

Structure and Packing Arrangement of Molecular Compounds. II. (1:1) 7,7,8,8-Tetracyanoquinodimethane-Dibenzo-*p*-dioxin

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The molecular structures of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and dibenzo-*p*-dioxin (DPDO) and their arrangement in a (1:1) crystalline complex were determined from three-dimensional integrated precession intensity data. The crystals are monoclinic with two units of the complex in a unit cell belonging to the space group $P2_1/c$ and having dimensions $a=7.037$ (2), $b=9.123$ (2), $c=15.009$ (3) Å and $\beta=100.45$ (3)°. The structure was solved by direct methods and was refined by the least-squares method to conventional and weighted discrepancy values $R=0.043$ and $r_w=0.040$ respectively. TCNQ and DPDO are arranged in columns in which unlike parallel molecules are stacked face to face. The separation between the planes of adjacent stacked molecules is 3.46 Å. The molecular geometry of TCNQ is close to that theoretically predicted for the neutral TCNQ species. These results indicate that relatively weak charge-transfer interactions are present in the crystalline complex. The DPDO molecule is planar with C–O bond distances averaging 1.376 Å, in agreement with other related structures. The thermal motion of DPDO is considerably more intense than that indicated for TCNQ. The average molecular motion observed in the present structure is compared with the motions found in several related structures of TCNQ complexes with regard to the relevant packing arrangements.

Introduction

This work is part of a study of mixed-stack π -molecular compounds which involve 7,7,8,8-tetracyanoquinodimethane (TCNQ) as the acceptor. Apart from the interest in finding a reasonably accurate geometry of the complex in these compounds, this study is also motivated by the desire to contribute to the understanding of the observed packing arrangements in terms of the electronic structures of the constituent molecules and to rationalize the average thermal motion in terms of the molecular environment. A qualitative discussion of the second aspect is given at the end of this paper for several related TCNQ complexes in which the constituent molecules can be reasonably well approximated by the rigid-body model. The first aspect is approached by semi-empirical calculations of electronic properties and some of the progress made so far is summarized in an accompanying paper of this series (Goldberg & Shmueli, 1973*b*).

The present work incidentally provided a convenient means to determine the molecular dimensions of dibenzo-*p*-dioxin (DPDO), which appears to be a difficult case in view of the intense diffuse scattering and a frequent twinning observed in the diffraction patterns of DPDO crystals.

The bulk of this paper is concerned with the determination and description of the crystal and molecular structures of TCNQ and of DPDO in their (1:1) complex.

Experimental

Crystals of TCNQ were obtained through the courtesy of Professor J. Jortner. A sample of colourless crystals

of DPDO was kindly supplied by Dr B. Fuchs. During the preliminary study, crystal data were obtained for DPDO from calibrated Weissenberg photographs and are compared below with those published by Wood & Williams (1941).

Dibenzo- <i>p</i> -dioxin, $C_{12}H_8O_2$, M.W. 184.2	
Present	Wood & Williams (1941)
$a=15.185$ (7) Å	15.2 Å
$b=5.084$ (3)	5.08
$c=11.736$ (7)	11.7
$\beta=100^\circ 17'$	$100^\circ 20'$
$Z=4$, $D_c=1.372$ g cm ⁻³	$Z=4$, $D_c=1.38$ g cm ⁻³
Space group $A2/a$ or Aa .	

DPDO does not appear to be a promising subject for study (at least at room temperature), since a very intense diffuse scattering and twinned reciprocal lattices appear in the patterns.

Equimolar solutions of DPDO and of TCNQ in acetonitrile were mixed and deep-green, elongated crystals of the complex were obtained by slow evaporation.

Microanalysis: found C, 74.34; H, 3.15; N, 14.56; calculated for 1:1 ratio of DPDO to TCNQ C, 74.22; H, 3.11; N, 14.43%.

Crystal data

($C_{12}H_8O_2$) ($C_{12}H_4N_4$), M.W. 388.4, m.p. 177°C.

Monoclinic

$a=7.037$ (2), $b=9.123$ (2), $c=15.009$ (3) Å;

$\beta=100.45$ (3)°, $U_{cell}=947.6$ Å³;

$D_m=1.36$ g cm⁻³, $Z=2$, $D_c=1.361$ g cm⁻³;

$\mu(\text{Mo } K\alpha)=1.0$ cm⁻¹.

Systematic absences: $0k0$ with k odd, $h0l$ with l odd.

Space group $P2_1/c$.

The unit-cell dimensions were obtained from their least-squares fit to 20 measurements on Weissenberg [$\lambda(\text{Cu } K\alpha_1) = 1.5405 \text{ \AA}$, $\lambda(\text{Cu } K\alpha_2) = 1.5443 \text{ \AA}$] and precession [$\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$] photographs. The $0kl$ and $h0l$ Weissenberg photographs used for this purpose were calibrated with powder lines from a thin (0.2 mm) copper wire. Preliminary exposures showed a marked tendency of the crystals to deteriorate when irradiated in open air. This was remedied by mounting the crystal in a glass capillary with 0.3 mm diameter and 0.1 mm wall thickness.

