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Hexamethylbenzene–Tetracyanoethylene (1:1) Complex at 113 K: Structure and Energy Calculations

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Hexamethylbenzene–tetracyanoethylene (HMB–TCNE), $C_{12}H_{18}.C_6N_4$, $P\bar{1}$; at 113 K: $a = 6.563$ (2), $b = 8.614$ (2), $c = 8.656$ (1) Å, $\alpha = 108.22$ (2), $\beta = 102.61$ (2), $\gamma = 111.74$ (2)°, $Z = 1$, $D_x = 1.207$ g cm^{-3}, $R = 0.077$. The structure is like that found at room temperature, except that the HMB molecule is observed to be slightly but significantly non-planar at low temperature, the methyl C atoms deviating alternately by about 0·02 Å from the molecular plane. The rotational positions of the methyl groups deviate by an average of 12° from those corresponding to D_{3d} molecular symmetry. The interplanar spacing between HMB and TCNE is 3·28 Å, about 2% smaller than at room temperature. The present structural parameters are appreciably more precise than those reported for the room-temperature structure. The apparent planarity of the HMB molecule in the latter is presumably the result of a dynamic disorder; the barrier to motion through the planar structure by rotation of the methyl groups (in a 'geared' fashion) is calculated to be about 10 kJ mol^{-1}. The TCNE molecule is found in two distinct orientations, in a ratio of about 5:1. These are related by a rotation of 90° about an axis through the molecular center and normal to the plane. Packing calculations confirm the existence of two approximately equal minima at 90°.

Introduction

Saheki, Yamada, Yoshioka & Nakatsu (1976) have recently published a description of the crystal structure at room temperature of the 1:1 HMB–TCNE complex. At the time that their account appeared we had completed a room-temperature study and were collecting data on another sample of the same substance at 113 K. Because our results at room temperature are similar to theirs, we will not present them here.

The unit cell reported here is the reduced cell (Santoro & Mighell, 1970; Mighell, Santoro & Donnay, 1969). The transformation matrix, **M**, from the unreduced cell of Saheki *et al.* (**a**′) to that used here (**a**) (*i.e.* **a** = **Ma**′) is

$$\mathbf{M} = \begin{pmatrix} 0 & 0 & 1 \\ \bar{1} & 0 & \bar{1} \\ 0 & \bar{1} & 0 \end{pmatrix}.$$

The dark-red needles were obtained from an equimolar solution of TCNE and HMB in benzene that was allowed to evaporate to dryness. They are very fragile and cannot be cut without being fragmented into polycrystalline specimens. At low temperature there is no need to mount the specimen in a capillary or otherwise enclose it. We collected data on a small crystal (about 0·15 × 0·25 × 0·37 mm) at 113 K using the apparatus described by Strouse (1976), with a $P\bar{1}$ Syntex diffractometer. Intensities of all unique reflections from $2\theta = 0$ to 115° were measured with graphite-monochromatized Cu $K\alpha$ radiation in the bisecting θ–2θ scan mode. In the parallel mode we measured the available reflections from $2\theta = 114$ to 154°. In all, 1211 intensities were measured (of 1685 accessible in principle). For 1174 reflections the corresponding $|F|$ was $>2\sigma(F)$, and these were used in the least-squares refinement.

We started with the structure we had found at room temperature. The parameters were essentially those described by Saheki *et al.* (1976). Our results differed from theirs only in that we found no conclusive evidence of disorder at room temperature, and we did locate the H atoms, although some of their positions were clearly unreliable. The C and N positions were refined first isotropically and then anisotropically with the low-temperature data. A difference Fourier synthesis then showed clearly the positions of all nine unique H atoms. There was also a peak of height about 1·1 e Å^{-3}, corresponding to the ethylenic C atoms of a disordered TCNE molecule, as found by Saheki *et al.* at room temperature. The positions of the disordered

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atoms are related to those of the corresponding atoms of the major molecule by a rotation of 90° around the normal to the molecular plane through the molecular center.

The disorder was described and refined in three different ways. First, we estimated the fraction of the low-occupancy TCNE by varying the relative weights of the ethylenic C atom of the principal [TC(1)] and the alternative [TDC(1)] molecules. The refinement, in which 141 parameters were varied, converged at $R = 0{\cdot}078$. The relative occupancy of the major and minor TCNE molecules was 0·84:0·16, not far from the value of 0·75:0·25 found by Saheki *et al.* at room temperature. The length of the central bond of the low-weight TCNE molecule was 1·29 (3) Å.

