C_2 (2) $0\cdot0192 = 0\cdot35t_E^2 + 0\cdot62t_F^2 + 98\varphi_N^2 + u_{22}^2$ (6)

N (2) $0\cdot0211 = 0\cdot11t_E^2 + 0\cdot89t_F^2 + 1\cdot86\varphi_N^2 + u_{32}^2$ (7)

O (2) $0\cdot0243 = 0\cdot91t_F^2 \qquad + 6\cdot42\varphi_N^2 + u_{42}^2$ (8)

C_1 (3) $0\cdot0158 = 0\cdot96t_E^2 \qquad + 1\cdot02\varphi_N^2 + u_{13}^2$ (9)

C_2 (3) $0\cdot0155 = 0\cdot63t_E^2 + 0\cdot37t_F^2 + 1\cdot111\varphi_N^2 + u_{23}^2$ (10)

N (3) $0\cdot0137 = 0\cdot88t_E^2 + 0\cdot11t_F^2 \qquad + u_{33}^2$ (11)

O (3) $0\cdot0165 = 0\cdot91t_E^2 \qquad + 0\cdot69\varphi_N^2 + u_{43}^2.$ (12)

The maximum value of t_F^2 (from (5)) is 0·0210 and this corresponds (from (10)) to a minimum t_E^2 of 0·0122 if $\varphi_N^2 = u_{23}^2 = 0$; but t_E^2 can be less if $\varphi_N^2 \neq 0$.

In order to explain the consistently larger values of B_2, t_F^2 must be considerably larger than t_E^2 unless there are big internal vibrations along the (2) directions.

It seems that we must choose between large values of u_{22}^2, u_{32}^2 (and u_{12}^2), which correspond with $\varphi_N^2 \geq 0\cdot0016$, or a large value of u_{43}^2 and medium u_{13}^2, which correspond with t_E^2, t_F^2 and φ_N^2 equal or near to 0·0116, 0·0193, 0·0010 respectively, and for which

$$0\cdot15(\varphi_L^2\sin^2(1\cdot2+\psi) + \varphi_M^2\cos^2(1\cdot2+\psi)) + u_{12}^2 = 0\cdot0008.$$

There seems no physical reason why the internal vibrations along the (2) axes should be large, but u_{43} and u_{13} correspond to movements of O and of C approximately along the [101] (H-bonding) direction, which are not impossible. It would be interesting to see whether neutron-diffraction studies would show an even larger H movement in this direction, or might indicate that some or all of u_{43} and u_{13} is due to bond anisotropy and not vibration.

The most reasonable positions of the in-plane libration axes would seem to be either [101] and its normal in the molecular plane ($\psi = -35\cdot5°$), or along and perpendicular to the line joining centro-symmetrical oxygen atoms ($\psi = 0°$). The former would be the axis common to a string of molecules along the [101] direction; the latter would be (or be near to) the axis of inertia of the single molecule. These two alternatives would give

$C_1(1)$ $0\cdot0298 = 0\cdot98t_G^2 + 0\cdot61\varphi_L^2 + 1\cdot30\varphi_M^2 + u_{11}^2$
$C_2(1)$ $0\cdot0411 = 0\cdot97t_G^2 + 2\cdot05\varphi_L^2 + 0\cdot03\varphi_M^2 + u_{21}^2$ $\psi =$
N (1) $0\cdot0436 = 0\cdot99t_G^2 + 0\cdot25\varphi_L^2 + 1\cdot62\varphi_M^2 + u_{31}^2$ $-35\cdot5$
O (1) $0\cdot0616 = 1\cdot00t_G^2 + 2\cdot36\varphi_L^2 + 4\cdot65\varphi_M^2 + u_{41}^2$

$C_1(1)$ $0\cdot0298 = 0\cdot98t_G^2 + 0\cdot01\varphi_L^2 + 1\cdot90\varphi_M^2 + u_{11}^2$
$C_2(1)$ $0\cdot0411 = 0\cdot97t_G^2 + 1\cdot60\varphi_L^2 + 0\cdot48\varphi_M^2 + u_{21}^2$ $\psi = 0°$
N (1) $0\cdot0436 = 0\cdot99t_G^2 + 1\cdot32\varphi_L^2 + 0\cdot55\varphi_M^2 + u_{31}^2$
O (1) $0\cdot0616 = 1\cdot00t_G^2 \qquad + 7\cdot01\varphi_M^2 + u_{41}^2$

Trial solutions show, however, that for $\psi = -35\cdot5°$ (and directions in this region) the equations always lead to rather large out-of-plane vibrations of C_2 and/or N. By taking $\psi = 0°$ it is possible to avoid postulating such large intra-molecular vibrations, al-

