# The Crystal Structure of the 1:1 Complex of [3.3]Paracyclophane with Tetracyanoethylene*

By Joel Bernstein and K. N. Trueblood

*Department of Chemistry,† University of California, Los Angeles, California* 90024, *U.S.A.*

Tetracyanoethylene (TCNE) and [3·3]paracyclophane (PC) form a 1:1 complex, $C_6N_4.C_{18}H_{20}$, that crystallizes in $P\bar{1}$, with $a=8\cdot533$, $b=8\cdot538$, $c=7\cdot705$ Å, $\alpha=103\cdot33$, $\beta=110\cdot78$, $\gamma=104\cdot01°$, and one formula unit in the unit cell. The structure was solved by the study of Patterson sections, calculated from three-dimensional diffractometer data, and was refined by full-matrix least-squares methods to $R=0\cdot055$ for 1634 reflections. Molecules are stacked in columns along the [111] direction, which is the needle axis of the crystal, with the TCNE and aromatic ring planes approximately parallel to each other. The geometry of the PC molecule is not significantly different from that in crystals of uncomplexed PC, except for a slightly greater mutual parallel displacement of the rings. TCNE is disordered by rotation about an axis through its center and normal to its plane; two orientations occur with relative weight about 3:1. Other orientations appear to be prohibited by potentially very short $N\cdots H$ and $N\cdots C$ contacts between adjacent columns of molecules.

## Introduction

Cram & Bauer (1959) investigated the charge-transfer spectra of tetracyanoethylene (TCNE) with a series of paracyclophanes and compared the results with those for substituted benzenes, which had been studied by Merrifield & Phillips (1958). Cram & Bauer concluded, tentatively, that the strongest $\pi$-base of the paracyclophane series is [3.3]paracyclophane (PC) using as a criterion the fact that its complex absorbed at the longest wavelength. Merrifield & Phillips postulated a quasi-parallel arrangement of donor and acceptor molecules of complexes of TCNE with aromatic hydrocarbons.

Since these early spectrophotometric studies, the crystal structures of both moieties in the TCNE:[3.3] PC complex have been determined (Gantzel & Trueblood, 1965; Bekoe & Trueblood, 1960, 1964; Little, Pautler, & Coppens, 1970); and TCNE has been studied by electron diffraction (Hope, 1968), so that the precise molecular geometry of the individual molecules in the absence of complexing is known.

Recently, Herndon & Feuer (1968) reported the results of all-valence-electron calculations on molecular $\pi$-complexes of TCNE with a number of aromatic hydrocarbons. Although they did not report such calculations for any paracyclophanes, they predicted a preferred orientation for TCNE in its complex with *p*-xylene, which may, to a first approximation, be considered analogous to [3.3]PC. Moreover, their calculations support the predictions of isomeric donor-acceptor complexes first proposed by Orgel & Mulliken (1957), although they did not state specifically which isomeric complexes are predicted for *p*-xylene. On the basis of molecular orbital calculations, Kuroda, Amano, Ikemoto & Akamatu (1967) have also predicted the

existence of isomeric complexes of TCNE with both pyrene and naphthalene. The calculated variation in energy, with rotation about an axis perpendicular to the molecular plane of the TCNE, in these complexes is so small (in agreement with the calculations of Herndon & Feuer) that no strongly preferred rotational orientation of the TCNE molecule would be expected. They calculated the energy barrier hindering the rotation of the TCNE relative to either molecule to be less than 1 kcal.mole$^{-1}$.

In spite of the extensive interest in complexes involving TCNE as an acceptor, only four crystal structures of such complexes have been reported: 1:1 complex with naphthalene (Williams & Wallwork, 1967); complex with 1:1 perylene (Kuroda, Ikemoto & Akamutu, 1966); 1:1 complex with pyrene (Ikemoto & Kuroda, 1967); complex with ferrocene (Adman, Rosenblum, Sullivan & Margulis, 1967). Unfortunately none of these determinations was highly precise. Williams & Wallwork observed slight disordering of the naphthalene molecule in the final difference map; Herbstein & Snyman (1969) have recently analyzed this disorder. It seems possible that the structure of the pyrene complex may also be disordered, but a test of this hypothesis must await the availability of more precise data.

The present study was undertaken to determine both the mutual arrangement of the molecules in the complex and the effects of complexing on the molecular geometry of each constituent.

## Experimental

Irregular needle-shaped crystals of the 1:1 complex of [3·3] PC with TCNE were supplied by Cram & Sheehan (1969). Suitable samples were obtained by fracturing the crystals; most fragments were still elongated parallel to the original needle axis. Some were twinned, with the twinning line paralleling the needle axis. The

---

crystals are triclinic; a later statistical analysis of intensity data indicated the space group to be $P\bar{1}$. Cell constants obtained from least-squares refinement with 79 values of $\sin \theta/\lambda$ (Ni-filtered Cu $K\alpha$ radiation, $\lambda(\alpha_1) = 1\cdot54050$, $\lambda(\alpha_2) = 1\cdot54434$ Å) are:

$$a_0 = 8\cdot533 \pm 0\cdot002 \text{ Å} \quad \alpha = 103\cdot33 \pm 0\cdot02°$$
$$b_0 = 8\cdot538 \pm 0\cdot002 \quad \beta = 110\cdot78 \pm 0\cdot02$$
$$c_0 = 7\cdot705 \pm 0\cdot001 \quad \gamma = 104\cdot01 \pm 0\cdot02 .$$

In this fully reduced cell the needle axis is [111]. Unit-cell volume is 477·23 Å$^3$, and the density calculated for a cell containing one formula weight of complex is 1·268 g.cm$^{-3}$. Observed density is 1·256 g.cm$^{-3}$.

Intensities of the diffraction maxima were measured on a Picker manual diffractometer, with Ni-filtered Cu radiation. Because of the high vapor pressure of the crystals, the specimens were sealed in lithium borate capillaries. Even so, the intensity of three monitor reflections decreased substantially during data collection, with an accompanying increase in the amount of material of color similar to that of the sample deposited on the capillary walls, presumably as a result of sublimation. Because of this intensity decrease three different crystals were used; the smallest measured $0\cdot07 \times 0\cdot15 \times 0\cdot27$ mm and the largest measured $0\cdot12 \times 0\cdot24 \times 0\cdot41$ mm. Intensity data from all three crystals were put on a common scale by means of a scale factor calculated from the unweighted average of the intensity ratios for 20 reflections measured for each crystal. The intensities of 2057 unique reflections were measured for $\sin \theta/\lambda < 0\cdot64$. Net counts for 1634 of these were significantly positive and these reflections were considered observed. The maximum error in $F^2$ due to absorption is calculated at about 6% and the average error is considerably less. No absorption corrections were made.

### Determination and refinement of the structure

Mulliken (1952) and Prout & Wright (1968) have noted that charge-transfer complexes involving molecules that are planar (or have planar portions) frequently form needle-shaped crystals in which the complexes stack with their planes approximately perpendicular to the needle axis. Preliminary examination of data for the present crystal suggested strongly that its structure might be of this type. The 111 reflection was twice as intense as any other and the spacing of the (111) planes is about 3·17 Å. This distance corresponds closely to the observed separation between the aromatic rings in the [3.3]PC molecule (Gantzel & Trueblood, 1965) and to the usual separation between donor and acceptor components in complexes of TCNE with planar hydrocarbons. Thus, the expected repeat distance in a TCNE-PC complex with parallel planes is about 9·5–9·6 Å, just the repeat distance along the [111] direction of the present cell [9·63 Å along the body diagonal, 9·52 Å perpendicular to the (111) planes].

Intensity statistics (Howells, Phillips & Rogers, 1950) indicated the space group to be centrosymmetric. Since each component of the complex has a potential center of symmetry and only one formula unit exists in the cell, it seemed reasonable to place one molecule with its center at the origin, the other with its center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and to search for solutions with the planes of the TCNE molecule and the aromatic rings approximately parallel to (111). Several attempts to solve the structure and obtain the molecular orientations by direct methods, with the program of Long (1965), failed. Others, have also reported some difficulties using direct methods in $P\bar{1}$. However, the structure was readily solved by use of sharpened Patterson sections parallel to the (111) planes. A large number of peaks, corresponding to the vectors predicted on the basis of the idealized geometry of a *para*-substituted benzene ring and a TCNE molecule, was present in, or near, the zero section. Thirteen of these vectors lay within 0·44 Å of the (111) plane. The approximate displacement of one aromatic ring relative to the other in the same molecule was found, as before (Gantzel & Trueblood, 1965), from the relation of the strong 3·2 Å inter-ring vector and the normal to the least-squares plane of the vectors defining the rings.