Integrated precession intensity data were collected with Mo $K\alpha$ radiation from ten layers ($h0l$ – $h3l$ and $hk0$ – $hk5$). The intensities of 2911 reflexions were recorded with the aid of a Joyce–Loebl microdensitometer but only those of 1578 reflexions could be reliably estimated. The ‘unobserved’ reflexions were assigned the value $\frac{1}{2}I_{\min}$, where I_{\min} is the weakest observed intensity. Each observation was provided with a weighting parameter given by $w_o(I) = I^2/\sigma^2(I)$, where I is the (relative) intensity and $\sigma(I)$ is the corresponding estimate of error, derived from a statistical analysis of the microdensitometer readings. Lorentz and polarization factors were applied to the data and all the reflexions were brought to a common scale by a least-squares procedure similar to that described by Rollett & Sparks (1960). 228 reflexions, common to different layers, were involved in the correlation of the data which included the averaging of multiple and symmetry related observations and the calculation of relative weights. Altogether, 1314 independent F_o values, including 641 unobserveds, were available for study. Absorption corrections were not applied. Most of the computer programs used in this work have been mentioned elsewhere (Goldberg & Shmueli, 1971).

Structure determination and refinement

Attempts at an interpretation of the three-dimensional Patterson synthesis yielded nothing beyond confirming that the molecules of the complex are stacked along the a axis. Structure determination by this method was probably prevented by the severe overlap of the vector sets of the two symmetry related and differently oriented units of the complex. It was therefore decided to try and solve the structure by direct methods.

Normalized structure amplitudes, with $|E| > 1.0$, corresponding to observed reflexions, were used with the routines *SIGMA2* and *CONVERGE* (Germain, Main & Woolfson, 1971) which produced the Σ_2 listing and selected the starting set of signs shown in Table 1. This starting set was then input to the multisolution routine of Long (1965) and the solution which was associated with the highest consistency index ($C = 0.76$) turned out to be the correct one, as the corresponding E map revealed the positions of all fifteen heavy atoms in the asymmetric unit. The discrepancy index, based on 569 reflexions with $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$, was $R = 0.17$ after the fifth cycle of overall refinement of the E -map model.

Allowance for individual isotropic vibration lowered R to 0.13 after three additional cycles which were based on all the observed reflexions. Constant weights were employed in these calculations. The weighting scheme adopted in the subsequent anisotropic refinement rounds was $w = 4w_o/F_o^2$, where w_o is the experimental weighting parameter assigned to each reflexion during the processing of the data.

Table 1. Starting set of signs

	h	k	l	E
Origin-specifying reflexions	4	1	$\bar{2}$	+3.27
	8	2	$\bar{3}$	+3.26
	1	2	$\bar{13}$	+2.69
Reflexions whose signs were permuted	2	1	0	3.24
	4	1	$\bar{1}$	2.93
	2	1	$\bar{1}$	2.68
	2	0	$\bar{2}$	2.63

In order to enhance the speed of the computation, each molecule was kept in a separate block of the matrix of normal equations. The various stages of the refinement are summarized in Table 2.

Table 2. Summary of the refinement

Stage	Parameters refined	No. of reflexions	R
(1)	x, y, z of non-H atoms, overall vibration, scale	569	0.170
(2)	x, y, z, U (isotropic) of non-H atoms, scale	673	0.130
(3)*	x, y, z, U^U of non-H atoms, scale	672	0.080
(4)	x, y, z of all the atoms, U^U of non-H atoms, U (isotropic) of hydrogens, scale	672	0.045
(5)†	As in stage (4)	671	0.043

* The strong $20\bar{2}$ reflexion was excluded at this stage (probable extinction).

† The 210 reflexion was also omitted (probable extinction).

After completion of stage (3) a difference synthesis was calculated and approximate positional parameters of all the hydrogen atoms were derived therefrom.

The final discrepancy indices, based on 671 observed reflexions, are $R = 0.043$ and $r(\text{weighted}) = 0.040$.

Atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964) for carbon, oxygen and nitrogen and were given by the exact quantum-mechanical expression (*International Tables for X-ray Crystallography*, 1962) for hydrogen. These free-hydrogen form factors were replaced in the final cycle with those obtained from the f curve of Stewart, Davidson & Simpson (1965).

The final atomic positional and thermal parameters, together with their estimated standard deviations, are given in Tables 3 and 4 respectively. A list of observed and calculated structure factors can be obtained from the authors on request.

Table 3. Atomic fractional coordinates

The e.s.d.'s are given in parentheses in units of the last decimal place.

	<i>x</i>	<i>y</i>	<i>z</i>
DPDO			
O(1)	0.4996 (3)	0.4000 (4)	0.5711 (2)
C(2)	0.4566 (4)	0.3584 (5)	0.4821 (3)
C(3)	0.4102 (5)	0.2144 (6)	0.4629 (5)
C(4)	0.3658 (7)	0.1696 (9)	0.3727 (7)
C(5)	0.3652 (7)	0.2680 (13)	0.3064 (6)
C(6)	0.4093 (5)	0.4124 (9)	0.3237 (4)
C(7)	0.4550 (4)	0.4564 (6)	0.4124 (3)
H(3)	0.409 (5)	0.164 (5)	0.518 (2)
H(4)	0.341 (5)	0.073 (5)	0.370 (3)
H(5)	0.336 (5)	0.242 (6)	0.247 (3)
H(6)	0.419 (5)	0.497 (5)	0.279 (3)
TCNQ			
C(1')	0.9755 (4)	0.3562 (5)	0.5297 (2)
C(2')	0.9497 (3)	0.3887 (4)	0.4347 (2)
C(3')	0.9770 (4)	0.5362 (5)	0.4091 (2)
C(4')	0.8959 (4)	0.2824 (4)	0.3715 (2)
C(5')	0.8654 (4)	0.3110 (4)	0.2760 (2)
N(6')	0.8402 (4)	0.3323 (4)	0.2003 (2)
C(7')	0.8650 (4)	0.1326 (5)	0.3934 (3)
N(8')	0.8381 (4)	0.0134 (4)	0.4076 (3)
H(1')	0.959 (3)	0.252 (4)	0.552 (2)
H(3')	0.963 (3)	0.561 (3)	0.348 (2)