Table 4. *Range of values of t_E^2, t_F^2 and φ_N^2 and corresponding values of the internal vibrations u_{id}^2*

t_E^2	t_F^2	φ_N^2	u_{22}^2	u_{32}^2	u_{42}^2	u_{13}^2	u_{23}^2	u_{53}^2	u_{43}^2
0·0122	0·0210	0	0·0025	0·0011	0·0052	0·0041	0	0·0006	0·0054
0·0130	0·0197	0	0·0024	0·0022	0·0065	0·0033	0	0·0001	0·0067
0·0130	0·0170	0·0009	0·0032	0·0029	0·0030	0·0024	0	0·0004	0·0063
0·0116	0·0193	0·0010	0·0021	0·0007	0·0003	0·0037	0	0·0014	0·0052
0·0124	0·0162	0·0015	0·0034	0·0025	0	0·0024	0	0·0010	0·0042
0·0138	0·0135	0·0016	0·0044	0·0046	0·0017	0·0010	0	0·0001	0·0029
0·0138	0·0124	0·0020	0·0047	0·0048	0·0002	0·0006	0	0·0002	0·0026

though as Table 5 shows, u_3 is still fairly large; but it can be reduced by giving ψ a small positive value. [It may be true, however, that N does have an independent out-of-plane vibration, tending to pyramidal rather than plane bonds.]

Table 5. *Values of* t_G^2, φ_L^2 *and* φ_M^2 *consistent with minimum values of* u_{id}^2, *for* $\psi = 0°, 5°, 10°, 15°$

t_G^2	φ_L^2	φ_M^2	u_{11}^2	u_{21}^2	u_{31}^2	u_{41}^2
$\psi = 0°$ (range of values)						
0·0204	0·0120	0·0050	0	0	0·0048	0·0062
0·0181	0·0128	0·0062	0	0	0·0054	0
0·0125	0·0160	0·0070	0·0012	0	0·0063	0
$\psi = 5°$ (best value)						
0·0173	0·0141	0·0062	0·0007	0	0·0034	0
$\psi = 10°$ (best value)						
0·0176	0·0150	0·0060	0·0004	0	0·0006	0
$\psi = 15°$ (best value)						
0·0183	0·0145	0·0055	0	0·0022	0	0·0005

Table 5 shows that $\psi = 10°$, that is, an axis making an angle of $10°$ with $O \cdots -O$ and $51\cdot4°$ with $C_2 \cdots -C_2$ in the molecular plane, is a most probable libration axis, together with its normal *in* the molecular plane, and N the normal to the molecular plane. But if $\psi = 0°$, then $\overline{u_{31}^2}$ is approximately 0·005. Table 6 gives a summary of the best set of all parameters, for which the non-rigid-body vibrations are minimum.

Conclusion

The vibration pattern that emerges is one in which the chains of molecules extended along [101] and linked by hydrogen bonds are behaving like a bundle of sinuous and somewhat elastic ribbons. The easy movements are those by which the atoms move out of the plane of the ribbon, either by a translational or librational movement of the molecule as a whole. Translation of the molecule within the chain is slightly more difficult and rigid-body libration about the normal to the molecular plane much more so. There seems to be an independent (non-rigid-body) movement of the oxygen atom along the [101] direction, which is accompanied by a smaller movement of the

C_1 atom to which it is directly attached; and possibly even of N and C_2, the latter along the direction (2). The N atom may have an out-of-plane vibration, tending towards pyramidal bonding; but this is not proved.
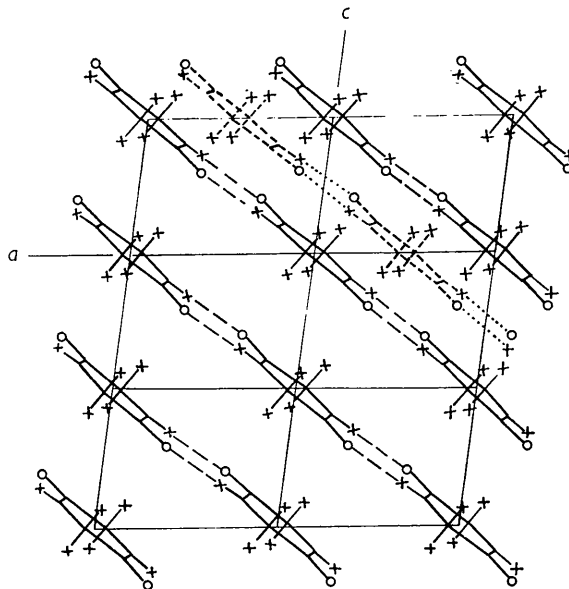

Fig. 2. Diagram to show chains of molecules along [101] directions in one (010) plane. One chain of molecules of the next sheet (through $\frac{1}{2}$, $\frac{1}{2}$, 0) is also shown.

Low-temperature measurements on this substance would be of particular interest, as one would expect that the non-rigid-body movements would not be temperature-dependent, but that the t and φ values should be reduced. The coefficient of expansion is probably a minimum along [101] and a maximum normal to (10$\bar{1}$). Neutron-diffraction experiments could indicate whether the non-rigid-body movements found for O and C are really due, in whole or in part, to bonding anisotropy.