A Fourier synthesis, which was phased conservatively with only the six atoms of the aromatic ring, revealed the other eight atoms in the asymmetric unit (three in the PC molecule, five in the TCNE molecule), at positions in accord with the expected geometry and packing. Full-matrix least-squares refinement was then started, with observed reflections only. The form factors used were N and C (valence) (Hoerni & Ibers, 1954) and H (bonded) (Stewart, Davidson & Simpson, 1965). The computer program was that of Gantzel, Sparks & Trueblood [ACA (old), No. 317 modified] which minimizes $\sum w(\Delta|F|)^2$. A $1/\sigma$ weighting scheme was used.

In the initial least-squares cycles, only reflections with $\sin \theta/\lambda$ below 0·4 were included; atomic temperature factors were isotropic. As refinement progressed, increasing numbers of reflections were included and anisotropic temperature factors were introduced. When the conventional discrepancy index, $R$, had fallen to 0·128, a difference Fourier synthesis clearly showed all 10 unique hydrogen atoms. After several further least-squares cycles, with the positions of the hydrogen atoms allowed to shift but the isotropic temperature factors of these atoms held constant at 4·5 Å$^2$, another difference map was plotted. It showed a peak of height about 1·2 e.Å$^{-3}$, surrounded by a through extending to $-0\cdot5$ e.Å$^{-3}$, not far from the central carbon atom of the TCNE molecule. This peak persisted even after further least-squares refinement when isotropic temperature factors for the hydrogen atoms were allowed to vary; this refinement converged to an $R$ value of 0·093.

The unexplained peak height of about 1·2 e.Å$^{-3}$ was situated in the plane of the TCNE molecule, about

1 Å from each (equivalent) central carbon atom, and nearly on the perpendicular bisector of the central C=C bond (Fig. 1). This position is very near that which would be occupied by the central carbon atom of TCNE if the molecule were rotated by 90° about an axis normal to its plane and passing through its center. Examination of a TCNE model shows that the molecule has approximate fourfold symmetry, if the two central atoms are disregarded. Thus, a 90° disorder of TCNE about its center and in its plane would result very nearly in superposition of carbon atom TC(2) on TC(3) (see Fig. 2) and TC(3) on TC(2'); a primed number denotes an atom related by the molecular center of symmetry to the corresponding unprimed atom. The corresponding mutual displacements of the nitrogen atoms from each other after a 90° rotation would only be about 0·4 Å. Thus, such a disorder would manifest itself in the difference map predominantly near the central carbon atoms and only slightly, if at all, in the region of the other atoms in the molecule.

Least-squares calculations were then begun with a disordered model. Initially, only the central carbon atom was considered to be disordered, with a weight of 20% in the alternative position. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Four cycles of refinement resulted in a drop of the $R$ index to 0·061; shifts in the final cycle were very small. The length of the central C–C bond, which had been significantly short in the ordered refinement (1·286 Å), increased to 1·323 Å for the higher-weight orientation, which was in better agreement with the value 1·339 Å found in monoclinic TCNE (Bekoe & Trueblood, 1964). (The length of this bond in the lower-weight molecule, at this stage, was 1·35 Å.)

It was clear at this point that the disordered model was a good one. However, because the alternative orientation of the molecule had a relatively low weight, it seemed preferable to assign an isotropic (rather than an anisotropic) temperature factor to the central carbon atom of the molecule. Several cycles of refinement. with this assignment led to the same $R$ index as before. The final $B$ of the lower-weight central carbon was only 2·1 Å², a value low enough to suggest that the degree of disordering might in fact be somewhat higher than 20%. Since our current least-squares program did not permit refinement of occupancy factors, we tested varying proportions of disordering, with the results indicated in Fig. 3. At the same time, we introduced two additional nitrogen atoms to allow for the disorder of this atom as well, because the C–C–N bond angles in the lower-weight orientation were only 151·6 and 152·0° and those for the higher-weight orientation also departed appreciably (although much less) from the expected near-linear arrangement, these being 171·0 and 171·4°. Calculations were made for five different relative occupancies, varying from 10% to 30% of the lower-weight orientation, at 5% intervals. The only permitted variations were in the parameters of the three disordered atoms: the central

carbon atom [TC(1) for the higher-weight orientation, TDC(1) for that of lower weight] and the two nitrogen atoms [TN(2) and TDN(2), TN(3) and TDN(3)]. The three atoms with lower weight were assigned isotropic temperature factors; those with higher weight were refined anisotropically. Each refinement series started with the same initial parameters and was carried through three cycles to convergence. Fig. 3 shows, as a function of occupancy of the lower-weight form, plots of final isotropic temperature factors for the disordered atoms [TDC(1), TDN(2), and TDN(3)], final $R$ index, and final weighted sum of the residuals (on an arbitrary scale). These graphs are all consistent with the conclusion that the degree of disorder is about $25 \pm 3\%$; this value corresponds to the most reasonable relative values of the temperature factors (nitrogen atoms would be expected to have somewhat higher
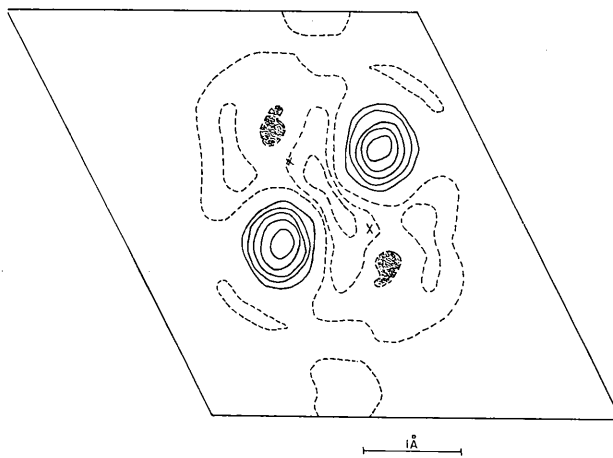


Fig. 1. Section of difference Fourier synthesis at $R = 0.093$ in plane parallel to (111) and passing through the point $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Contour interval is 0·20 e.Å$^{-3}$; negative contours are dashed. Minimum contour is at 0·20 e.Å$^{-3}$. Shaded portions include local maxima in regions of negative electron density. Crosses specify input positions of central atoms of TCNE.
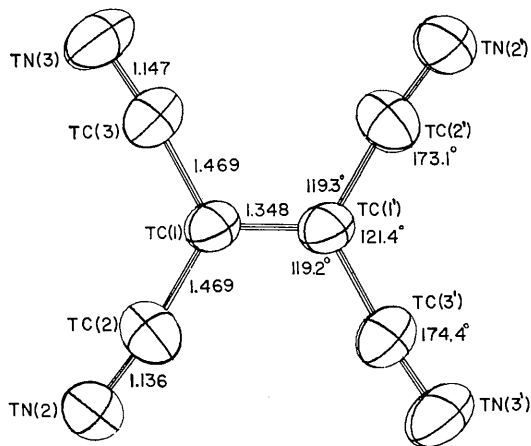


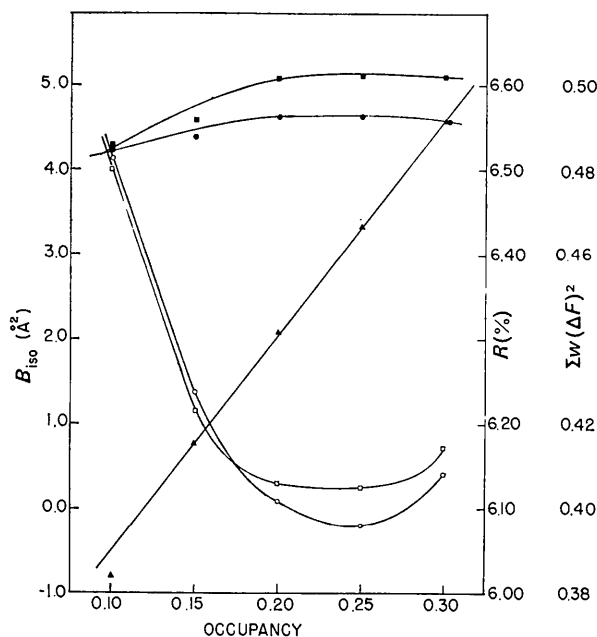Fig. 2. Bond lengths and angles of TCNE, including corrections for riding motion.

corresponding to these parameters are listed in Table 3. Anisotropic temperature factors of the carbon atoms in the [3.3] PC molecule were used in analyzing possible rigid-body motion (Cruickshank, 1956); results are given in Table 4. The largest discrepancy between any observed and calculated $U_{il}$ was about 11% [for $U_{11}$ of PC(1)], but the average discrepancy was less than 5%. Because the TCNE molecule is disordered and because wagging motion of the cyano groups in cyano-olefins is always observed, it is not surprising that thermal parameters of the TCNE-molecule atoms do not fit a rigid-body model.