Crystal structure

Since the molecules of TCNQ and DPDO are located on centres of the space group $P2_1/c$, the unit cell is crossed by two differently oriented stacks which are related by screw axis and glide plane operations (Fig. 1).

The molecules in a stack have their natural axial systems almost exactly parallel, the normals to the planes of TCNQ and DPDO forming angles of $11^\circ 14'$ and

$11^\circ 28'$ respectively with the [100] direction. Fig. 2 shows details of the molecular overlap resulting from the inclinations of the axial systems of TCNQ and DPDO with respect to the stacking axis.

The observed mixed-stack arrangement of this complex is typical of donor-acceptor π -molecular com-

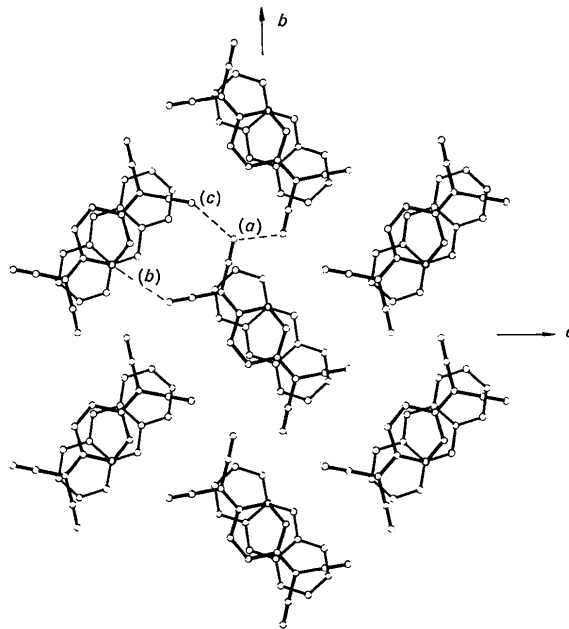


Fig. 1. Projection of part of the structure on the bc plane. The interatomic contacts marked in the figure are (a) N(8') at $x, 1-y, z$ to N(8') at $2-x, 1+y, 1-z$ 3.26 Å; (b) N(6') at $x, 1-y, z$ to C(1') at $x, 1\frac{1}{2}+y, z-\frac{1}{2}$ 3.36 Å; (c) N(8') at $x, 1-y, z$ to N(6') at $2-x, \frac{1}{2}-y, \frac{1}{2}-z$ 3.43 Å.

Table 4. Atomic thermal parameters $U^{ij} \times 10^4$ (Å²)

The e.s.d.'s are given in parentheses in units of the last decimal place. The anisotropic temperature factor is in the form $\exp[-2\pi^2(h_i a^i)(h_j a^j) U^{ij}]$ where h_i and a^i are reflexion indices and reciprocal unit-cell edges respectively.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
DPDO						
O(1)	828 (15)	804 (27)	727 (22)	-100 (15)	154 (24)	44 (13)
C(2)	452 (18)	530 (32)	915 (38)	-53 (19)	30 (39)	87 (20)
C(3)	570 (24)	827 (48)	1393 (55)	40 (24)	33 (55)	159 (30)
C(4)	627 (28)	938 (59)	2182 (102)	37 (34)	-519 (74)	77 (41)
C(5)	588 (26)	1784 (95)	1460 (75)	152 (42)	-681 (80)	10 (35)
C(6)	560 (23)	1236 (54)	840 (40)	76 (28)	-147 (52)	108 (22)
C(7)	458 (18)	700 (36)	705 (35)	-20 (19)	-84 (36)	57 (18)
TCNQ						
C(1')	545 (18)	479 (27)	519 (22)	54 (18)	112 (29)	149 (15)
C(2')	420 (15)	402 (25)	531 (22)	104 (15)	79 (26)	136 (14)
C(3')	561 (18)	589 (29)	405 (21)	84 (18)	78 (29)	115 (16)
C(4')	484 (16)	491 (26)	529 (22)	53 (16)	8 (27)	105 (14)
C(5')	615 (19)	604 (30)	627 (25)	25 (16)	-84 (27)	119 (17)
N(6')	1066 (20)	854 (30)	608 (20)	26 (17)	-44 (23)	160 (16)
C(7')	602 (19)	553 (26)	629 (25)	55 (21)	-55 (33)	27 (16)
N(8')	894 (20)	625 (24)	1005 (28)	-45 (17)	-13 (27)	95 (17)

Isotropic vibration parameters of the hydrogen atoms

H(3) 7.2 (1.3)	H(5) 9.7 (1.6)	H(1') 5.7 (0.8)
H(4) 8.2 (1.4)	H(6) 9.2 (1.4)	H(3') 3.8 (0.7)

Table 5. Results of the rigid-body motion analysis

All the tensors are referred to the axial system of the tensor of inertia defined below. l_i and t_i are unit vectors along the principal axes of the libration tensor L and translation tensor T , respectively.