Next, plausible positions were calculated for the cyano C and N atoms of the low-weight molecule, and these positions were refined isotropically. Occupancies were also refined. After convergence the conventional R was 0·078; R_w $\{=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}\}$ was 0·108. The ethylenic bond of the low-weight TCNE had increased slightly to 1·30 Å, but the molecule was non-planar and the resolution of the major and minor TCNE molecules was very poor.

Finally, the disorder was treated by representing the low-weight TCNE as a rigid body, with the geometry of the higher-weight molecule. In all, 145 parameters were varied in eight refinement cycles. These included the relative occupancy of the two TCNE molecules, the three angles fixing the orientation of the minor TCNE (its position being fixed, since it is on a center of symmetry), and isotropic temperature factors for the five atoms of this group. R at convergence was 0·077 ($R_w = 0{\cdot}106$). As judged by Hamilton's (1974) test, this model was the best of those tried: $\mathscr{R}_{4,1029} = 1{\cdot}019$, better than the 0·5% level of confidence. The parameters from this refinement* were taken as final; the final occupancies were 0·84 (1) and 0·16.† Positional parameters are given in Table 1.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

Positions are $\times 10^4$ for anisotropic atoms, $\times 10^3$ for isotropic atoms. E.s.d.'s of the least significant digits are given in parentheses.

	x	y	z	B (Å^2)
C(1)	1102 (4)	1210 (3)	1801 (3)	
C(2)	1106 (4)	1932 (3)	552 (3)	
C(3)	−22 (4)	716 (3)	−1256 (3)	
C(4)	2279 (6)	2517 (4)	3740 (3)	
C(5)	2315 (5)	4011 (3)	1133 (3)	
C(6)	−48 (5)	1509 (4)	−2594 (3)	
TC(1)	5483 (5)	455 (4)	892 (4)	
TC(2)	5322 (9)	−503 (7)	1979 (6)	
TN(3)	5196 (15)	−1244 (9)	2875 (6)	
TC(4)	6716 (7)	2457 (5)	1776 (9)	
TN(5)	7706 (11)	4047 (4)	2510 (7)	
TDC(1)	541*	84	−2	1·6 (4)
TDC(2)	673	254	156	2·5 (13)
TDN	779	390	282	2·3 (6)
TDC(4)	498	100	−165	1·8 (6)
TDN(5)	464	113	−295	2·7 (13)
H(4*A*)	136 (6)	213 (5)	426 (5)	4·2 (8)
H(4*B*)	204 (7)	360 (6)	397 (6)	7·1 (11)
H(4*C*)	380 (10)	278 (7)	437 (7)	9·4 (15)
H(5*A*)	152 (7)	467 (5)	163 (5)	5·7 (9)
H(5*B*)	297 (9)	443 (6)	25 (6)	8·1 (12)
H(5*C*)	396 (7)	475 (5)	214 (5)	5·2 (8)
H(6*A*)	156 (7)	210 (5)	−264 (5)	6·3 (10)
H(6*B*)	−101 (8)	52 (6)	−382 (5)	6·3 (9)
H(6*C*)	−29 (7)	264 (6)	−214 (5)	5·6 (9)

* The position parameters allowed to vary for the minor TCNE were the three molecular angles. The final values were: φ 0·00 (1); θ 3·12 (1); and ρ −1·59 (2) rad (Strouse, 1970).

Discussion

A drawing of the HMB molecule, with its dimensions, is shown in Fig. 1. Librational corrections (Cruickshank, 1956) varied from 0·002 to 0·004 Å for bond distances. The librational motion at 113 K is small, and the fit to the rigid-body model (Table 2) is excellent. In contrast, at room temperature we found the librational amplitude about the normal to the molecular plane to be greater than 8°, and the fit poor (see below). The dimensions of the TCNE molecule (Fig. 2) are less reliable because of the disorder; furthermore, libra-

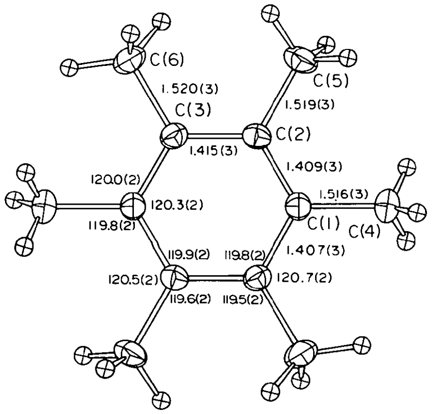

Fig. 1. The HMB molecule. Dimensions include small librational corrections. The C—H distances average 0·98 Å (range 0·86–1·05 Å), the C—C—H angles average 113° (range 109–120°) and the H—C—H angles average 105° (range 91–121°). Thermal ellipsoids are scaled to enclose 50% probability; H atom radii are set to 0·1 Å.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33550 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Scattering factors for N, C_{val} and bonded H were taken from *International Tables for X-ray Crystallography* (1974). All calculations were made on an IBM 360-91 computer with programs written in this laboratory and with the programs of Strouse (1970), Boyd (1968), Williams (1969) and Johnson (1965).

tional corrections for TCNE were not possible because one negative eigenvalue was found for libration when an attempt was made to treat the major TCNE as a rigid body.