Fig. 3. Variation with fraction of TCNE disorder of: isotropic temperature factors for three disordered atoms [▲, TDC(1); ●, TDN(2); ■, TDN(3)], discrepancy index (○), and weighted sum of residuals on arbitrary scale (□).

values) and to minima in both $R$ and the weighted sum of the squares of the residuals.

As a final stage in the structure analysis, secondary extinction corrections were made (Zachariasen, 1963), leading to a drop in $R$ to 0·056. Three more cycles of least-squares refinement (using the 25% disordered model for the TCNE) led to the final parameters, corresponding to $R = 0·055$ (observed reflections only) or $R = 0·082$ (all reflections).

Final position parameters, with their estimated standard deviations are given in Table 1. Final temperature factors are given in Table 2. Structure factors

Table 1. *Final position parameters** × 10^4*

|  | $x$ | $y$ | $z$ |
|---|---|---|---|
| PC(1) | 1656 (3) | 1034 (3) | 2847 (3) |
| PC(2) | 2529 (3) | 0865 (3) | 1641 (3) |
| PC(3) | 2296 (3) | 1645 (3) | 0209 (3) |
| PC(4) | 1338 (3) | 2764 (3) | 0217 (3) |
| PC(5) | 0482 (3) | 2929 (3) | 1435 (3) |
| PC(6) | 0541 (3) | 1985 (3) | 2700 (3) |
| PC(7) | −0686 (3) | 1860 (3) | 3712 (3) |
| PC(8) | −2638 (3) | 0674 (3) | 2308 (3) |
| PC(9) | −2977 (3) | −1237 (3) | 1347 (3) |
| PH(1) | 1771 (32) | 0393 (30) | 3741 (34) |
| PH(2) | 3200 (27) | 0096 (25) | 1696 (29) |
| PH(4) | 1175 (28) | 3327 (28) | −0746 (32) |
| PH(5) | −0253 (32) | 3634 (30) | 1297 (35) |
| PH(7a) | −0095 (32) | 1434 (30) | 4863 (36) |
| PH(7b) | −0707 (34) | 3078 (34) | 4324 (33) |
| PH(8a) | −3322 (27) | 0734 (27) | 3131 (31) |
| PH(8b) | −3113 (28) | 1162 (27) | 1265 (31) |
| PH(9a) | −2491 (32) | −1702 (30) | 2369 (35) |
| PH(9b) | −4337 (34) | −1968 (30) | 0660 (34) |
| TC(1) | 4937 (4) | 4661 (4) | 5687 (4) |
| TC(2) | 3866 (3) | 5113 (3) | 6690 (4) |
| TC(3) | 5854 (3) | 3462 (3) | 6116 (4) |
| TN(2) | 3018 (9) | 5316 (9) | 7514 (10) |
| TN(3) | 6502 (11) | 2527 (10) | 6552 (12) |
| TDC(1) | 4487 (11) | 5431 (12) | 5149 (13) |
| TDN(2) | 3378 (29) | 5268 (34) | 7839 (35) |
| TDN(3) | 6303 (38) | 2616 (39) | 6855 (41) |

* E.s.d.'s in parentheses are in units of the least significant digit.

Table 2. *Final temperature-factor parameters** × 10^4*

|  | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |  | $B(\text{Å}^2)$ |
|---|---|---|---|---|---|---|---|---|
| PC(1) | 0158 (4) | 0154 (4) | 0179 (5) | 0110 (8) | 0139 (8) | 0154 (8) | PH(1) | 4·8 (6) |
| PC(2) | 0148 (4) | 0139 (4) | 0190 (5) | 0128 (7) | 0142 (8) | 0129 (8) | PH(2) | 3·4 (5) |
| PC(3) | 0131 (4) | 0140 (4) | 0177 (5) | 0073 (7) | 0130 (8) | 0109 (8) | PH(4) | 3·8 (4) |
| PC(4) | 0174 (5) | 0150 (4) | 0214 (5) | 0131 (8) | 0167 (9) | 0182 (9) | PH(5) | 5·4 (5) |
| PC(5) | 0156 (4) | 0148 (5) | 0233 (6) | 0130 (8) | 0165 (9) | 0146 (9) | PH(7a) | 5·3 (6) |
| PC(6) | 0135 (4) | 0134 (4) | 0174 (5) | 0075 (7) | 0125 (8) | 0072 (8) | PH(7b) | 5·6 (6) |
| PC(7) | 0152 (5) | 0192 (5) | 0196 (6) | 0103 (8) | 0164 (9) | 0099 (9) | PH(8a) | 3·6 (4) |
| PC(8) | 0153 (5) | 0199 (5) | 0221 (6) | 0149 (9) | 0199 (10) | 0132 (10) | PH(8b) | 3·7 (5) |
| PC(9) | 0157 (5) | 0177 (5) | 0193 (6) | 0090 (8) | 0178 (9) | 0134 (9) | PH(9a) | 4·7 (5) |
|  |  |  |  |  |  |  | PH(9b) | 4·6 (5) |
| TC(1) | 0171 (6) | 0127 (6) | 0225 (7) | 0135 (10) | 0190 (12) | 0135 (11) |  |  |
| TC(2) | 0206 (6) | 0182 (5) | 0254 (7) | 0104 (9) | 0260 (11) | 0125 (10) | TDC(1) | 3·3 (1) |
| TC(3) | 0212 (6) | 0153 (5) | 0242 (6) | 0151 (9) | 0165 (10) | 0165 (10) | TDN(2) | 4·9 (5) |
| TN(2) | 0208 (11) | 0205 (9) | 0282 (13) | 0175 (18) | 0289 (22) | 0196 (19) | TDN(3) | 6·1 (6) |
| TN(3) | 0289 (12) | 0189 (9) | 0305 (14) | 0274 (17) | 0199 (24) | 0223 (19) |  |  |

* Temperature factor for carbon, nitrogen (not disordered):
$$\exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right].$$
The e.s.d.'s in parentheses are in units of the least significant digit given for the corresponding parameter.

Table 3. *Observed and calculated structure factors*

The three columns list, respectively, $h$, $10F_o$, and $10F_c$. Letter $U$ means 'too weak to be observed'.

Table 4. *Rigid-body translational and librational tensors for [3.3] PC†*

$$T = \begin{pmatrix} 0.038 & 0.001 & -0.001 \\ & 0.038 & 0.005 \\ & & 0.040 \end{pmatrix} Å^2 \qquad L = \begin{pmatrix} 6.5 & 2.2 & 1.4 \\ & 3.1 & 1.9 \\ & & 5.7 \end{pmatrix} (°)^2$$

| Principal axes | Eigenvalue | | Direction cosines of eigenvector | |
|---|---|---|---|---|
| T | 0.044 Å$^2$ | 0.052 | −0.600 | −0.798 |
| | 0.039 | 0.933 | 0.312 | −0.180 |
| | 0.034 | 0.357 | −0.734 | 0.578 |
| L | 9.0 (°)$^2$ | 0.702 | 0.434 | 0.565 |
| | 4.7 | −0.638 | 0.043 | 0.768 |
| | 1.7 | −0.311 | 0.899 | −0.309 |

† $\langle \sigma(T) \rangle$ is about 0.001 Å$^2$ and $\langle \sigma(L) \rangle$ is about 0.5 (°)$^2$. Reference axes are a, c* × a, and c*.