(a) DPDO

Tensor of inertia:		Eigenvalues‡			Eigenvectors*		
		199	l	-1.021	-6.624	-9.527	
		926	m	-0.960	-6.005	11.300	
		1125	n	-6.896	1.816	2.615	
Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)							
Tensor		11	12	13	22	23	33
$L(\text{rad}^2)$		923 (417)	-32 (65)	139 (123)	17 (63)	-114 (54)	1313 (53)
$T(\text{Å}^2)$		7287 (289)	-782 (283)	-686 (313)	5598 (408)	-59 (410)	4975 (720)
R.m.s. amplitudes				Principal axes†			
L		6.7°	l_1	0.3029	-0.0870	0.9491	
		5.4	l_2	0.9528	0.0053	-0.3036	
		0.3	l_3	0.0214	0.9962	0.0845	
T		0.28 Å	t_1	0.9177	-0.3300	-0.2212	
		0.23	t_2	0.2126	0.8784	-0.4280	
		0.22	t_3	0.3356	0.3457	0.8763	
R.m.s. discrepancy				0.0119 Å ²			

(b) TCNQ

Tensor of inertia:		Eigenvalues‡			Eigenvectors*		
		395	l	-0.991	-6.515	-9.737	
		1849	m	-0.948	-6.133	11.111	
		2243	n	-6.902	1.777	2.649	
Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)							
Tensor		11	12	13	22	23	33
$L(\text{rad}^2)$		1030 (91)	22 (11)	52 (20)	86 (22)	-36 (12)	225 (12)
$T(\text{Å}^2)$		5684 (107)	-70 (104)	499 (111)	3902 (150)	45 (151)	3604 (174)
R.m.s. amplitudes				Principal axes†			
L		5.8°	l_1	-0.9978	-0.0211	-0.0632	
		2.8	l_2	-0.0561	-0.2465	0.9675	
		1.6	l_3	-0.0359	0.9689	0.2447	
T		0.24 Å	t_1	0.9749	-0.0309	0.2207	
		0.20	t_2	0.0013	-0.9895	-0.1445	
		0.19	t_3	0.2229	0.1411	-0.9646	
R.m.s. discrepancy				0.0053 Å ²			

(c) TCNQ, quinonoid part only

Tensor of inertia:		Eigenvalues‡			Eigenvectors*		
		72	l	-0.947	-6.558	-9.700	
		254	m	-0.972	-6.093	11.171	
		326	n	-6.905	1.757	2.533	
Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)							
Tensor		11	12	13	22	23	33
$L(\text{rad}^2)$		1180 (201)	60 (88)	-29 (107)	162 (51)	-14 (34)	190 (33)
$T(\text{Å}^2)$		5654 (104)	38 (102)	561 (129)	3789 (133)	187 (135)	3351 (283)
R.m.s. amplitudes				Principal axes†			
L		6.2°	l_1	0.9978	0.0591	-0.0294	
		2.5	l_2	0.0473	-0.3285	0.9433	
		2.2	l_3	0.0461	-0.9426	-0.3306	
T		0.24 Å	t_1	0.9730	0.0397	0.2272	
		0.20	t_2	0.0991	-0.9615	-0.2564	
		0.18	t_3	0.2083	0.2720	-0.9395	
R.m.s. discrepancy				0.0045 Å ²			

* Referred to the reciprocal base vectors a^* , b^* , and c^* .

† Referred to the unit vectors l, m, n .

‡ In units of atomic weight $\times \text{Å}^2$.

pounds (Prout & Wright, 1968; Herbstein, 1971). However, the relatively large separation of 3.46 Å between the planes of adjacent stacked TCNQ and DPDO suggests that any charge-transfer interaction present is probably rather weak.

Sideways packing is characterized by a small number of close approaches between cyano groups of TCNQ in adjacent columns and by the absence of contacts, shorter than the sum of van der Waals radii (Pauling, 1960) of the atoms concerned, involving the donor molecule. The staggering mode of adjacent stacks, which completes the description of the packing arrangement, is illustrated in Fig. 3.

Thermal motion

The different vibrational behaviour of the two molecules, already apparent from Table 4, is illustrated by the thermal ellipsoids in the best plane projections of TCNQ and DPDO (Fig. 5). The major component of the average motion of DPDO appears to be an extensive libration of the molecule in its own plane, *i.e.* about an axis of highest inertia. This apparently unusual type of motion seems to be rather common in crystals of molecular compounds in which the packing restrictions on the constituent molecules are dissimilar (Herbstein, 1971). As for possible indications of orientational disorder being concealed by the observed thermal motion of DPDO, none could be found in the electron density and difference density best plane sections through the molecule. However, the librational motion of DPDO, indicated by Fig. 5 and by the rigid-body motion analysis below, is immediately apparent in the electron-density map.

The anisotropic vibration parameters of TCNQ and DPDO were analysed in terms of rigid-body models based on the libration and translation tensors (Cruickshank, 1956*a*). The quantities describing the molecular motions, resulting from these analyses, are shown in Table 5.

The r.m.s. discrepancy between the experimental and calculated thermal parameters of DPDO, $\langle(\Delta U_{ij})^2\rangle^{1/2}$

$=0.0119 \text{ \AA}^2$, is rather large. This may reflect some unknown misfit to the rigid-body model but is more probably due to systematic errors which were absorbed in the large vibration parameters. The corresponding percentage discrepancy is $100 \sum|\Delta U|/\sum U = 13.8\%$.

