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

BY ISRAEL GOLDBERG AND URI SHMUELI

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

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 $a = 8\cdot437$ (2), $b = 7\cdot253$ (3), $c = 8\cdot571$ (4) Å, $\alpha = 105\cdot61$ (5), $\beta = 71\cdot41$ (3), and $\gamma = 101\cdot60$ (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 $R = 0\cdot071$ and weighted $r = 0\cdot070$. 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 $3\cdot38$ 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

which a preliminary report was published elsewhere (Goldberg & Shmueli, 1971a). Some results of semi-empirical calculations pertaining to interplanar separations and to modes of molecular overlap observed in these complexes are also included.

Experimental

Crystals of TCNQ were obtained through the courtesy of Professor J. Jortner. Equimolar solutions of TCNQ
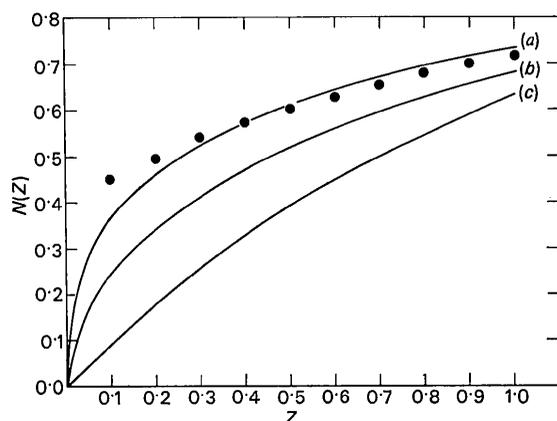

Fig. 1. Results of the $N(z)$ test; (a) bicentric, (b) centric, (c) acentric. Solid circles denote experimental distribution.

and of commercial (EGA) phenazine in acetonitrile were mixed, and deep red crystals of the complex were obtained from the hot mixture by letting it cool slowly.

Microanalysis confirmed the $1:1$ ratio of TCNQ to phenazine.

Crystal data

$(C_{12}H_8N_2)$ $(C_{12}H_4N_4)$, M.W. 384·4, m.p. 214–215 °C. Triclinic
$a = 8·437$ (2), $b = 7·253$ (3), $c = 8·571$ (4) Å
$\alpha = 105·61$ (5), $\beta = 71·41$ (3), $\gamma = 101·60$ (3)°
$V = 474·8$ Å^3
$D_m = 1·34$ g cm^{-3}, $Z = 1$, $D_c = 1·344$ g cm^{-3}
Space group $P\bar{1}$ or $P1$
μ(Mo $K\alpha$) = 0·9 cm^{-1}.