## Crystal and molecular structure

A portion of the molecular arrangement in the crystal is depicted in Fig.4. There are no unusually short contacts between molecules of the same type (no intermolecular $N \cdots N$ contacts less than 4 Å and only one $H \cdots H$ contact less than 2·5 Å, Table 5), indicating that interactions between TCNE and PC dominate the packing scheme. The shortest interatomic distances between molecules are given in Table 5 and are illustrated in Fig. 4. Distances of atoms in TCNE from a number of least-squares planes, defined by atoms in one benzene ring of the PC, are given in Table 6. The least-squares plane of the four unsubstituted benzene-carbon atoms of the PC, and the least-squares plane of the TCNE molecule, are inclined to each other by only 2°. The close parallelism of the planes of the two molecules appears to be characteristic of TCNE com-

plexes; the angle is also 2° in TCNE:pyrene (Ikemoto & Kuroda, 1967) and 0° in TCNE:naphthalene (Williams & Wallwork, 1967). The absence of any out-of-plane groups on either molecule apparently minimizes steric interference.

Table 5. *Shortest intermolecular distances\**

Within one column of molecules

| | | | | | |
|---|---|---|---|---|---|
| PC(1)$\cdots$TC(1) | 3·25 Å | | PC(6)$\cdots$TC(1) | 3·45 Å |
| PC(1)$\cdots$TC(3) | 3·33 | | PC(7)$\cdots$TN(2) | 3·49 |
| PC(2)$\cdots$TC(1) | 3·47 | | PC(1)$\cdots$TDC(1') | 3·43 |
| PC(2)$\cdots$TC(3) | 3·37 | | PC(2)$\cdots$TDC(1') | 3·26 |
| PC(3)$\cdots$TC(1') | 3·47 | | PC(3)$\cdots$TDC(1') | 3·49 |
| PC(3)$\cdots$TC(2') | 3·33 | | PC(6)$\cdots$TDC(1) | 3·42 |
| PC(4)$\cdots$TC(1') | 3·35 | | PC(9')$\cdots$TDN(2') | 3·42 |
| PC(4)$\cdots$TC(3') | 3·37 | | | |
| PC(5)$\cdots$TC(3') | 3·36 | | PH(9b')$\cdots$TN(2') | 2·71 |
| PC(6)$\cdots$TC(2) | 3·32 | | PH(9b')$\cdots$TDN(2') | 2·55 |
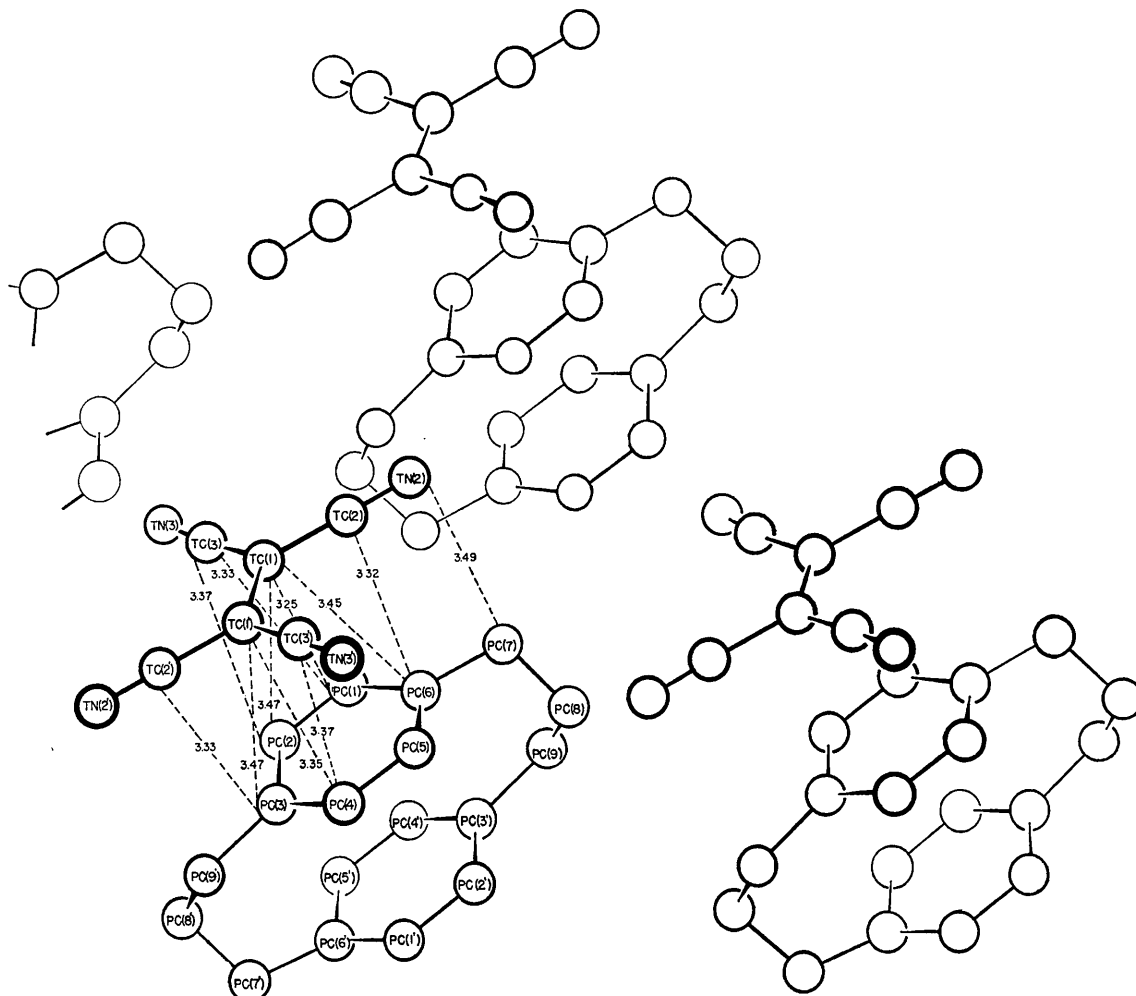


Fig. 4. View of the structure along $b$ axis, showing $C \cdots C$ and $C \cdots N$ intermolecular distances less than 3·5 Å, except for that between PC(5) and TC(3'), 3·36 Å, which cannot easily be shown.

Table 5 (cont.)

Between different columns of molecules

| | | |
|---|---|---|
| TN(2)·····PC(8') (011) | 3·49 Å |
| TN(2)·····PH(4) (001) | 2·90 |
| TN(2)·····PH(7b') (011) | 2·83 |
| TN(2)·····PH(8b') (011) | 2·91 |
| TDN(2)···PH(4) (001) | 2·87 |
| TDN(2)···PH(9a') (001) | 2·90 |
| TN(3)·····PH(2') (101) | 2·89 |
| TN(3)·····PH(8a) (100) | 2·80 |
| TDN(3)···PH(2') (101) | 2·85 |
| PH(7a)····PH(1') (001) | 2·53 |
| PH(7a)····PH(9a') (001) | 2·38 |
| PH(8b')···PH(9b) (100) | 2·51 |

* All C···C and C···N distances less than 3·5 Å, all C···H and N···H distances less than 2·9 Å, and all H···H distances less than 2·55 Å. E.s.d.'s: 0·01 Å for C···C, C···N; 0·04 Å for N···H; 0·06 Å for H···H.

Primed atoms are related to unprimed ones by a center of symmetry in the particular molecule indicated. The triple of numbers in parentheses after certain atoms indicates the unit translations along a, b, and c for the molecule in which that atom is situated. In the absence of such a triple of numbers, the molecule is assumed to be that designated in Table 1.



Fig. 5. Stacking of molecules along the body diagonal of the unit cell (indicated by dashed line).