The ten atoms of the TCNE molecule are planar, with a maximum deviation of 0·006 Å, and this plane makes an angle of 0·2° with the plane of the HMB molecule, 3·28 Å away. To a first approximation, the HMB molecule has D_{3d} symmetry: adjacent C atoms of the ring are above or below the ring plane by 0·004–0·005 Å, the methyl C atoms are displaced in the same direction as the attached aromatic C by 0·018–0·024 Å, and the methyl groups are approximately staggered (see Fig. 3). The H atoms are 0·22 to 0·81 Å from the molecular plane; the methyl groups are rotated an average of 12° from the positions corresponding to D_{3d} symmetry. While the deviations of the methyl C atoms from the molecular plane are small, they are significant with respect to the e.s.d.'s of the positions of the atoms and are consistent with what one would expect for an ordered HMB molecule. In contrast, at room temperature, Saheki *et al.* and we, quite independently, found all C atoms of the HMB molecule in this complex to be coplanar within experimental error (about 0·01 Å). Furthermore, at room temperature the apparent r.m.s. vibration amplitude of the methyl C atoms normal to the HMB plane is unusually large, about 0·30 Å, and cannot be interpreted in terms of rigid-body motion of the molecule. The observed thermal parameters might correspond to a real motion of the methyl groups but they are also consistent with a static disorder in which the methyl C atoms are displaced about 0·09 Å above and below the plane.

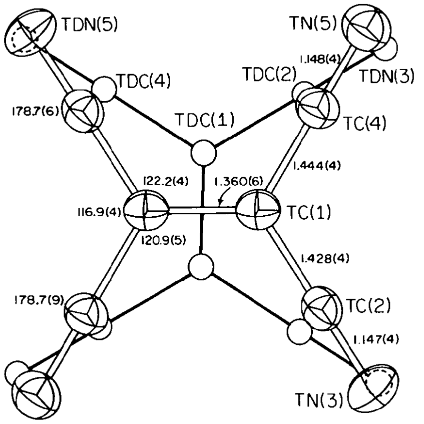

Fig. 2. Dimensions for the major TCNE molecule, without librational corrections (see text). The low-weight molecule was constrained to the average dimensions of the major molecule. The poor resolution of the two molecules is indicated by the distances TC(2)–TDC(4) 0·37, TC(4)–TDC(2) 0·22, TN(3)–TDN(5) 0·10, and TN(5)–TDN(3) 0·33 Å. [TDC(4) and TDN(5) are at position II,100; see Table 3.]

Table 2. *Rigid-body-motion parameters for HMB in the present structure* (*at* 113 K)

Direction cosines are expressed relative to axes parallel to **a**, **c*** × **a**, **c***. The r.m.s. value of ΔU_{ij} is 1·0 × 10^{-3} Å^2, comparable to the average e.s.d. of U_{ij} (1·1 × 10^{-3} Å^2). The normal to the least-squares plane of the HMB molecule has direction cosines 1·0000, 0·0007, 0·0020.

	Principal axes	Direction cosines (× 10^4)		
T	0·0248 (Å^2)	7728	6105	1734
	0·0213	2828	−867	−9552
	0·0186	−5681	7873	−2397
L	12·3 (°)^2	−239	−9856	1677
	6·8	9961	−92	879
	5·7	−851	1691	9819

In the present low-temperature structure, on the other hand, the r.m.s. amplitude of vibration of the methyl groups normal to the plane is relatively small and can be interpreted entirely in terms of rigid-body motion of the molecule (Table 2). The decrease in the interplanar spacing between the molecules of HMB and TCNE (3·28 Å at 113 K as contrasted with 3·35 Å at room temperature) is consistent with the decrease in apparent vibrational amplitudes normal to the plane, whether these represent dynamic or static disorder. The energy calculations reported below suggest that the disorder is dynamic.

