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Structure and Packing Arrangement of Molecular Compounds. V.* Constrained Refinement of a Disordered (1:1) Tetracyanoethylene–Naphthalene Structure†

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The previously made suggestion that the apparent thermal motion of naphthalene in the (1:1) naphthalene–tetracyanoethylene complex conceals orientational disorder has been confirmed by a constrained refinement based on the published data. It appears that the disorder in the above structure, at room temperature, is due mainly to usual van der Waals interactions.

Introduction

A well known feature of molecular complexes is the fact that the environments of the constituent molecules are in general dissimilar. It follows, in the case of π-molecular compounds, that the forces experienced by the donor and by the acceptor may be rather different and hence a different pattern of thermal motion of such molecules is hardly surprising. However, the disparity of the thermal parameters of naphthalene and tetracyanoethylene in their 1:1 complex (Williams & Wallwork, 1967; hereafter referred to as WW) required further investigation as it is unusually large (Fig. 1). Thus, WW suggested in the original paper that a small contribution of disordered orientations may explain the observed peaks in their difference map of naphthalene. The in-plane libration, however, was considered to be genuine. Herbstein & Snyman (1969) studied this problem with the aid of electron density and difference density maps as well as by examining the thermal parameters of the naphthalene carbon atoms. They concluded that a minor orientational disorder is in fact present in this complex and that the published structure of naphthalene (WW) corresponds to a superposition of two orientations in which the molecules are rotated in a plane by ± 7·5° away from the published orientation. We have arrived at a qualitatively similar conclusion (Shmueli & Goldberg, 1973) which differs from that of Herbstein & Snyman (1969) in the angular deviation from the published orientation. The results of our approach, illustrated in Fig. 2, are based on evaluating a potential curve corresponding to the motion of naphthalene about a direction associated with the suspiciously large libration amplitude. The method is easy to apply but like other approaches it may only generate a hypothesis that still needs to be tested.

As far as we know, cases of minor orientational disorder were, so far, not confronted directly with observed structure amplitudes, although the constrained refinement that makes such a confrontation possible was long since recognized (Pawley, 1963) as an appropriate method in cases of disorder.

Following the results obtained in our study of disorder *via* potential calculations we decided to investigate this problem with the aid of constrained refinement techniques and thereby to assess the applicability of these methods to cases of apparently false thermal motion. In this communication we report our results on the π-molecular compound (1:1) tetracyanoethylene (TCNE)–naphthalene. Apart from naphthalene, the TCNE molecule in this complex was also of interest

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since two minima in the potential curve were found upon rotating TCNE about its plane normal (Fig. 2), indicating a situation very similar to that observed in the TCNE–paracyclophane complex (Bernstein & Trueblood, 1971).

The constrained refinement of the TCNE–naphthalene complex described below is based on the F_o data published by WW.

Refinement of the structure

The structure of the 1:1 complex of TCNE and naphthalene was solved by WW from three-dimensional counter data and was refined by WW to a conventional reliability index $R=0{\cdot}130$. The above refinement was based on heavy atoms only, using 512 independent reflexions and assuming the space group $C2/m$ ($Z=2$), as inferred from negative piezo- and pyro-electric tests. Intensity statistics of the published data indicate a hypercentric distribution and thus support the correct choice of the above space group.

Some computational details of the least-squares routine employed in the present work are given in the Appendix. In this work the index of the published structure for the 512 reflexions is 0·128, the slight difference from $R=0{\cdot}130$, reported by WW, probably being due to the use of different scattering factor curves. Unit weights are used throughout the calculations.

Since the dimensions of the naphthalene in the published structure were rather seriously distorted the input atomic parameters were evaluated on the basis of the molecule found in the naphthalene crystal (Abrahams, Robertson & White, 1949) and refined by Cruickshank (1957). These dimensions were averaged so as to impart to naphthalene an *mm* symmetry. The modified molecule was then inserted into the unit cell of TCNE–naphthalene with its molecular axes coinciding with those of the published naphthalene (WW). The atomic parameters of TCNE, on the other hand, were not altered or refined except for the occupancies of the two perpendicular orientations of TCNE (see below).