Table 6. Some least-squares planes*†‡

| | I | II | III | IV |
|---|---|---|---|---|
| $l_1$ | 0·4028 | 0·4600 | 0·4310 | 0·4240 |
| $l_2$ | 0·6257 | 0·5180 | 0·5727 | 0·5494 |
| $l_3$ | 0·6680 | 0·7211 | 0·6974 | 0·7200 |
| D(Å) | −1·544 | −1·499 | −1·604 | −4·807 |

Deviations of atoms (Å)

| | | | | |
|---|---|---|---|---|
| PC(1) | −0·002 | 0·154 | −0·002 | −3·17 |
| PC(2) | 0·002 | 0·161 | 0·002 | −3·19 |
| PC(3) | −0·001 | 0·000 | −0·083 | −3·32 |
| PC(4) | 0·158 | 0·000 | −0·002 | −3·26 |
| PC(5) | 0·159 | 0·000 | 0·002 | −3·22 |
| PC(6) | 0·001 | 0·000 | −0·076 | −3·26 |
| PC(7) | −0·289 | −0·290 | −0·364 | −3·51 |
| PC(8) | −1·734 | −1·777 | −1·832 | −4·98 |
| PC(9') | −0·231 | −0·228 | −0·315 | −3·59 |
| PH(1) | −0·08 | 0·19 | −0·02 | −3·15 |
| PH(2) | −0·09 | 0·18 | −0·04 | −3·22 |
| PH(4) | 0·17 | −0·10 | −0·05 | −3·33 |
| PH(5) | 0·19 | −0·08 | −0·03 | −3·26 |
| PH(7a) | −0·06 | 0·07 | −0·07 | −3·19 |
| PH(7b) | 0·35 | 0·25 | 0·23 | −2·93 |
| PH(8a) | −1·79 | −1·83 | −1·89 | −5·01 |
| PH(8b) | −1·88 | −2·04 | −2·04 | −5·21 |
| PH(9a') | −0·38 | −0·50 | −0·53 | −3·83 |
| PH(9b') | 0·68 | 0·71 | 0·61 | −2·67 |
| TC(1) | 3·22 | 3·31 | 3·20 (3·22) | 0·012 |
| TC(2) | 3·24 | 3·28 | 3·19 (3·23) | 0·024 |
| TC(3) | 3·10 | 3·37 | 3·16 (3·25) | 0·003 |
| TN(2) | 3·19 | 3·20 | 3·12 (3·29) | −0·017 |
| TN(3) | 2·99 | 3·41 | 3·13 (3·28) | −0·007 |
| TDC(1) | 3·31 | 3·27 | 3·22 (3·20) | 0·008 |
| TDN(2) | 3·35 | 3·40 | 3·31 (3·11) | 0·171 |
| TDN(3) | 3·02 | 3·43 | 3·16 (3·26) | 0·026 |

* $l_1$, $l_2$, $l_3$ are direction cosines relative to a, c*×a, c*, re-respectively. D is the distance of the plane from the origin.
† Bold-face type indicates that atom was used to define the plane. Negative deviations are in the direction of the origin.
‡ Numbers in parentheses indicate distances for centro-symmetrically related atoms.



Fig. 6. View of the complex in a direction normal to least-squares plane of the aromatic ring. TCNE molecule depicted with solid lines represents about 75% occupancy, that shown dashed about 25%.

As anticipated, the molecules stack along a line almost parallel to the body diagonal of the unit cell (Fig. 5). A view of the complex normal to the molecular planes is given in Fig. 6, showing the disorder in the TCNE; this is discussed later. The normals to the least-squares planes of the TCNE and PC (planes III and IV of Table 6) make angles of 3·8 and 3·0° respectively with the [111] direction and angles of 6·8 and 8·7° with the normal to (111). This arrangement of molecules in the crystal corresponds to Prout & Wright's (1968) type A for space group P1̄, each molecule in the complex occupying a center of symmetry. The geometry of [3.3]PC in this crystal structure is illustrated in Figs. 7, 8, and 9. For clarity, hydrogen atoms have been omitted from all but one of these Figures. Pertinent information for hydrogen atoms is summarized in Tables 7 and 8. The bending of the

aromatic rings out of the planar conformation (Fig. 7) shows the same pattern as in the uncomplexed molecule and, as expected, is much less than in the [2.2] compound (Hope, Bernstein, & Trueblood, 1971) and its diolefin (Coulter & Trueblood, 1963). The deformation angle $\alpha$ (average 6·3°) is apparently unchanged



Fig. 7. Out-of-plane distortion of one ring of PC molecule, viewed edge-on.
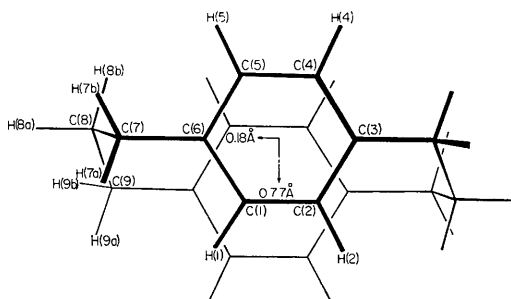


Fig. 8. View of the [3.3] PC molecule normal to the plane of the aromatic rings. Displacement of the center of one ring relative to the center of the other is shown.

on complexing (it is 6·4° in the crystal of [3.3] PC). Moreover, $\beta$, the angle of bending of the exocyclic C–C bonds out of the plane, exhibits qualitatively the pattern found earlier, being different (2·3 and 5·0°) on the two ends of the molecule (2·5 and 4·6° in the uncomplexed molecule). This difference at the two ends of the molecule results from the mutual parallel displacement of the two aromatic rings relative to one another; this displacement is slightly greater in the present structure than in the uncomplexed molecule. The increase in displacement is reflected in a decrease in the perpendicular distance between the planes C(1)–C(2)–C(4)–C(5) and C(1')–C(2')–C(4')–C(5'), from 3·26 in pure [3.3] to 3·20 Å in the present crystal. It also results in a closer approach of H(8b) to C(2') and H(2') than in the uncomplexed molecule, by about 0·1 and 0·2 Å respectively, and similar increases in the distances of H(8b) from C(5) and H(5).

Dihedral angles in the methylene bridge are 63° (6–7–8–9) and 70° (7–8–9–3'); these values agree very closely with those for the uncomplexed molecule (65 and 70°), and with the conformation of *gauche* n-butane, where the angle is 63° (Bonham & Bartell, 1959). The difference in the fold angles around atoms PC(3) (2·8°) and PC(6) (6·1°) [*i.e.*, the angle between the planes PC(5)–PC(6)–PC(7) and PC(1)–PC(6)–PC(7), and between the equivalent planes at atom PC(3)] also reflects the slight distortion that results from the parallel displacement of the rings.

Table 7. *Bond distances and angles in* [3.3] PC\*†‡

| 1–2 | 1·389 Å | 6–1–2 | 121·9° | 6 –1–H(1) | 120° |
|---|---|---|---|---|---|
| 2–3 | 1·398 | 1–2–3 | 120·6 | 2 –1–H(1) | 118 |
| 3–4 | 1·402 | 3–4–5 | 121·2 | 1 –2–H(2) | 119 |
| 4–5 | 1·384 | 4–5–6 | 121·2 | 3 –2–H(2) | 120 |
| 5–6 | 1·399 | | | 3 –4–H(4) | 119 |
| 6–1 | 1·389 | 2–3–4 | 117·2 | 5 –4–H(4) | 120 |
| | | 5–6–1 | 117·2 | 4 –5–H(5) | 118 |
| | | | | | |
| 6–7 | 1·510 | | | 6 –5–H(5) | 121 |
| 9–3' | 1·517 | 2–3–9' | 121·4 | | |
| | | 4–3–9' | 121·4 | 6 –7–H(7a) | 110 |
| | | | | | |
| 7–8 | 1·541 | 1–6–7 | 120·9 | 6 –7–H(7b) | 110 |
| 8–9 | 1·537 | 5–6–7 | 121·7 | 8 –7–H(7a) | 113 |
| | | | | 8 –7–H(7b) | 107 |
| | | | | | |
| 1–H(1) | 0·97 | 6–7–8 | 113·4 | 7 –8–(H8a) | 106 |
| 2–H(2) | 0·97 | 7–8–9 | 117·1 | 7 –8–H(8b) | 108 |
| 4–H(4) | 0·96 | 8–9–3' | 115·8 | 9 –8–H(8a) | 107 |
| 5–H(5) | 0·97 | | | 9 –8–H(8b) | 110 |
| 7–H(7a) | 1·05 | | | 8 –9–H(9a) | 110 |
| 7–H(7b) | 1·05 | | | 8 –9–H(9b) | 111 |
| 8–H(8a) | 1·00 | | | 3'–9–H(9a) | 110 |
| 8–H(8b) | 1·00 | | | 3'–9–H(9b) | 106 |
| 9–H(9a) | 0·97 | | | | |
| 9–H(9b) | 1·04 | | | H(7a)–7–H(7b) | 109 |
| | | | | H(8a)–8–H(8b) | 108 |
| | | | | H(9a)–9–H(9b) | 103 |

\* Carbon atoms are identified merely by their numbers. Hydrogen-atom numbers are the same as those of the carbon atom to which the hydrogen atom is bonded.