The conformation of the hexamethylbenzene molecule is of great interest because a planar geometry would require severe overcrowding of the six methyl groups (Coulson & Stocker, 1959; Coulson, 1970). Neutron diffraction studies (Hamilton, Edmonds, Tippe & Rush, 1969) and electron diffraction (Karl, Wang & Bauer, 1975) indicate that the benzene ring is planar

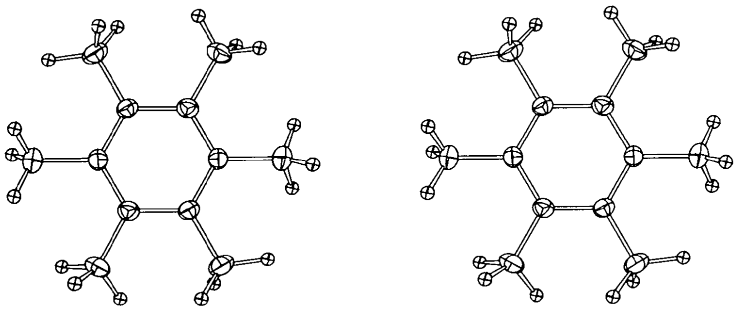

Fig. 3. Stereoview of the hexamethylbenzene molecule, with H atom radii arbitrarily set to 0·1 Å.

but that the methyl groups are displaced alternately from the plane. Energy-minimization calculations are in agreement with this model. We used Boyd's (1968) program to calculate the minimum-energy geometry for an isolated hexamethylbenzene molecule. The force constants and potential functions have been described previously (Boyd, Breitling & Mansfield, 1973; Maverick, Smith, Kozerski, Anet & Trueblood, 1975), except that in the present study the C_A—C_A—C—H torsional potential was given a sixfold form with a barrier height of 0·602 kJ mol^{-1}. The result was a molecule with approximate D_{3d} symmetry, with the aromatic C atoms (C_A) displaced ±0·135 Å from the least-squares plane of the benzene ring. The methyl groups are staggered, in agreement with our experimental results and with Hamilton *et al.* (1969). The calculated minimum-energy molecule shows a considerably larger deviation from planarity than that actually observed in the present structure.

To investigate the possibility that the planarity and large apparent vibrational amplitudes observed at room temperature are a consequence of dynamic disorder, we estimated the barrier heights for ring inversion by rotation of the methyl groups. This was done by 'driving' to convergence six C_A—C_A—C—H angles, one for each methyl group, in small steps over the 120° path, allowing all other degrees of freedom to vary. When the six methyl groups were rotated by driving six angles in the same direction, the planar intermediate had six H···H contacts of 1·83 Å each, and its potential energy was 30·5 kJ mol^{-1} greater than the minimum on either side. However, when alternate methyl groups were rotated in opposite directions, in a 'geared' fashion, the twelve shortest H···H distances in the planar intermediate were 2·20 Å and the barrier height was 10·0 kJ mol^{-1}. The C···C contacts and H—C—H angles were also less strained for the 'geared' rotational mode.

It is also possible to describe the inversion of the hexamethylbenzene ring by driving the six C—C_A—C_A—C torsion angles. In the calculated minimum-energy conformation this angle is ±9·2°. Although the barrier by this path was calculated to be quite high (probably more than 40 kJ mol^{-1}) the minimum is rather flat. In a nearly planar structure corresponding to that of the present crystal study, with H atoms still in the staggered arrangement, the torsion angle is about ±1° and the energy (after allowing all other degrees of freedom to vary to convergence) is only about 5 kJ mol^{-1} greater than the minimum.

Our calculated barrier by the lowest-energy path, synchronous 'geared' rotation of the methyl groups, 10·0 kJ mol^{-1}, is somewhat larger than the reported values of 4–8 kJ mol^{-1} from neutron diffraction, NMR, and IR and Raman spectroscopy (Hamilton *et al.*, 1969; Allen & Cowking, 1967; Ware, Williamson & Devlin, 1968; Ron & Hyams, 1972), but smaller than that of about 15 kJ mol^{-1} from third-law entropies (Overberger, Steele & Aston, 1969).

Further approximate potential-energy calculations were undertaken to compare the two positions occupied by the TCNE molecule in the crystal. The position of the HMB molecule was not varied. The intermolecular potential energy was approximated using the program *PCK*5 (Williams, 1969). The potential functions and force constants were those of Williams; N was treated as C, and all C—H distances were lengthened from the crystal-structure values to 1·10 Å. The summation limits were 3·65 Å for C···C, 3·03 Å for C···H, and 2·88 for H···H. Two minima, 90° apart, had the same energy to within 1 kJ mol^{-1}. The two positions found in the crystal structure correspond to those of the calculated minima to within a few hundredths of an ångström.