Atomic scattering factors for carbon and nitrogen atoms were taken from Hanson, Herman, Lea & Skillman (1964) while those for hydrogen atoms are from Stewart, Davidson & Simpson (1965). The internal geometry of naphthalene was kept fixed while its orientation parameters were taken as the angles through which the input molecule has to be rotated in the same sense about each of its axes of inertia. This set of parameters was preferred to the Eulerian angles in view of singularity problems occuring with the latter. The average motion of the carbon skeleton was assumed to be governed by the libration and translation tensors **L** and **T** respectively. No screw tensor is needed since the molecule must occupy (at least) a crystallographic centre of symmetry. The eventually disordered naphthalene molecules must also have equal occupancies. For convenience of interpretation, the asymmetric unit was chosen as a complete naphthalene molecule with an occupancy factor of 0·25 and a quarter of TCNE as in the previous work (WW). As naphthalene was placed with its centre at the origin, the disordered model could be generated with the operations of the point group $2/m$. No attempt was made at refining individual atomic parameters of naphthalene.

In the refinement process summarized in Table 1 the orientational and thermal parameters are refined simultaneously by the full-matrix method. The input value of φ_N was taken from the result shown in Fig. 2.

As far as the structural detail and the number of refined parameters are concerned, stage 2 of the present calculation may be compared with the final cycle of the published refinement (WW). There are 15 and 23 naphthalene-defining refined parameters in the present and in the previous (WW) refinements, respectively. After this stage the hydrogens of naphthalene were inserted

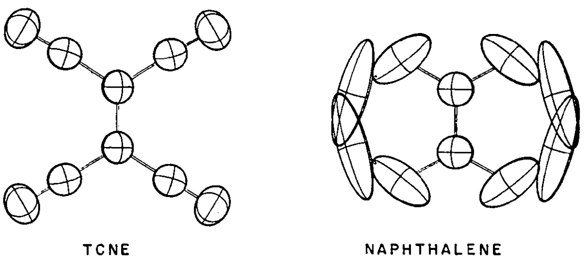

Fig. 1. Thermal ellipsoids of TCNE and of naphthalene calculated from published (WW) atomic parameters.

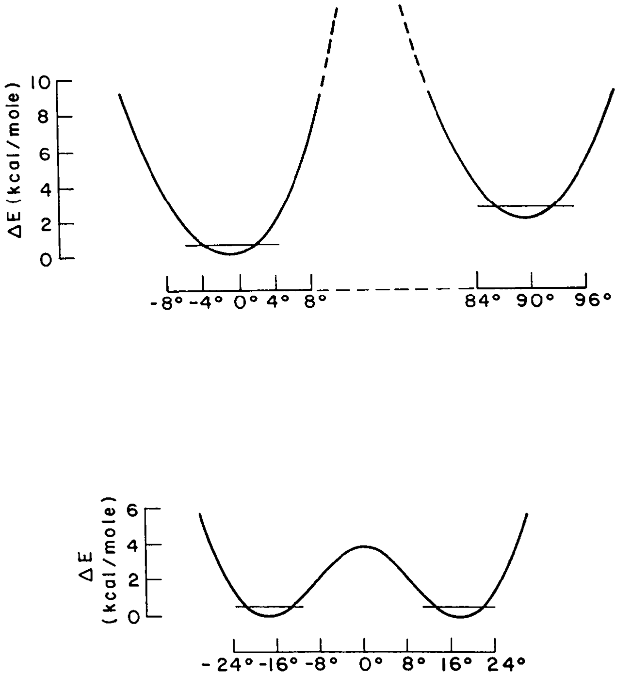

Fig. 2. Rotation potentials of TCNE (upper) and of naphthalene with modified (see text) geometry. The rotation potential of TCNE is based on a disordered model resulting from the present work.