† Corrected for librational effects (Cruickshank, 1956).

‡ E.s.d.'s: C–C, 0·004 Å; C–H, 0·03 Å; C–C–C angles, 0·25°; C–C–H and H–C–H angles, 2°.

Table 8. *Nonbonded intramolecular distances in* [3.3]PC*

| | | | | | |
|---|---|---|---|---|---|
| 8–2′ | 3·07 Å | | | | |
| H(8b)–2′ | 2·77 | 1–5 | 2·37 Å | 1–4 | 2·75 Å |
| H(8b)–5 | 3·01 | 2–4 | 2·39 | 2–5 | 2·76 |
| 8–H(2′) | 2·84 | 3–1 | 2·42 | 3–6 | 2·83 |
| | | 3–5 | 2·42 | | |
| H(8b)–H(2′) | 2·25 | 6–2 | 2·42 | Angles: | |
| | | 6–4 | 2·42 | | |
| 1–4′ | 3·29 | | | 4–2–5′ | 101·9° |
| 2–5′ | 3·29 | 7–1 | 2·52 | 5–1–4′ | 102·3 |
| 3–6′ | 3·13 | 7–5 | 2·54 | 2–1–4′ | 86·7 |
| | | 7–9 | 2·62 | 4–5–2′ | 85·6 |
| 6–9 | 3·18 | 9–2′ | 2·54 | | |
| 7–3′ | 3·30 | 9–4′ | 2·55 | | |
| 6–2′ | 3·30 | 8–3′ | 2·58 | | |
| 5–8 | 3·26 | 8–6 | 2·55 | | |
| 1–3′ | 3·21 | | | | |

* All C–C distances less than 3·5 Å, all H···H distances smaller than 2·6 Å and with at least four intervening carbon atoms, and all C···H distances less than 3·2 Å and with at least three intervening carbon atoms. Carbon atoms are identified by their numbers; hydrogen-atom numbers are the same as those of the carbon atom to which the hydrogen atom is bonded. Given angles define the parallel displacement of the rings; they would all be 90° in an idealized molecule with exactly superimposed rings.

All bond distances and angles for the present [3.3] molecule (Fig. 9) are within 3σ of those found earlier; the largest discrepancy between bond lengths for the

two structures is for the C(8)–C(9) distance, 0·012 Å, which is probably not significant.

Aromatic hydrogen atoms are displaced slightly toward the inside of the molecule from the plane of the half-aromatic ring to which they are attached (planes I and II of Table 6), just as in [2.2] PC (Bekoe & True-blood, 1964; Hope, Bernstein & Trueblood, 1971), its diolefin (Coulter & Trueblood, 1963), its octafluoro analog (Hope, Bernstein & Trueblood, 1971), and un-complexed [3.3] (Gantzel & Trueblood, 1965). The average displacement in the present structure is about 0·09 Å, with only a small deviation from the average.

The dihedral angle between the two half-aromatic rings is 7·6°, also within one e.s.d. of the observed value (8°) for the uncomplexed [3.3]PC. Remaining features of the molecular geometry are very similar to those discussed by Gantzel & Trueblood (1965) and do not warrant further comment. The similarity of the molecular geometries of the complexed and uncom-plexed PC* indicates that, at least within the present precision, no changes have occurred in this molecule as a result of complex formation. The indicated motion of the molecule is not large and the pattern is quite

* Although in both crystals in which it has been studied the [3.3]PC molecule is centrosymmetric and, thus, in 'chair' form in relation to the three-carbon bridges between the rings, the 'boat' form predominates over the 'chair' by 2:1 in solution in CDCl₃ at −88°C (Anet & Brown, 1969).
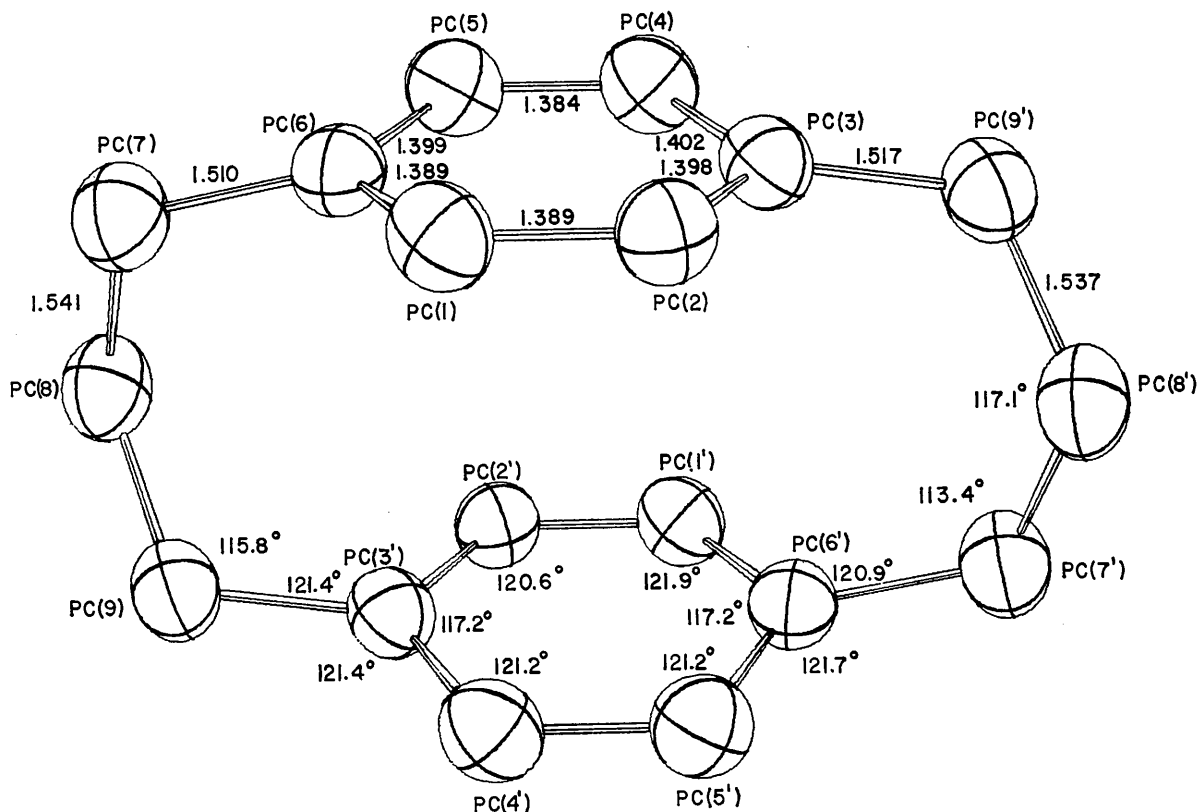


Fig. 9. Bond lengths and angles of [3.3]PC, including corrections for molecular libration.

plausible. Principal libration (Table 4), with a root-mean-square amplitude of 3°, is about an axis not far (18°) from the normal to the plane of the aromatic rings.