The shortest intramolecular and intermolecular non-bonded contacts in the crystal are listed in Table 3. The only H···H distances shorter than 2·6 Å are intramolecular; the only C···C and C···N distances shorter than 3·4 Å are within the columns of molecules along the *a* axis [see Fig. 3 of Saheki *et al.* (1976)], and the shortest of those at low temperature is 3·25 Å [between C(6) and TN(3)]. The principal intermolecular contacts are between N and H atoms. Because the H positions of Table 1 are systematically in error (the true C—H distances surely being near 1·10 Å), we have recalculated the intra- and intermolecular contacts, assuming the C—C—H and H—C—H angles

Table 3. *Some short intramolecular and intermolecular distances* (Å)

Position (I) is *x,y,z*; position (II) is *−x,−y,−z*. The three digits after the position indicate translations parallel to **a**, **b** and **c**.

From	To	At position	Observed distance	With ideal C–H distances
Intramolecular				
H(4*A*)	H(6*B*)		2·10	2·01
H(4*B*)	H(5*A*)		2·48	2·43
H(4*B*)	H(5*C*)		2·45	2·44
H(4*C*)	H(6*B*)		2·57	2·57
H(5*B*)	H(6*A*)		2·37	2·35
H(5*B*)	H(6*C*)		2·21	2·19
Intermolecular				
TC(2)	H(6*A*)	II,100	2·91	2·87
TN(3)	H(6*A*)	II,100	2·53	2·46
TN(3)	H(6*B*)	I,101	2·84	2·75
TN(3)	H(6*C*)	II	2·83	2·81
TN(5)	H(5*A*)	I,100	2·68	2·59
TN(5)	H(5*C*)	I	2·72	2·68
TN(5)	H(6*C*)	II,110	2·88	2·84
TN(5)	H(4*B*)	II,111	3·01	2·94
TN(5)	H(4*B*)	I,100	3·07	2·98
H(4*A*)	H(6*A*)	I,001	2·66	2·46
H(4*A*)	H(6*B*)	I,001	2·84	2·59
H(5*A*)	H(6*C*)	II,010	2·66	2·47
H(5*B*)	H(5*B*)	II,110	2·66	2·58

to be the same as those observed but making all C—H bond lengths 1·10 Å. The effect of this calculation on the non-bonded contacts listed in Table 3 is indicated by the entries in the column headed 'With ideal C—H distances'.

Thus the crystal structure shows the features predicted by the potential-energy calculations. The HMB C atoms are not coplanar, although they are more so than the minimum-energy structure for an isolated molecule. The flatness of the minimum with respect to planarity facilitates a shorter TCNE–HMB interplanar spacing. The TCNE molecules in the two alternative positions have very similar non-bonded interactions with the HMB.

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The Crystal Structure of Guanidinium Pyromellitate Trihydrate Monoperhydrate

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The structure of $[C(NH_2)_3]_4(O_2C)_2C_6H_2(CO_2)_2.3H_2O.H_2O_2$ has been solved using microdensitometer-measured data and refined to $R = 0{\cdot}096$. The space group is $P\bar{1}$ [$a = 7{\cdot}35$ (2), $b = 10{\cdot}03$ (2), $c = 10{\cdot}24$ (2) Å, $\alpha = 105{\cdot}5$ (3), $\beta = 116{\cdot}4$ (2), $\gamma = 72{\cdot}3$ (2)°] and the H_2O_2 molecules substitute in two equivalent water molecule positions with site occupancy of approximately one-half. All of the H atoms of the guanidinium ions are involved in the hydrogen-bonding scheme. The hydrogen peroxide molecules accept three hydrogen bonds and donate two. The carboxyl groups of the pyromellitate fragment are twisted by 15·9 and 84·5° with respect to the benzene ring, values significantly different from those found in pyromellitic acid dihydrate (21·4 and 74·5°).

Introduction

The title compound is of interest since it is one of a relatively small number of compounds containing hydrogen peroxide of crystallization (perhydrates) which are reasonably stable. It is also only the second salt hydrate perhydrate to be studied structurally, the first being guanidinium oxalate dihydrate monoperhydrate (Adams & Pritchard, 1976). Perhydrates have many technological uses and some basic structural work is necessary to lay a foundation for 'chemical engineering' of stable, industrially useful peroxide carriers (Adams, Pritchard & Thomas, 1976).

Experimental

12·7 g of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) and 18 g of guanidinium carbonate