Table 1. *Summary of the refinement of naphthalene*

Input parameters

TCNE – as published
Naphthalene – 'ideal' geometry (see text)
$\varphi_L=\varphi_M=0,\ \varphi_N=17{\cdot}0°$
$T_{ii}=0{\cdot}05$ Å^2, $T_{ij}=0$ for $i\neq j$
$L_{ii}=0{\cdot}01$ rad^2, $L_{ij}=0$

Parameters refined (naphthalene only)	R(%)	r(%)	φ_N
φ_N, **L**, **T**, scale (based on heavy atoms)	10·4	9·7	11·2°
φ_L, φ_M, φ_N, **L**, **T**, scale (based on heavy atoms)	9·1	9·1	11·4
φ_L, φ_M, φ_N – all atoms, **L**, **T** – heavy atoms, scale	9·0	8·5	11·3
Published structure (structure-factor calculation)	12·8	11·2	

at chemically reasonable positions with C–H = 1·07 Å. Their fixed isotropic vibration parameters were taken as one third of the trace of **U**, where **U** is the vibration tensor of the carbon atoms to which the hydrogen is bonded. **U** was evaluated from the **L** and **T** tensors of the naphthalene and from the coordinates of this carbon after stage 2 of the refinement. It is seen that inclusion of the hydrogen atoms into the refinement had a small effect on the conventional R index but was reflected to a greater extent in the weighted reliability index, $r=[\sum w(F_o-K|F_c|)^2/\sum wF_o^2]^{1/2}$. The final R and r values, reached in this refinement, are 0·090 and 0·085 respectively.

At this stage a section of the difference density $\Delta\varrho$, passing through the best plane of the two disordered naphthalenes, was computed. The values of $\Delta\varrho$ range from $-0{\cdot}15$ eÅ^{-3} in the region of ring centres to 0·1 eÅ^{-3} along the carbon skeleton. The published difference density map (WW) contains in the latter region peaks ranging from $-0{\cdot}5$ to 0·5e Å^{-3}.

Following the refinement of the disordered naphthalene model, the second orientation of TCNE was generated by rotating the molecule about its plane normal through 90° and by transforming the anisotropic vibration tensors assuming that TCNE in both orientations has an identical thermal behaviour. With this model, the assumption that the second orientation may be populated can be rejected as being wrong since the occupancy factor of the perpendicular orientation dropped after four cycles from 0·20 to nearly zero.

The crystal data, initial and final coordinates of

Table 2. *Results of refinement*

Crystal data

$a=7{\cdot}26$, $b=12{\cdot}69$, $c=7{\cdot}21$ Å. $\beta=94{\cdot}4°$, space group $C2/m$, $Z=2$.

Rigid-body parameters

(*a*) Positional

$\varphi_L=-4{\cdot}1\ (3)°$ $\varphi_M=0{\cdot}9\ (1)°$ $\varphi_N=11{\cdot}3\ (1)°$
$\varrho_L=0$ $\varrho_M=0$ $\varrho_N=0$ (not refined)

(*b*) Thermal*

$$\mathbf{L}[\sigma(\mathbf{L})]\times10^5=\begin{pmatrix}449\ (300) & 33\ (113) & -97\ (155)\\ & 262\ (81) & -11\ (89)\\ & & 856\ (94)\end{pmatrix}\text{rad}^2$$

$$\mathbf{T}[\sigma(\mathbf{T})]\times10^5=\begin{pmatrix}4978\ (211) & -58\ (191) & -226\ (176)\\ & 5032\ (245) & 62\ (307)\\ & & 4689\ (432)\end{pmatrix}\text{Å}^2$$

	Eigenvalues	Eigenvectors		
L	28·8°^{2}	−0·2104	0·0003	−0·9776
	14·2	−0·9066	−0·3742	0·1950
	8·4	−0·3657	0·9274	0·0790
T	0·0516 Å^2	−0·8130	0·4296	−0·3930
	0·0498	−0·3359	−0·8974	−0·2861
	0·0456	−0·4756	−0·1006	0·8739