The extensive libration of DPDO about the plane normal is well supported by the analysis. Libration about the long axis also appears to be large; yet, it is less certain in view of the large standard deviation of L_{11} . The third, quite inappreciable, amplitude of libration about the O---O line is consistent with the probable inhibition of this type of motion by contacts of peripheral atoms of DPDO with the cyano groups of adjacent TCNQ molecules in the same stack.

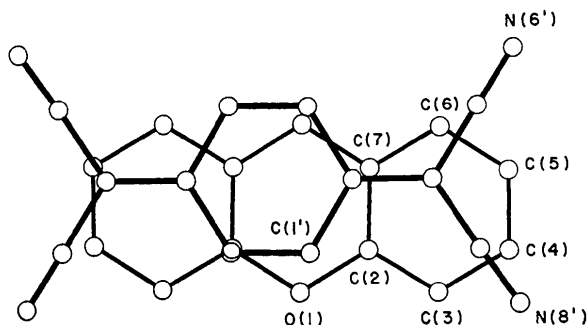


Fig. 2. Projection of two adjacent stacked molecules on the best plane of the quinonoid part of TCNQ.

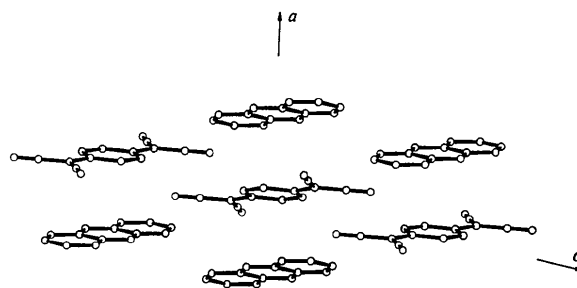


Fig. 3. The packing arrangement viewed down the *b* axis.

Table 6. Bond distances

	Distance (Å)			Distance (Å)	
	Uncorr.	Corr.		Uncorr.	Corr.
DPDO			TCNQ		
O(1)–C(2)	1.369 (6)	1.380	C(1')–C(2')	1.436 (5)	1.444
C(2)–C(3)	1.372 (7)	1.383	C(2')–C(3')	1.424 (6)	1.429
C(2)–C(7)	1.374 (7)	1.390	C(2')–C(4')	1.361 (5)	1.363
C(3)–C(4)	1.394 (13)	1.404	C(4')–C(5')	1.434 (5)	1.441*
C(4)–C(5)	1.340 (14)	1.355	C(4')–C(7')	1.431 (6)	1.437*
C(5)–C(6)	1.368 (14)	1.379	C(1')–C(11')	1.344 (5)	1.347
C(6)–C(7)	1.372 (7)	1.383	C(5')–N(6')	1.135 (5)	1.166*
C(7)–O(8)	1.360 (7)	1.372	C(7')–N(8')	1.131 (5)	1.163*
C(3)–H(3)	0.95 (4)		C(1')–H(1')	0.94 (3)	
C(4)–H(4)	0.90 (5)		C(3')–H(3')	1.02 (4)	
C(5)–H(5)	0.91 (5)				
C(6)–H(6)	1.04 (5)				

* Corrected on the assumption of riding motion (Busing & Levy, 1964).

The translational motion of DPDO is very nearly isotropic and rather similar to that indicated for TCNQ.

An analysis based on all the heavy atoms of TCNQ, with $\langle(\Delta U_{ij})^2\rangle^{1/2} = 0.0053 \text{ \AA}^2$ and $R = 10.1\%$, indicates qualitatively that the largest libration of TCNQ takes place about a direction 4° away from its long axis while the motion about the other two directions is much more restricted. A considerable improvement of fit is achieved by removing the cyano groups from the analysis (their somewhat independent motion, repeatedly reported in the literature, was also observed in the present case) as the r.m.s. discrepancy, $\langle(\Delta U_{ij})^2\rangle^{1/2}$, and percentage discrepancy are now reduced to 0.0045 \AA^2 and 8.9% respectively. The resulting rigid-body tensors and the directions of their principal axes were only slightly modified by considering the quinonoid skeleton rather than the whole molecule.

These results, here of main interest in connexion with the correction of bond distances, will be compared below with those obtained for some closely related TCNQ complexes.

Preliminary rigid-body motion analyses, carried out prior to the introduction of the hydrogen atoms into the refinement, gave for TCNQ and for DPDO almost identical results to those described in Table 5. It is perhaps worth noting that a marked out-of-plane vibration of the oxygen atoms in DPDO, not accounted for by the rigid-body motion analysis, also appears in the related 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Boer, van Remoortere, North & Neuman, 1972) and in 2,7-dichlorodibenzo-*p*-dioxin (Boer & North, 1972).

Molecular geometry

The molecules of TCNQ and DPDO are planar, within the experimental error. The equations of the best molecular planes are

$$6.90x - 1.81y - 2.62z = 1.23 \text{ \AA} \text{ for DPDO}$$

$$6.90x - 1.78y - 2.65z = 4.69 \text{ \AA} \text{ for TCNQ}$$

where x, y, z are fractional coordinates of a point in the plane and the right-hand sides of the equations are distances of the planes from the unit-cell origin.