The unit-cell dimensions were obtained from their least-squares fit to 41 measurements of high-angle reflexions on Weissenberg [λ(Cu $K\alpha_1$) = 1·5405, λ(Cu $K\alpha_2$) = 1·5443 Å] and precession [λ(Mo $K\alpha$) = 0·7101 Å] photographs. Powder lines from a thin copper wire were superimposed on the Weissenberg photographs used for the determination of the cell constants. A crystal of approximate dimensions $0·15 \times 0·65 \times 0·65$ mm was selected for the collection of intensity data. The intensities were obtained by the integrated precession method, with Mo $K\alpha$ radiation, from 10 layers (h0l–
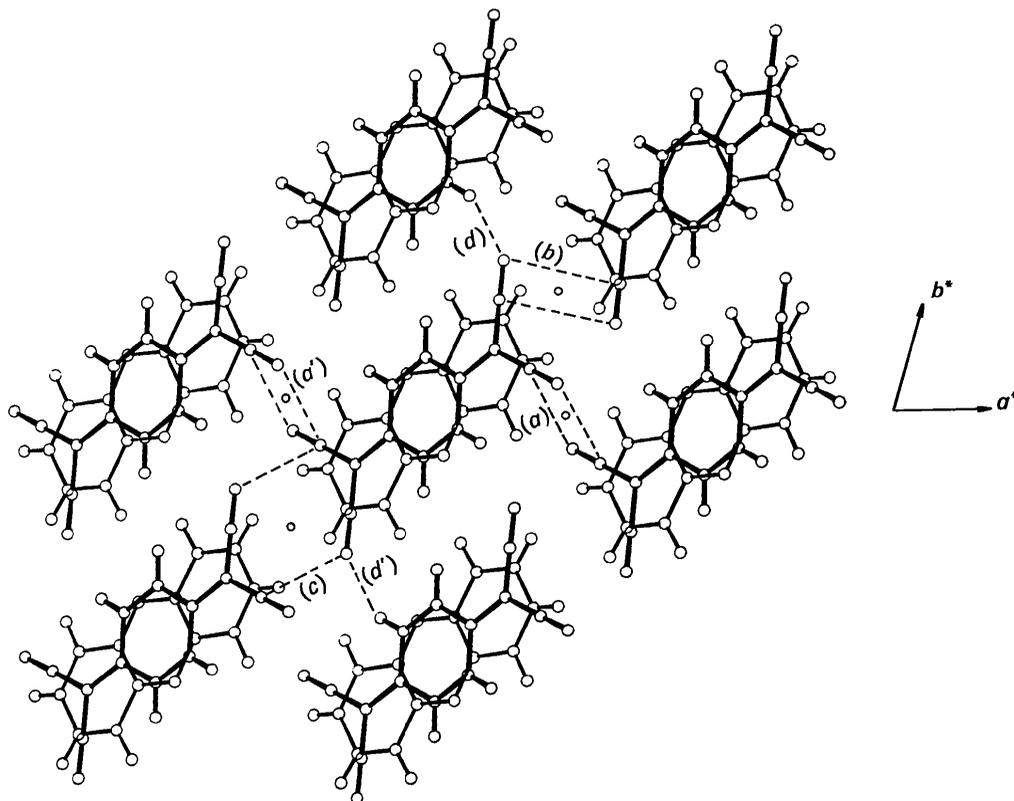

Fig. 2. Projection of the structure down the c axis. The contacts marked in the figure are explained in Table 5. The projection was drawn using the program ORTEP (Johnson, 1965).

$h4l$, $0kl-4kl$), and were measured with a Joyce–Loebl recording microdensitometer. Of the 2680 available reflexions the intensities of 1250 were too weak to be reliably estimated and were assigned the value $\frac{1}{3}I_{min}$, I_{min} being the weakest observed intensity. The processing of the data included relative weighting of the observations, application of Lorentz and polarization corrections and cross-scaling of the reflexions on different layers. 584 reflexions which appeared on more than one layer were used in the least-squares scaling procedure. Altogether, 2207 independent F_o values, including 968 unobserveds, were available for the study. Absorption corrections were not applied.

Since both TCNQ and phenazine are centrosymmetric, the assumption that the space group is $P\bar{1}$ is very plausible. This is further supported by the results of the $N(z)$ (Fig. 1) and intensity moment tests. The observed hypersymmetric intensity distribution agrees fairly well with the bicentric distribution derived by Rogers & Wilson (1952). The theoretical moments of z, based on the relevant distribution function (equation (15); Rogers & Wilson, 1953) and those based on the Wilson (1949) statistics, are compared with the experimental moments in Table 1. These results are shown here not only for giving additional support to the space group assumption but also in order to illustrate the hypersymmetry which, although harmless in the present structure, may be rather annoying in non-centrosymmetric cases (Rogers & Wilson, 1953; Goldberg & Shmueli, 1973b).

Table 1. Results of the moment test

	Experimental		Theoretical	
		$P1$	$P\bar{1}$	$P\bar{1}$ (bicentric)
$\langle z^2 \rangle$	4·49–5·27	2	3	$4\frac{1}{2}$
$\langle z^3 \rangle$	37·84–75·14	6	15	$37\frac{1}{2}$

The theoretical moments in columns 2 and 3 are based on the Wilson (1949) distribution. The moments were computed from overlapping equal groups of 100 to 200 reflexions in a $\sin^2 \theta$ range; their average values are shown in the first column. Lower and upper limits of the average experimental moment range correspond to averaging over 100 to 200 reflexion groups respectively. All 2207 independent reflexions were used.