Atomic fractional coordinates of naphthalene (× 10^4)†

	Input			Final			
	x	y	z	x	y	z	B_{iso}
C(3)	0	556	0	−204	543	−29	
C(4)	1565	1104	832	1131	1272	755	
C(4′)	−1565	1104	−832	−1941	887	−870	
C(5)	3041	559	1616	2779	922	1550	
C(5′)	−3041	559	−1616	−3189	173	−1608	
H(4)	1565	1947	832	822	2097	711	5·1
H(4′)	−1565	1947	−832	−2250	1711	−914	5·1
H(5)	4207	981	2236	3769	1477	2133	6·0
H(5′)	−4207	981	−2236	−4488	441	−2235	6·0

Atomic fractional coordinates and anisotropic vibration tensors of TCNE – as published (WW).

* The rigid-body tensors, as well as their eigenvectors, are referred to the inertial system of the modified published naphthalene (see text).

† A final atomic position vector is given by $r=\mathbf{A}[\mathbf{M}(\varphi_L\varphi_M\varphi_N)\mathbf{r}_o+\boldsymbol{\varrho}]$, where $\mathbf{r}_o$ is the initial position of this atom referred to the principal axes of inertia of the published naphthalene (WW), modified as described in the text. The form of **M** is given in the Appendix, while **A** is a transformation matrix relating the working (inertial) and the crystal systems. The positions of only half of the naphthalene atoms belonging to the chosen asymmetric unit are given in the Table. The second part of the molecule can be obtained by applying an inversion through the origin.

naphthalene and the refined parameters are presented in Table 2. Thermal ellipsoids of naphthalene carbons based on the anisotropic vibration tensors from the published structure (WW) and on the **L** and **T** tensors obtained in the present work are shown in Fig. 3.

Description of the structure and discussion

The above results show conclusively that the published average motion of naphthalene in its (1 : 1) TCNE complex (WW) conceals a minor orientational disorder of this molecule. This is in agreement with the suggestions based on difference maps (Herbstein & Snyman, 1969) and on potential calculations (Shmueli & Goldberg, 1973). As far as the actual amount of disorder present is concerned, the in-plane deviation from the published orientation ($\varphi_N = 11{\cdot}3^\circ$, Table 2) lies between the values of 7·5 and 17°, deduced from difference map and potential calculations respectively. However, the in-plane rotation through φ_N is also followed by a rotation through 0·9° about the twofold axis (φ_M) and by another about a line passing through the molecular centre and lying in the mirror plane of the space group $C2/m$ ($\varphi_L = -4{\cdot}1^\circ$) [we recall that L, M, N are the molecular axes of the published naphthalene structure (WW)]. That is, a complete, although small, reorientation takes place on transition to the present disordered model.

Introduction of hydrogen atoms, at reasonable positions, into the published structure (WW), modified as described above results in short contacts between two of these hydrogens and the nitrogen atoms of TCNE from a neighbouring stack. Thus, for example, the C(5)···N contact of 3·47 Å (in the modified published structure) is normal, as noted by WW who report the value of 3·54 Å for this contact. However, the H(5)···N distance of 2·42 Å is 0·3 Å shorter than the sum of the appropriate van der Waals radii (Pauling, 1960). It is seen from Fig. 4 that in either of the disordered arrangements this contact is considerably relaxed as the relevant contacts become: C(5)···N = 3·51, C(5')···N' = 3·59, H(5)···N = 2·55 and H(5')···N'2·63 Å.

The thermal motion of naphthalene (Table 2) is now described in terms of a nearly isotropic translation tensor and an anisotropic tensor of libration. The largest r.m.s. amplitude of libration, 5·4°, is associated with the plane normal of the molecule. This result seems to be reasonable since the rotation about the long axis of the modified published structure ($\varphi_L = 4{\cdot}1^\circ$) not only contributes to the relaxation of H···N short contacts but probably also imparts to the molecule a greater lattitude of in-plane motion as follows from a careful consideration of the packing arrangement.