I am indebted to my colleagues at University College for computational assistance and to Dr R. A. Sparks for a Mercury programme converting $\alpha_i \ldots \eta_i$

Table 6. *The best set of translational and librational (amplitudes)^2 and r.m.s., together with residual intramolecular vibrations* u_{id}^2 *and* $(\overline{u_{id}^2})^{\frac{1}{2}}$

t_E^2	t_F^2	t_G^2	φ_L^2	φ_M^2	φ_N^2	u_{11}^2	u_{21}^2	u_{31}^2	u_{41}^2
0·0116	0·0193	0·0176	0·0150	0·0060	0·0010	0·0004	0	0·0006	0

	u_{12}^2	u_{22}^2	u_{32}^2	u_{42}^2	u_{13}^2	u_{23}^2	u_{33}^2	u_{43}^2	
	0	0·0021	0·0007	0·0003	0·0037	0	0·0014	0·0052	

$(\overline{u^2})^{\frac{1}{2}}$ translations along			$(\overline{\varphi^2})^{\frac{1}{2}}$ librations about		
[101]	[010]	$\perp$ (10$\bar{1}$)	L	M	N
0·11 Å	0·14 Å	0·13 Å	0·12(7·0°)	0·08(4·7°)	0·03(1·8°) radians

u_{11}	u_{21}	u_{31}	u_{41}	u_{12}	u_{22}	u_{32}	u_{42}	u_{13}	u_{23}	u_{33}	u_{43}
0·02 Å	0	0·025	0	0	0·045	0·025	0·015	0·06	0	0·035	0·07

to thermal parameters relative to a, b, c^*. My thanks are due also to Mrs Varwell for help with diagrams; to the Wellcome Trust for a grant for computing and to the University of London Central Research Fund for tape-editing equipment. I must particularly thank Dr R. E. Marsh for most useful suggestions in relation to the orientation of the libration axes.

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A Detailed Refinement of the Crystal Structure of Sodium Tropolonate

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A refinement of the crystal structure of sodium tropolonate, including anisotropic temperature factors, has been carried out using Sasada & Nitta's three-dimensional data. The differential Fourier synthesis and the least-squares methods were used and the two results are compared.

Introduction

The crystal and molecular structure of sodium tropolonate $NaC_7H_5O_2$ was studied by Sasada & Nitta (1956) with three-dimensional line synthesis through atomic centers. The standard deviation of their final bond lengths suggested that more accurate values for the interatomic distances could be obtained by further refinement of their data.

There have been several structure analysis of tropolone derivatives, i.e. cupric tropolone, $C_{14}H_{10}CuO_4$ by Robertson (1951); purpurogallin by Taylor (1952) and by Dunitz (1952); tropolone by Kiruta & Kubo (1953); tropolone hydrochloride, $C_7H_7ClO_2$, by Sasada, Osaki & Nitta (1954) and Sasada & Nitta (1957); tribromo-tropolone, $C_7H_3Br_3O_2$, by Kubo, Kurita & Kimura (1954); 2-bromo-3-hydroxy-tropone, $C_7O_2H_5Br$ and 7-bromo-3-hydroxy-tropone by McDonald (1955). All these results except tropolene hydrochloride (1957) were based on one projection of the X-ray data only, or by electron diffraction. Tropolone hydrochloride was refined with three-dimensional data in a similar manner to that of sodium tropolonate.

Since no complete three-dimensional refinement of a structure containing a tropolone ring have been completed we have undertaken this further refinement on the sodium salt using anisotropic temperature factors. A subsidiary purpose of the work was the more complete testing of the differential synthesis and anisotropic structure factor refinement programs which have been written for the IBM 650 computer (Shiono, 1957, 1959).

The numbering of atoms in the tropolonate ion, I,

is the same as used in the earlier paper. The space group of the crystal structure is $P2_1/c$ with 4 molecules in the unit cell,

$$a = 13\cdot91, \ b = 3\cdot69, \ c = 11\cdot67 \text{ Å}, \ \beta = 93\cdot1°.$$

I
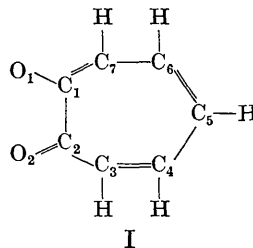
Three-dimensional refinement by the Fourier method

All the observed data in the Table 2* and Table 3 of the paper by Sasada & Nitta (1956) were used in this refinement. The final coordinates and temperature factors were taken as the starting parameters. Cyclic computations of structure factors followed by the differential synthesis with both observed and calculated structure factors were used to refine the parameters by means of an IBM 650.

The atomic scattering factors for Na, O and C used are those by Berghuis *et al.* (1955). An overall temperature factor of $3\cdot3$ Å^2 was applied in the first calculation of structure factors, and this was changed to $3\cdot2$ Å^2

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* All the values in the Table 2 were multiplied by a factor of 2 in order to bring them to the normal scale of the Table 3.