Most of the computer programs used in this study have been described elsewhere (Goldberg & Shmueli, 1971b).

Determination and refinement of the structure

The unit-cell contents and the assumed symmetry require that both TCNQ and phenazine be located on centres of symmetry in the triclinic unit cell. Packing considerations supported by an (010) Patterson projection indicated that a probable arrangement, consistent with symmetry requirements, is a sandwich-type stacking of the molecules along the c axis. Hence, it was assumed that the molecular planes of TCNQ and of phenazine are parallel and that the same holds for the

long axes of the molecules. Comparison of the vector set based on the above model, with a sharpened three-dimensional Patterson synthesis, readily led to approximate positional parameters of all the non-hydrogen atoms in both molecules. A few cycles of an overall isotropic refinement of the trial structure so derived led to $R=0.174$ and to acceptable interatomic distances. All the observed reflexions were used in this refinement. Constant weights were used in isotropic calculations, while weights given by $w = 4w_o/F_o^2$, where w_o is an experimental weighting parameter assigned to each reflexion during the processing of the data, were employed in anisotropic refinement rounds. The parameters of each molecule were 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	R
(1)	x,y,z of non-H atoms U_{iso} (overall), scale	0·174
(2)	x,y,z, U_{iso} of non-H atoms, scale	0·139
(3)	x,y,z, U^{ij} of non-H atoms, scale	0·098
(4)	x,y z of all the atoms U^{ij} of non-H atoms, scale	0·077
(5)*	x,y,z of all the atoms U^{ij} of non-H atoms, U_{iso} of hydrogens, scale	0·071

* The $10\bar{2}$ reflexion, which was probably affected by extinction, was excluded at this stage.

Hydrogen atoms were inserted at chemically reasonable positions and were introduced, with free atom scattering factors (*International Tables for X-ray Crystallography*, 1962), into the refinement. During stage (4) the isotropic vibration parameters of the hydrogen atoms were kept fixed at $u_H = 0.05$ Å^2. In the final cycle of refinement of all the atomic parameters, the free-atom scattering factors of the hydrogens were replaced by those taken from the f curve of Stewart, Davidson & Simpson (1965).
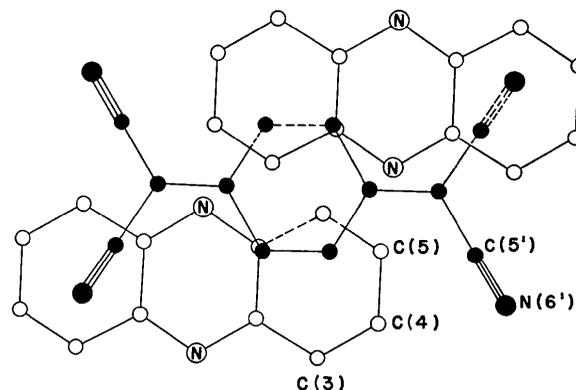

Fig. 3. Molecular overlap. The molecules are projected onto the best plane through phenazine.

The final discrepancy indices are $R=0.071$ and r(weighted)$=0.070$. The final value of $[\sum w\Delta^2/(n-m)]^{1/2}$ is 1.36 for $n=1238$ and $m=160$.

The scattering factors for carbon and nitrogen were taken from Hanson, Herman, Lea & Skillman (1964).

A list of observed and calculated structure amplitudes can be obtained from the authors upon request. The atomic positional and thermal parameters, output from the last cycle, are presented in Tables 3 and 4 respectively, together with their estimated standard deviations.