It should be kept in mind that this study is based on an assumed molecular geometry of naphthalene.

The theoretical work of Kuroda, Amano, Ikemoto & Akamatu (1967) shows that the increase of the calculated charge transfer energy as a result of a rotation of the naphthalene molecule through ~12° about the plane normal, the starting point being the published structure, is less than 0·1 kcal mole^{-1}. It is therefore possible to neglect as a first approximation the charge-transfer interactions and calculate the lattice energy with semi-empirical (exp −6) functions. We did this with the *PCK*6 program of Williams (1972) and the

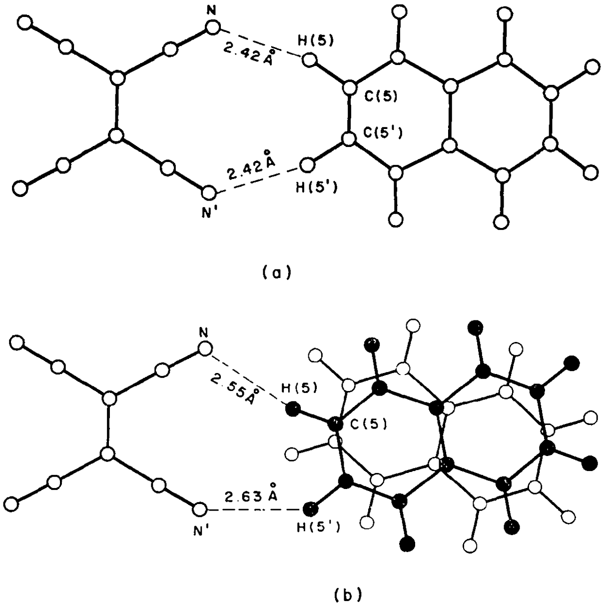

Fig. 4. Short contacts between neighbouring TCNE and naphthalene molecules in (*a*) the modified published structure and (*b*) the refined disordered structure.

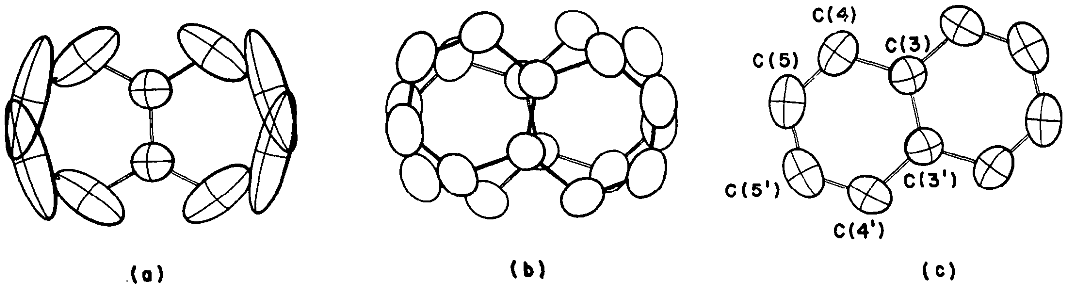

Fig. 3. Comparison of thermal ellipsoids of naphthalene in (*a*) the published (WW) structure and (*b*) the present structure. The numbering of the atoms is given in (*c*) where a single orientation of naphthalene is displayed.

result was that the modified published structure (A) is less stable by about 5 kcal mole^{-1} than two other structural models which are based on disorder of naphthalene. In one of the models the orientation of naphthalene with respect to the unit-cell axes is identical at the two possible sites (B) while in the other model the molecules at (0,0,0) and at ($\frac{1}{2}$,$\frac{1}{2}$,0) deviate from the published structure in opposite senses (C). The results are $-32{\cdot}8$ kcal mole^{-1}, $-38{\cdot}1$ kcal mole^{-1} and $-37{\cdot}7$ kcal mole^{-1} for structures A, B and C, respectively. It is of interest to note that the H$\cdots$N short contacts mentioned above, are the main contributors to the destabilization of structure A. There are probably many more possible local arrangements characterized by somewhat different lattice energies and violating the $C2/m$ symmetry. Structures (B) and (C) were chosen to approximate two extreme packing modes.