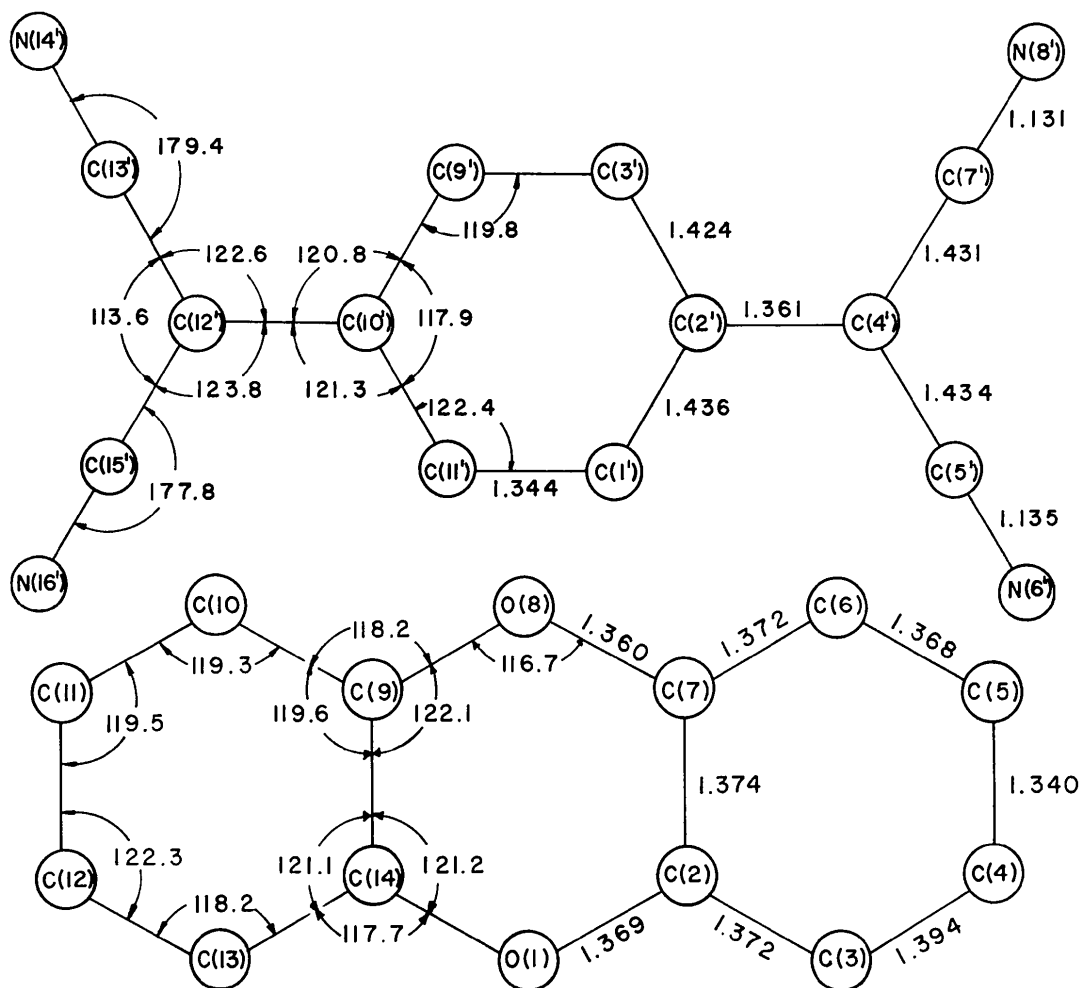


Fig. 4. Molecular geometry. Bond distances (Å) shown are not corrected for libration.

Internal consistency of chemically equivalent bonds in TCNQ is rather satisfactory, as the largest discrepancy [between C(1')-C(2') and C(2')-C(3') in TCNQ] is about 1.5σ , where σ is the standard deviation of the difference between the relevant bond lengths (Table 6). The molecular geometry of TCNQ, as shown in Table 6 and in Fig. 4, suggests, by comparison with a summary of TCNQ dimensions in other structures (Hoekstra, Spoelder & Vos, 1972), that TCNQ in the present structure is predominantly neutral. The quinonoid bond distance (1.363 Å), known to be sensitive to the molecular charge, also agrees with the corresponding distance theoretically predicted for the TCNQ species (Lowitz, 1967; Jonkman & Kommandeur, 1972). Thus, the molecular dimensions of TCNQ and

the relatively large interplanar spacing (3.46 Å) lead to the conclusion that the ground state of the TCNQ-DPDO complex is mainly of no-bond nature.

The molecular dimensions of DPDO could not be accurately estimated, presumably owing to the intense thermal motion. In particular, the C(4)-C(5) bond (1.340 Å) and the estimated standard deviations of the peripheral carbon-carbon bond distances in DPDO, seem to be significantly affected by the large in-plane molecular vibration. As is usually the case, libration corrections did not cope with the situation. The bond lengths in the central heterocyclic ring of DPDO seem to be much less affected by the librational motion, presumably because of their proximity to the centre of libration. Indeed, the approximately corrected average