Crystal structure

A projection of the structure down the [001] direction, to which the axes of the stacks formed by TCNQ and phenazine molecules are parallel, is shown in Fig. 2. The mean molecular planes of unlike molecules in the stack are very nearly parallel and the long axes of phenazine and of TCNQ also have the same orientation. The mean planes of adjacent molecules are separated by an average distance of 3.38 Å, which is shorter than that observed in the TCNQ–dibenzo-p-dioxin complex (3.46 Å; Goldberg & Shmueli, 1973a) but which lies well within the range observed for a variety of π molecular compounds. Fig. 3 shows the

Table 3. *Atomic fractional coordinates*

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

	x	y	z
Phenazine			
N(1)	−0·0598 (3)	0·1610 (4)	−0·0187 (3)
C(2)	0·0742 (4)	0·1823 (5)	0·0389 (3)
C(3)	0·1601 (5)	0·3706 (6)	0·0817 (4)
C(4)	0·2969 (5)	0·3941 (8)	0·1403 (5)
C(5)	0·3575 (5)	0·2345 (8)	0·1558 (4)
C(6)	0·2804 (4)	0·0537 (7)	0·1153 (4)
C(7)	0·1360 (4)	0·0210 (6)	0·0559 (3)
H(3)	0·108 (5)	0·485 (6)	0·072 (4)
H(4)	0·361 (5)	0·516 (6)	0·170 (5)
H(5)	0·447 (5)	0·245 (5)	0·192 (4)
H(6)	0·324 (4)	−0·066 (5)	0·125 (4)
TCNQ			
C(1′)	0·0113 (4)	0·1991 (5)	0·5160 (4)
C(2′)	0·1315 (4)	0·1230 (5)	0·5592 (3)
C(3′)	0·1137 (4)	−0·0832 (5)	0·5401 (4)
C(4′)	0·2593 (4)	0·2424 (4)	0·6140 (3)
C(5′)	0·2840 (4)	0·4443 (6)	0·6236 (4)
N(6′)	0·3057 (4)	0·6062 (5)	0·6301 (4)
C(7′)	0·3819 (4)	0·1721 (5)	0·6632 (3)
N(8′)	0·4779 (4)	0·1174 (4)	0·7039 (3)
H(1′)	0·018 (5)	0·341 (6)	0·533 (4)
H(3′)	0·193 (4)	−0·134 (4)	0·566 (3)

Table 5. *Some interstack close approaches*

			Coordinates* of the second atom		Contact marks in Fig. 2
N(6′)····C(3′)	3·39 Å	x,	$y+1$,	z	–
N(6′)····H(3′)	2·53	x,	$y+1$,	z	d
N(14′)···H(11′)	2·53	x,	$y-1$,	z	d'
N(8′)····C(15′)	3·28	$x+1$,	y,	z	a
N(16′)···C(7′)	3·28	$x-1$,	y,	z	a'
N(6′)····C(13′)	3·48	$x+1$,	$y+1$,	z	b
N(14′)···C(7′)	3·48	$x-1$,	$y-1$,	z	c
C(3′)····N(16′)	3·43	$x+1$,	y,	z	–
C(6′)····N(16′)	3·48	$x+1$,	y,	z	–
N(8′)····C(13′)	3·49	$x+1$,	y,	$z+1$	–
N(8′)····H(13′)	2·67	$x+1$,	y,	$z+1$	–

* Coordinates pertain to an enlarged asymmetric unit which comprises the whole unit of the complex. The numbering of atoms is that used in Fig. 4. The centres of TCNQ and of phenazine are located at $(0,0,\frac{1}{2})$ and $(0,0,0)$ respectively.

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 of the form:

$$\exp\left[-2\pi^2(h_i a^i)(h_j a^j)U^{ij}\right]$$

where h_i and a^i, $i=1,2,3$, are reflexion indices and reciprocal unit-cell edges respectively.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
Phenazine						
N(1)	424 (16)	547 (20)	426 (13)	111 (15)	93 (12)	−126 (12)
C(2)	341 (18)	556 (23)	365 (15)	96 (18)	88 (14)	−122 (13)
C(3)	567 (25)	525 (27)	554 (21)	84 (22)	43 (17)	−151 (18)
C(4)	540 (28)	817 (34)	636 (23)	−82 (27)	−6 (21)	−234 (20)
C(5)	386 (24)	1094 (42)	576 (22)	39 (27)	63 (23)	−270 (19)
C(6)	424 (22)	775 (30)	481 (19)	143 (22)	106 (18)	−192 (16)
C(7)	304 (17)	626 (23)	346 (15)	136 (18)	112 (13)	−130 (13)
TCNQ						
C(1′)	338 (18)	342 (20)	560 (18)	31 (17)	127 (14)	−183 (15)
C(2′)	335 (18)	384 (20)	383 (14)	69 (17)	116 (12)	−89 (13)
C(3′)	396 (20)	432 (23)	502 (18)	102 (18)	145 (14)	−164 (16)
C(4′)	365 (19)	350 (19)	384 (15)	70 (16)	96 (13)	−100 (14)
C(5′)	448 (22)	474 (25)	618 (20)	−21 (19)	135 (17)	−223 (16)
N(6′)	690 (24)	501 (21)	1096 (24)	3 (19)	170 (18)	−459 (20)
C(7′)	350 (18)	364 (19)	431 (16)	38 (16)	101 (13)	−129 (14)
N(8′)	473 (18)	642 (21)	640 (17)	143 (16)	151 (14)	−241 (14)

Isotropic vibration parameters of the hydrogen atoms

H(3)	5·7 (1·0)	H(5)	4·4 (0·8)	H(1′)	5·8 (0·9)
H(4)	7·5 (1·1)	H(6)	4·6 (0·8)	H(3′)	2·8 (0·7)

Table 6. *Results of rigid-body motion analysis*

All the tensors in this Table 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) Phenazine

Tensor of inertia:

Eigenvalues			Eigenvectors*		
200 (at.wt. $-$ Å^2)	l	6·436	2·839	3·700	
939	m	4·713	$-6·667$	3·771	
1139	n	2·746	0·309	$-6·750$	

Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)

Tensor	11	12	13	22	23	33
L(rad^2)	469 (13)	37 (20)	41 (38)	237 (20)	43 (17)	494 (17)
T (Å^2)	3930 (93)	-1398 (91)	278 (107)	3868 (130)	-183 (131)	3178 (232)

	R.m.s. amplitudes		Principal axes†		
	4·2°	l_1	$-0·5910$	$-0·1858$	$-0·7850$
L	3·8	l_2	$-0·7964$	$-0·0205$	0·6045
	2·7	l_3	$-0·1284$	0·9824	$-0·1359$
	0·23 Å	t_1	0·7092	$-0·6891$	0·1491
T	0·18	t_2	0·0369	$-0·1750$	$-0·9839$
	0·16	t_3	0·7041	0·7032	$-0·0987$

R.m.s. discrepancy 0·0035 Å

(b) TCNQ

Tensor of inertia:

Eigenvalues			Eigenvectors		
409 (at.wt. $-$ Å^2)	l	6·554	2·720	3·686	
1832	m	4·513	$-6·723$	3·905	
2240	n	2·804	0·074	$-6·680$	

Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)

Tensor	11	12	13	22	23	33
L(rad^2)	1098 (74)	126 (9)	5 (17)	8 (19)	18 (11)	112 (11)
T (Å^2)	3902 (92)	-327 (90)	-283 (95)	2936 (127)	66 (130)	3612 (150)

	R.m.s. amplitudes		Principal axes†		
	6·0°	l_1	$-0·9935$	$-0·1137$	$-0·0066$
L	1·9	l_2	$-0·0224$	0·1389	0·9901
	0·0	l_3	$-0·1116$	0·9838	$-0·1406$
	0·20 Å	t_1	$-0·8460$	0·2521	0·4698
T	0·19	t_2	$-0·4410$	0·1643	$-0·8823$
	0·17	t_3	$-0·2996$	$-0·9536$	$-0·0278$

R.m.s. discrepancy 0·0040 Å^2

(c) TCNQ, quinonoid part only

Tensor of inertia:

Eigenvalues			Eigenvectors*		
73 (at.wt. $-$ Å^2)	l	6·501	2·765	3·711	
255	m	4·675	$-6·694$	3·643	
328	n	2·658	0·381	$-6·813$	

Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)