The result of refining the occupancy of TCNE in the two orientations, shown in Fig. 2, is in agreement with the published structure. The rather obvious reason for the presence of two minima 90° apart is the fact that the nitrogen atoms involved in shortest interstack contacts lie approximately on the corners of a square. It was pointed out by Wallwork (1973) that the perpendicular (unoccupied) orientation was in fact considered in the early stages of the structure determination. It is seen (Fig. 2) that the perpendicular orientation corresponds to a minimum which is shallower by about 2 kcal mole^{-1} than the occupied one. If we add to it 0·7 kcal mole^{-1}, which is the increase in the charge-transfer energy calculated by Kuroda *et al.* (1967) for a 90° rotation, we obtain $\exp(-E/kT)=\exp(-4{\cdot}2)=0{\cdot}015$ for the expected fraction of molecules in this minimum. This reasonably small occupancy again speaks in favour of semi-empirical calculations, however approximate they may be.

It should be pointed out that in the calculation of the rotation potential in Fig. 2, a disordered model of naphthalene resulting from the present refinement was used. The rotation potential of TCNE presented elsewhere (Shmueli & Goldberg, 1973) was calculated on the basis of the modified published structure of naphthalene (WW) and shows, as was expected, two equal minima. A disordered model of naphthalene was not used at that stage as the amount of disorder was uncertain.

The results obtained in this study differ significantly from those indicated by either rotation potentials or difference maps. As far as the first method is concerned, its limitations were discussed in detail elsewhere (Shmueli & Goldberg, 1973), the most important being the approximate nature of the functions employed and the assumption of uncorrelated motion of molecules in the solid. It is therefore not expected that the results of this method be very accurate, especially where large deviations from equilibrium are involved. However, a plausible result can be obtained in most cases and may serve as a useful starting point for a more rigorous test. The difference map, on the other hand, is apparently more objective, as it is based in part on the observed structure amplitudes. However, in cases of false thermal motion, there may be serious errors involved in the calculated structure amplitudes, since the correct atomic thermal parameters are in principle unknown unless a refinement of the disordered model has been carried out.

We thank Professor Fred Hirshfeld for supplying his constrained refinement routine and Professor Wallwork for communicating his unpublished results on the TCNE orientation problem. The computations were done with a CDC–6600 at the Tel-Aviv University Computation Centre.

APPENDIX

For the purpose of this work, the local version of *ORFLS* was modified, in a manner similar to that indicated by Pawley (1971), so that geometrical and thermal constraints can be simultaneously applied. Rather than Eulerian matrices, which may lead to singularity problems, we choose as orientation-defining parameters three angles $\varphi_x,\varphi_y,\varphi_z$, through which the input rigid group has to be rotated about the unit vectors parallel to the axes of the working (Cartesian) system and referred to the origin of this group. The rotation matrix employed has the form

$$\mathbf{M}(\varphi_x\varphi_y\varphi_z)=\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\varphi_x & \sin\varphi_x\\ 0 & -\sin\varphi_x & \cos\varphi_x\end{pmatrix}\begin{pmatrix}\cos\varphi_y & 0 & -\sin\varphi_y\\ 0 & 1 & 0\\ \sin\varphi_y & 0 & \cos\varphi_y\end{pmatrix}\begin{pmatrix}\cos\varphi_z & \sin\varphi_z & 0\\ -\sin\varphi_z & \cos\varphi_z & 0\\ 0 & 0 & 1\end{pmatrix} \qquad (1)$$

and premultiplies the input atomic position vector referred to the local origin. In the text, x,y,z are replaced by L,M,N, respectively, as the inertial system has been used (see below). Each of the matrices in (1) represents an operator which rotates a vector in a clockwise sense when looking from the origin towards the negative end of the axis appearing as subscript.