Features of the molecular geometry found for TCNE in the present study are given in Table 9 and Fig. 2. Bond lengths have been corrected for thermal motion by the 'riding motion' method of Busing & Levy (1964). Molecular dimensions are compared in Table 10 with those found for uncomplexed monoclinic TCNE (Bekoe & Trueblood, 1960, 1964) and cubic TCNE (Little, Pautler & Coppens, 1971), for TCNE in the naphthalene complex (Williams & Wallwork, 1967) and in the pyrene complex (Ikemoto & Kuroda, 1967), and for gaseous TCNE (by electron diffraction) (Hope, 1968). Because of the disorder in the present structure, with its consequence that the positions of the cyano-carbon atoms of the two TCNE molecules are too close to be resolved, we cannot place much credence in the molecular dimensions involving these two atoms. Thus, the facts that for the present TCNE molecule (alone among those in Table 10) the C(2)–C(1)–C(3) angle appears greater than 120°, the C–C–N angles deviate about 6° from linearity, and the C(1)–C(2) and C(1)–C(3) distances are longer than in the other studies (except for the imprecisely determined pyrene complex) may reflect no more than an inaccuracy in the C(2) and C(3) positions. On the basis of a comparison of the maximum-absorption wavelength of the complexes (Table 10; Cram & Bauer, 1959; Dewar & Thomson, 1966), the [3.3]–TCNE complex appears to be intermediate in strength between those formed by naphthalene and pyrene and any effects on molecular geometry due to complex formation might be expected to reflect this ordering. While identical features of the geometry show some apparent changes much greater than $3\sigma$

between structures, there are no obvious trends that can be legitimately construed as resulting from complex formation for these three examples of complexed TCNE.

Table 9. *Distances and angles in* TCNE*†

| 1–1' | 1·348 (7) Å | 2–1–3 | 121·4 (3)° |
|---|---|---|---|
| 1–2 | 1·469 (5) | 2–1–1' | 119·3 (4) |
| 1–3 | 1·469 (5) | 3–1–1' | 119·2 (4) |
| 2–N(2) | 1·136 (10) | 1–2–N(2) | 173·1 (5) |
| 3–N(3) | 1·147 (10) | 1–3–N(3) | 174·4 (7) |
| 2–3 | 2·542 (5) | | |
| 2–3' | 2·766 (4) | 3–2–3' | 90·1 |
| N(2)–N(3) | 4·39 (1) | | |
| N(2)–N(3') | 4·07 (1) | | |
| D(1)–D(1') | 1·32 (2) | 2–D(1)–3' | 132 (1) |
| D(1)–2 | 1·51 (1) | 2–D(1)–D(1') | 114 (1) |
| D(1)–3 | 1·51 (1) | 3'–D(1)–D(1') | 114 (1) |
| 2–DN(2) | 1·10 (3) | D(1)–2–DN(2) | 162 (2) |
| 3–DN(3) | 1·08 (4) | D(1)–3–DN(3) | 166 (2) |
| DN(2)–DN(3) | 3·90 (5) | | |
| DN(2)–DN(3') | 4·46 (5) | | |
| N(2)—DN(2) | 0·34 (3) | | |
| N(3)—DN(3) | 0·34 (4) | | |

* Carbon atoms are designated by numbers only; nitrogen atoms are designated by numbers of the carbon atoms to which they are bonded. D indicates the lower weight (disordered) molecule.
† Bond lengths for ordered molecule have been corrected for thermal motion on the assumption of riding motion; e.s.d.'s in parentheses are in units of the least significant digit.

The geometrical features of the lower-weight molecule (except for the central TDC(1)–TDC(1') bond, which is well enough resolved to be independent of the atoms in the higher-weight molecule) are reported in Table 9 only for reference and do not warrant further discussion. Clearly, the atomic positions are very imprecise.

Table 10. *Comparison of* TCNE *in various phases*

| | TCNE Monoclinic[a] | TCNE Cubic[b] | Naphthalene: TCNE[c] | Pyrene: TCNE[d] | [3·3] PC: TCNE[e] | Gaseous TCNE[f] |
|---|---|---|---|---|---|---|
| C=C | 1·339 (8) Å | 1·344 (1·357) (3) Å | 1·351 (14) Å | 1·309 (12) Å | 1·348 (7) Å | 1·357 (4) Å |
| C–C | 1·442 (5) | 1·439 (1·433) (2) | 1·426 (7) | 1·472 (13) | 1·469 (5) | 1·435 (4) |
| | 1·441 (5) | | | 1·464 (12) | 1·469 (5) | |
| C≡N | 1·135 (6) | 1·153 (1·166) (2) | 1·131 (8) | 1·113 (12) | 1·136 (10) | 1·162 (1) |
| | 1·133 (5) | | | 1·124 (12) | 1·147 (10) | |
| C=C–C | 121·0 (4)° | 122·2 (1)° | 120·9 (3)° | 121·4 (9)° | 119·3 (3)° | 121·1° |
| | 120·9 (4) | | | 120·3 (9) | 119·2 (4) | |
| C–C–C | 118·1 (3) | 115·6 (2) | 118·3 (6) | 118·3 (7) | 121·4 (4) | |
| C–C≡N | 179·1 (4) | 178·2 (2) | 178·7 (8) | 177·4 (9) | 173·1 (5) | |
| | 179·4 (4) | | | 176·7 (9) | 174·4 (7) | |
| $\lambda_{max}(m\mu)$[g] | — | — | 558 | 730 | 599 | — |

(a)  Bekoe & Trueblood (1964). C–C (but not C–N) distances are corrected for libration by method of Leung & Marsh (1958).
(b)  Little, Pautler & Coppens (1971). Distances are corrected for riding motion (Busing & Levy, 1964). Values in first set of parentheses for C=C, C–C, C N result when positions of $K$ and $L$ shells are refined separately.
(c)  Williams & Wallwork (1967).
(d)  Ikemoto & Kuroda (1967).
(e)  Present work; corrected for libration by method of Busing & Levy (1964).
(f)  Hope (1968), by electron diffraction.
(g)  $\lambda_{max}$ for complexes with naphthalene and pyrene from Dewar & Thompson (1966); for the PC complex, from Cram & Bauer (1959).

## Discussion

Examination of the present structure (Fig. 6) shows that the angle between the axes of the complex's components is within about 15° of that predicted by Herndon & Feuer (1968) for the TCNE:*p*-xylene complex, presumably a fair model for the present one. They calculated that the most stable orientation was with the molecular planes parallel, and with an angle of about 60° between the central double bond of the TCNE and the long axis of *p*-xylene. This angle is about 45° for both the higher-weight and lower-weight TCNE molecules relative to the long axis of PC. The relative population of TCNE in the two orientations (about 3:1) indicates that the difference in free energy between them is small, about 0·7 kcal.mole$^{-1}$. Herndon & Feuer calculated that the barrier to mutual rotation of the components of a complex between TCNE and a methylated benzene would be only a few kcal.mole$^{-1}$. Why then are there just two preferred orientations here, rather than a whole spectrum of them?

Study of a projection of the structure along the normal to the plane of a TCNE molecule (essentially along the [111] direction) provides a plausible explanation for the existence of two, and only two, angular orientations of TCNE relative to PC, solely on the basis of steric interactions.

Such a projection is shown in Fig. 10. The TCNE molecule(s) at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ are depicted at the center of the Figure, surrounded by six neighboring PC molecules in nearly the same plane, with their centers at the indicated positions. In the two observed positions of the TCNE molecule, each unique nitrogen atom is at, or near, a potential minimum with regard to nonbonded N···H and N···C contacts. Each nitrogen atom is, as indicated in Fig. 10 and Table 5, at a distance of 2·8 to 2·9 Å from a hydrogen atom in one of the surrounding PC molecules. The sum of the corresponding van der Waals radii is 2·6 to 2·7 Å. In these observed TCNE positions, the minimum N···C distance between columns of molecules is 3·49 Å (Table 5), well above the van der Waals sum of 3·1 to 3·2 Å.