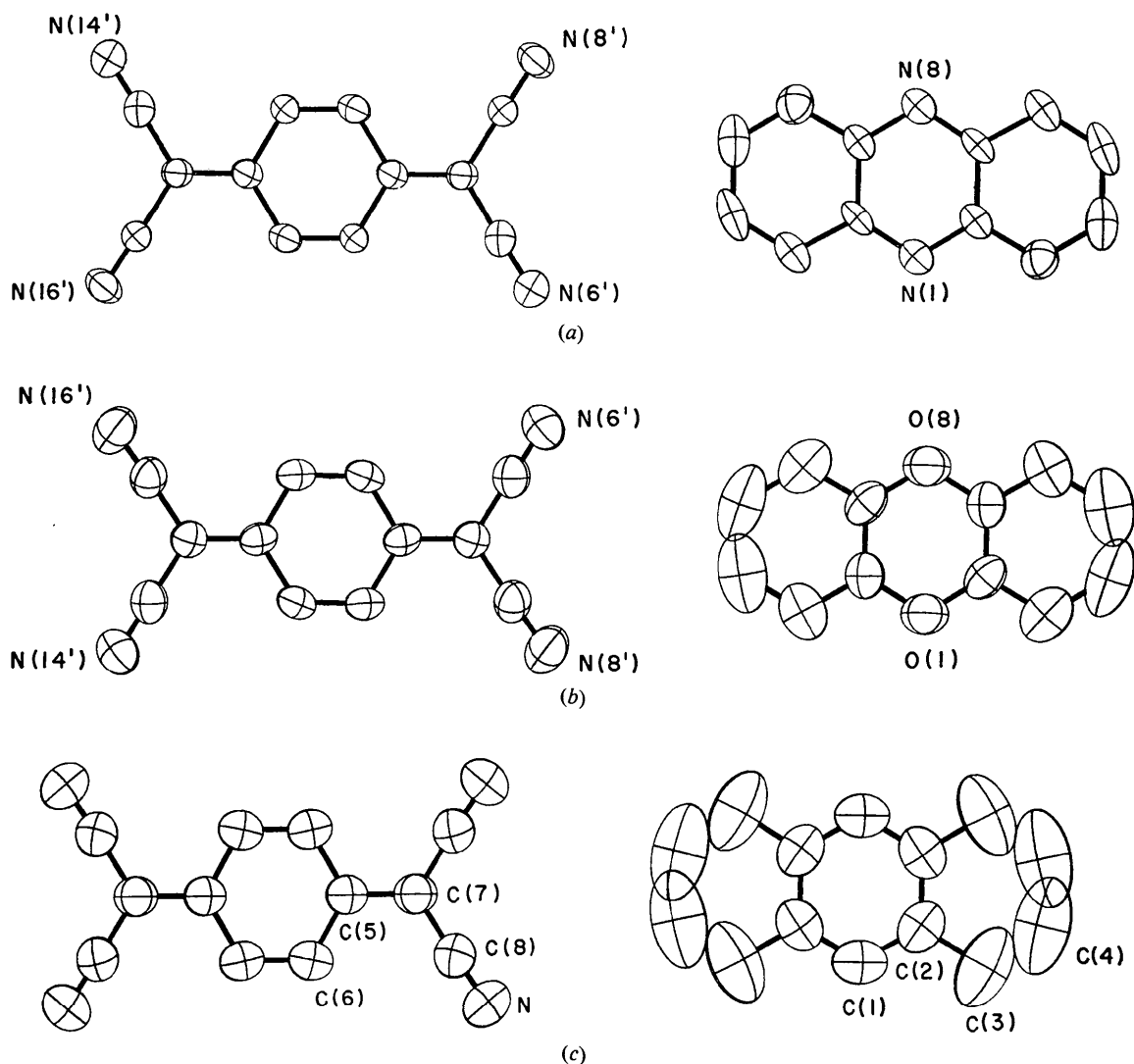


Fig. 5. 50% probability thermal ellipsoid representations of (a) TCNQ-phenazine (Goldberg & Shmueli, 1973*b*), (b) TCNQ-DPDO and (c) TCNQ-anthracene (Williams & Wallwork, 1968). The drawings were prepared from the observed thermal parameters with the program *ORTEP* (Johnson, 1965). The numbering of the atoms is the same as that given in the relevant papers.

C–O bond length of 1.376 Å is similar to that found in other structures (1.370 Å in furan, Fourme, 1969; 1.378 Å in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, Boer *et al.*, 1972; 1.37 Å in 2,7-dichlorodibenzo-*p*-dioxin, Boer & North, 1972). The recently estimated C–O bond length of 1.404 Å in dibenzofuran (Dideberg, Dupont & André, 1972) is not consistent with the above quoted results.

The maximal deviations from the best plane of DPDO (0.02 Å) and the rather limited (except for the oxygens) out-of-plane vibration of the atoms in DPDO suggest that the possibility of folding disorder being concealed by the thermal motion is not very likely. This possibility ought to be considered in view of the C–O bond distance (1.376 Å), which is indicative of a saturated central heterocyclic ring.

Comparison with other structures

The packing arrangement observed in DPDO–TCNQ is similar in several respects to that found in the structure of TCNQ–anthracene (Williams & Wallwork, 1968). Both structures are characterized by a rather loose packing, *i.e.* the interplanar separation between the unlike molecules is relatively large (> 3.45 Å) and no short interstack contacts are observed. In both cases the nearest approaches between molecules in adjacent stacks involve primarily the larger TCNQ molecules, whose thermal motion in DPDO and anthracene complexes is of comparable magnitude and which is relatively small when compared to the motion of the appropriate donors (Fig. 5). Since TCNQ is larger than either of the donors, DPDO and anthracene have a considerable amount of 'free' space in the corresponding structures. This is consistent with the libration amplitudes of anthracene and DPDO, about axes normal to the molecular planes, being relatively large (8.7 and 6.7° respectively). However, the molecular planes of DPDO and of TCNQ are slightly inclined with respect to the stacking axis while those in the anthracene–TCNQ structure are almost perpendicular to the direction of corresponding stack. Hence, DPDO is somewhat better exposed to interstack interactions, which is in keeping with the more limited libration of DPDO about the plane normal than that indicated for anthracene.