The working system can be either a Cartesian system based on the vectors $\mathbf{a}$, $\mathbf{b}^*$ and $\mathbf{a}\times\mathbf{b}^*$ or a system constructed from the eigenvectors of the tensor of inertia of the first input rigid group. The atomic positions are referred, *via* the the centroids of the groups to which they belong, to the unit-cell origin. Introduction of an inertial system offers a convenient way of interpreting the positional and thermal rigid-body parameters at the expense of providing for an eigenvalue–eigenvector subroutine and a few relevant statements. The reflexion indices are transformed to the working system only after the symmetry operations were applied to them. Atomic vibration tensors are expressed according to the usual **TLS** formalism (Schoemaker & Trueblood, 1968) and their derivatives with respect to the thermal and positional rigid-body parameters are explicitly evaluated in order to permit a simultaneous refinement of these parameters. It is also possible to apply only geometrical or only thermal constraints and treat a part of the structure in an unconstrained manner in which cases the derivatives are appropriately modified.

The general organization of the program was based in part on an *ORFLS* version modified by Professor F. L. Hirshfeld for a purpose similar to ours, but with some constraints different.

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The Crystal Structure of Sodium Diborate $Na_2O.2B_2O_3$

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Sodium diborate, $Na_2O.2B_2O_3$, is triclinic, space group $P\bar{1}$, with unit-cell dimensions at 22°C: $a=6\cdot5445\pm0\cdot0004$, $b=8\cdot6205\pm0\cdot0004$, $c=10\cdot4855\pm0\cdot0006$ Å, $\alpha=93\cdot279\pm0\cdot006$, $\beta=94\cdot870\pm0\cdot006$, $\gamma=90\cdot843\pm0\cdot006°$. The calculated density is $2\cdot272$ g cm^{-3} with four formula units in the cell. The structure was determined from three-dimensional X-ray data by direct methods. A full-matrix least-squares refinement resulted in an R index of 0·035 (0·040 for the weighted R index). The anion borate polymer in this structure forms layers composed of di-pentaborate groups and triborate groups with one non-bridging oxygen. This is a novel feature in diborates. Boron–oxygen bond lengths are normal, but with significant differences depending on the location within the groups. The sodium atoms are coordinated by six or seven oxygen atoms at distances ranging from 2·260 to 2·872 Å.

Introduction

Several of the anhydrous diborates have polymer structures built up from diborate groups. This is the case for lithium diborate, $Li_2O.2B_2O_3$ (Krogh-Moe, 1968), and cadmium diborate, $CdO.2B_2O_3$ (Ihara & Krogh-Moe, 1966). The structure of this cadmium compound is the first determined structure in an isomorphous series including the Mg, Mn, Fe, Co, Ni, Zn, Hg compounds (Ecker, 1966). Diborates containing groups other than the diborate group are known, however. Potassium diborate (Krogh-Moe, 1972*a*) has, in addition to diborate groups, di-triborate groups. Barium diborate (Block & Perloff, 1965) has a single framework based on di-triborate and di-pentaborate groups. The structure reported for sodium diborate in the present paper provides yet another example of a diborate with a novel combination of groups.

Sodium diborate exists in more than one modification (Jenkel, 1936; Milman & Bouaziz, 1968). The phase studied here crystallizes from the melt (or glass) below the melting point 742°C down to about 650°C. It appears to be the stable phase, at least in the temperature range mentioned. Vila & Font-Altaba (1955) have reported unit-cell dimensions for what appears to be the same phase, though their values differ appreciably from those obtained by us.

Experimental

Anhydrous sodium diborate was prepared by dehydrating and melting borax, $Na_2O.2B_2O_3.10H_2O$, (p.a.