However, if either TCNE molecule is rotated, both N···H and N···C distances decrease rapidly. A rotation of either TCNE molecule by as little as 15° in either direction gives short N···PC(8) or N···PC(9) contacts of 2·9 to 3·0 Å. With further rotation these distances drop even more prohibitively; a 45° rotation of either TCNE molecule in either direction gives N···C contacts of 2·4 Å or less. The N···H contacts become similarly unfavorable; after a 45° rotation, one nitrogen atom of each molecule is about 2·0 Å from each of two hydrogen atoms, and the other nitrogen atom of each molecule is about 1·8 Å from each of two other hydrogen atoms. No vertical adjustments of the molecules can compensate for these prohibitively close contacts, because the interplanar N···C and N···H distances are already near the minimum (Table 5).
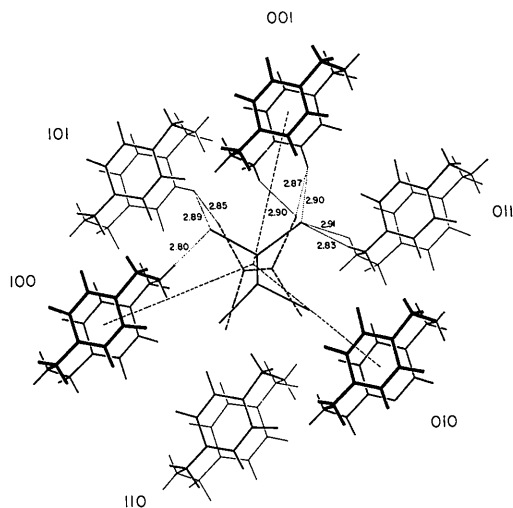


Fig. 10. View of a portion of the structure along the normal to the plane of the TCNE molecule, showing the surroundings of the TCNE molecule at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. The triple of numbers beside each PC molecule denotes the position of the center of that molecule in terms of unit-cell translations. Three lighter dashed lines radiating from the center of the drawing represent unit-cell edges. The eight unique N···H contacts between stacks (Table 5) are indicated by dots.

It seemed tempting to try to identify the two maxima in the visible region of the solution spectrum of the TCNE:PC complex (Cram & Bauer, 1959) with the two orientations of TCNE found in the crystal, but no such identification is justified by our results. The two new bands in the solution spectrum might seem (de Maine, 1957) to be attributable to two distinct orientational isomers, in which the central double bond of the TCNE molecule is oriented respectively parallel to, and perpendicular to, the line between the *para* carbon atoms of PC; these positions parallel the nodal planes of the two highest filled molecular orbitals of the PC molecule. However, these are *not* the orientations found in the crystal. They are, in fact, the orientations of maximum steric interaction with adjacent columns, as indicated above. Whatever may be the structure of the complex in solution, it seems clear that the dominating orientational forces in the crystal are steric. The intercolumnar interactions would not, of course, be present in a solution or in the vapor state; therefore, our findings are quite consistent with Herndon & Feuer's suggestion that there may be nearly free rotation in a complex of this kind when it is not constrained by its environment. This analysis underscores the difficulties in using evidence about the structure of a weak complex in one phase for drawing structural conclusions about similar complexes in other media.

## References

ADMAN, E., ROSENBLUM, M., SULLIVAN, S. & MARGULIS, T. N. (1967). *J. Amer. Chem. Soc.* **89**, 4540.
ANET, F. A. L. & BROWN, M. A. (1969). *J. Amer. Chem. Soc.* **91**, 2389.

BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1.

BEKOE, D. A. & TRUEBLOOD, K. N. (1964). A.C.A. Meeting, Bozeman, Montana, Abstract J-12, p. 87.

BONHAM, R. A. & BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3491.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.

COULTER, C. L. & TRUEBLOOD, K. N. (1963). *Acta Cryst.* **16**, 667.

CRAM, D. J. & BAUER, R. H. (1959). *J. Amer. Chem. Soc.* **81**, 5971.

CRAM, D. J. & SHEEHAN, M. (1969). *J. Amer. Chem. Soc.* **91**, 3553.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754, 757.

DEWAR, M. J. S. & THOMPSON, C. C. (1966). *Tetrahedron. Suppl.* **7**, 97.

GANTZEL, P. K. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 958.

HERBSTEIN, F. H. & SNYMAN, J. A. (1969). *Phil. Trans. Roy. Soc.* A **264**, 635.

HERNDON, W. C. & FEUER, J. (1968). *J. Amer. Chem. Soc.* **90**, 5914.

HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.

HOPE, H. (1968). *Acta Chem. Scand.* **22**, 1057.

HOPE, H., BERNSTEIN, J. & TRUEBLOOD, K. N. (1971). To be published.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

IKEMOTO, I. & KURODA, H. (1967). *Bull. Chem. Soc. Japan,* **40**, 2009.

KURODA, H., AMANO, T., IKEMOTO, I. & AKAMATU, H. (1967). *J. Amer. Chem. Soc.* **89**, 6056.

KURODA, H., IKEMOTO, I. & AKAMATU, H. (1966). *Bull. Chem. Soc. Japan,* **39**, 547.

LEUNG, Y. C. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 17.

LITTLE, R. G., PAUTLER, D. & COPPENS, P. (1971). To be published.

LONG, R. E. (1965). Ph.D. Thesis, Univ. of California, L.A.

MAINE, P. A. D. DE (1957). *J. Chem. Phys.* **26**, 1189

MERRIFIELD, R. E. & PHILLIPS, W. D. (1958). *J. Amer. Chem. Soc.* **80**, 2778.

MULLIKEN, R. S. (1952). *J. Amer. Chem. Soc.* **74**, 811.

ORGEL, L. E. & MULLIKEN, R. S. (1957). *J. Amer. Chem. Soc.* **79**, 4839.

PROUT, C. K. & WRIGHT, J. D. (1968). *Angew. Chem. (Int.)* **7**, 659.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* **22**, 899.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

---

# The Crystal and Molecular Structures of Hexakis(imidazole)cadmium(II) Nitrate, [Cd(C₃H₄N₂)₆](NO₃)₂, and Hexakis(imidazole)cadmium(II) Hydroxide Nitrate Tetrahydrate, [Cd(C₃H₄N₂)₆](OH)(NO₃).4H₂0

BY A. D. MIGHELL AND A. SANTORO

*Institute for Materials Research, National Bureau of Standards, Washington, D.C.* 20234, *U.S.A.*

The crystal and molecular structures of hexakis(imidazole)cadmium(II) nitrate, $Cd(C_3H_4N_2)_6$ $(NO_3)_2$, and hexakis(imidazole)cadmium(II) hydroxide nitrate tetrahydrate, $[Cd(C_3H_4N_2)_6]$ $(OH)$ $(NO_3).4H_2O$, have been determined by single-crystal X-ray diffraction techniques. $[Cd(C_3H_4N_2)_6](NO_3)_2$ crystallizes in the trigonal system, space group $R\bar{3}$. The lattice parameters (hexagonal axes) are $a=12\cdot633$ (2), $c=15\cdot049$ (2) Å, $Z=3$, $\varrho_o=1\cdot54$ g.cm$^{-3}$, $\varrho_c=1\cdot54$ g.cm$^{-3}$. The final three-dimensional full-matrix least-squares refinement resulted in an $R$ value of $3\cdot6\%$ based on 1343 observed reflections. $[Cd(C_3H_4N_2)_6]$ $(OH)$ $(NO_3).4H_2O$ crystallizes in the hexagonal system, space group $P6_3/m$. The lattice parameters are $a=9\cdot0376$ (8), $c=21\cdot729$ (3) Å, $Z=2$, $\varrho_c=1\cdot45$ g.cm$^{-3}$, $\varrho_o=1\cdot44$ g.cm$^{-3}$. The final three-dimensional full-matrix least-squares refinement resulted in an $R$ value of $5\cdot4\%$ based on 996 observed reflections. Both structures consist of discrete $Cd(C_3H_4N_2)_6^{2+}$ cations and $NO_3^-$ anions but as a result of the presence of water molecules and $OH^-$ ions in the hydroxide complex, the packing of the cations in the two structures is considerably different. The ligand imidazole molecules are coordinated through the pyridine type nitrogen atoms ($>N$) to the $Cd^{2+}$ ions with an average bond distance $Cd\cdots N$ of $2\cdot363$ Å and they are hydrogen bonded through the pyrrole type ($-N-H$) nitrogen atoms to the nitrate groups. However, to accommodate hydrogen bonding, there is considerable difference in the orientation of the imidazole rings in the two complexes. Specifically, each ring in one of the two complex cations is rotated, about the Cd–N(1) direction, approximately 130° with respect to its counterpart in the other cation. The bond distances and angles between the atoms of the imidazole molecules are practically identical in the two structures.

## Introduction

The imidazole group occurs in a number of biologically important molecules such as histidine and hypoxan- thine, and it plays an important rôle in the chemistry of several biological systems by providing possible bind- ing sites in metal–protein interactions and in other interactions involving hydrogen bonds (Hofmann,