The importance of packing restrictions as a factor controlling the thermal motion in such complexes can be appreciated by comparing TCNQ–anthracene (Williams & Wallwork, 1968) with TCNQ–*N,N'*-dimethyldihydrophenazine (Goldberg & Shmueli, 1973*a*). The latter complex has remarkably similar cell dimensions and packing arrangement to those of TCNQ–anthracene, but the libration of the donor about the mean-plane normal is relatively small (3.2°), probably owing to the additional methyl groups which effectively fill the 'free' space.

Another example is provided by the structure of the TCNQ–phenazine complex (Goldberg & Shmueli,

1973*b*). The centre of the phenazine molecule is shifted by about 2.6 Å in the diagonal direction (along the bisector of the angle between the long and short molecular axes) relative to the centre of TCNQ. The resulting large inclination of the parallel molecular planes with respect to the stacking axis in that structure (about 38°) allows the formation of short contacts between molecules in adjacent stacks. Accordingly, the thermal motion of phenazine is comparatively small (Fig. 5) and of different character.

A qualitative conclusion based on the above observations is that the different patterns of thermal motion indicated for phenazine, DPDO and anthracene in the corresponding (1:1) TCNQ complexes are consistent with the observed interstack packing. As indicated by theoretical considerations, the intrastack interactions have probably little to do with the in-plane motion discussed above. Thus, it was found in a number of studies of charge-transfer complexes (*e.g.* Lippert, Hanna & Trotter, 1969; Herndon & Feuer, 1968) that the barrier to free rotation of the donor relative to the acceptor is generally a very low one (< 0.5 kcal mole⁻¹ in the absence of methyl groups on the donor). Assuming that this is also the case in the TCNQ complexes discussed here, it follows that the dynamics of such crystals is determined mainly by the van der Waals and dipole–dipole interactions. Preliminary calculations carried out in this laboratory appear to support the above conclusion.

One must of course be aware of the possibility of orientational disorder being concealed by the observed thermal ellipsoids. The presence of such in-plane disorder of anthracene in its TCNQ complex was suggested by Herbstein (1971). As far as DPDO is concerned, this was also suspected but no direct evidence (electron and difference density maps) for disorder could be found. In any case, it is probable that the above type of orientational disorder as well as the thermal motion in crystals of π -molecular compounds are governed by similar interactions.

Since there exist in the literature a considerable number of compounds that are accused, with more or less certainty, of being orientationally disordered, it would be interesting to have some spectroscopic evidence on such crystals. Thus, for example, the average frequency of libration about the plane-normal of DPDO is estimated from an approximate expression given by Cruickshank (1956*b*) as 28 cm⁻¹, which is rather low. One would therefore expect to find in far infrared and Raman spectra of similar crystalline compounds low frequency bands polarized along or close to the stacking axis, provided the thermal motion indicated is genuine.

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Structure and Packing Arrangement of Molecular Compounds. III. (1:1) 7,7,8,8-Tetracyanoquinodimethane–Phenazine

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Crystals of the (1:1) 7,7,8,8-tetracyanoquinodimethane (TCNQ)–phenazine complex are triclinic, with one unit of the complex in a unit cell of dimensions $a=8.437$ (2), $b=7.253$ (3), $c=8.571$ (4) Å, $\alpha=105.61$ (5), $\beta=71.41$ (3), and $\gamma=101.60$ (3)°. The structure was solved from three-dimensional integrated precession intensity data by using Patterson methods and was refined by the least-squares method to a conventional $R=0.071$ and weighted $r=0.070$. TCNQ and phenazine are alternately stacked along the [001] direction and have their mean-plane normals inclined at about 38° with respect to the stacking axis. The average perpendicular separation between the molecular planes is 3.38 Å. Molecular geometries of TCNQ and of phenazine suggest that the constituent molecules in this compound are essentially neutral. Some quantitative aspects of intrastack packing arrangement found in several related TCNQ complexes are discussed.

Introduction

Crystal structures of (1:1) TCNQ compounds with anthracene (Williams & Wallwork, 1968), dibenzo-*p*-dioxin (Goldberg & Shmueli, 1973a) and phenazine (Goldberg & Shmueli, 1971a) have recently been determined. These three molecular compounds, and in particular the latter two, have donors of almost exactly similar shapes and of the same molecular symmetries. It is therefore hoped that the description and comparison of their crystal structures will provide suitable

material for a comparative study which may contribute to a better understanding of the importance of charge-transfer interactions in determining the packing arrangements observed in the crystal. The present status of the problem has been reviewed recently (Prout & Wright, 1968; Herbstein, 1971) and results of theoretical considerations of other π -complexes have been published (Kuroda, Amano, Ikemoto & Akamatu, 1967; Chesnut & Moseley, 1969).

This paper deals with the detailed description of the (1:1) TCNQ–phenazine crystalline complex, on