Tensor	11	12	13	22	23	33
L(rad^2)	1079 (156)	151 (68)	127 (84)	22 (39)	12 (26)	14 (25)
T (Å^2)	3865 (83)	-316 (80)	-205 (102)	3120 (104)	43 (106)	3606 (222)

	R.m.s. amplitudes		Principal axes†		
	6·0°	l_1	0·9838	0·1372	0·1154
L	0·2	l_2	0·0278	$-0·7528$	0·6576
	0·0	l_3	0·1771	$-0·6438$	$-0·7445$
	0·20 Å	t_1	$-0·8615$	0·3039	0·4067
T	0·19	t_2	$-0·3635$	0·1903	$-0·9120$
	0·17	t_3	$-0·3545$	$-0·9335$	$-0·0535$

R.m.s. discrepancy 0·0030 Å^2

* Referred to the reciprocal base vectors a*, b*, and c*.
† Referred to the unit vectors l, m, n.

molecular overlap in this complex to be strikingly different from the nearly complete and complete donor–acceptor superpositions found in TCNQ–dibenzo-*p*-dioxin (Goldberg & Shmueli, 1973*a*) and in TCNQ–anthracene (Williams & Wallwork, 1968) complexes respectively. These overlap modes will be discussed below in some detail. There are a considerable number of close approaches involving like and unlike molecules in different stacks. These are shown in Table 5. Of some interest is the extensive network of interstack close approaches between cyano groups (Fig. 2) which indicate that dipole–dipole interactions may be of importance in stabilizing the observed packing arrangement.

Thermal motion

The average molecular motion indicated for TCNQ and for phenazine is relatively limited, when compared with the motion indicated for TCNQ and in particular for the donors in some related structures (Goldberg & Shmueli, 1973*a*).

Rigid-body motion analyses were carried out for TCNQ and for phenazine by the method of Cruickshank (1956). Some results of these calculations are presented in Table 6.

The fit of phenazine to the rigid-body model is fairly good in view of the r.m.s. discrepancy, $\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.0052$ Å^2, between the experimental and calculated

Table 7. *Best planes*

(*a*) Deviations (Å × 10^3) of the TCNQ atoms from the best plane of the quinonoid group.

C(1')	C(2')	C(3')	C(4')	C(5')	N(6')	C*(7')	N*(8')
−3	−7	−3	5	83	159	−32	−75

(*b*) Equations of best planes.

$-2.656x - 0.383y + 6.814z = 3.407$ Å	quinonoid group
$-2.745x - 0.310y + 6.751z = 0$	phenazine

where x, y, z are fractional coordinates of a point in the plane and the right hand side is the distance of the plane from the unit-cell origin.

* Approaching the peripheral ring of phenazine overlapped by these atoms.

Table 8. *Bond distances*

	Distance (Å)			Distance (Å)	
	Uncorr.	Corr.		Uncorr.	Corr.
Phenazine			TCNQ		
N(1)–C(2)	1·338 (5)	1·343	C(1')–C(2')	1·430 (5)	1·435
C(2)–C(3)	1·423 (5)	1·429	C(2')–C(3')	1·442 (5)	1·449
C(2)–C(7)	1·431 (5)	1·438	C(2')–C(4')	1·364 (4)	1·365
C(3)–C(4)	1·363 (6)	1·369	C(4')–C(5')	1·420 (5)	1·431*
C(4)–C(5)	1·408 (8)	1·415	C(4')–C(7')	1·454 (5)	1·455*
C(5)–C(6)	1·349 (6)	1·355	C(1')–C(11')	1·340 (4)	1·341
C(6)–C(7)	1·419 (5)	1·424	C(5')–N(6')	1·140 (5)	1·172*
C(7)–N(8)	1·349 (4)	1·355	C(7')–N(8')	1·149 (5)	1·175*
C(3)–H(3)	1·04 (5)		C(1')–H(1')	0·99 (4)	
C(4)–H(4)	0·95 (4)		C(6')–H(3')	0·93 (4)	
C(5)–H(5)	0·89 (4)				
C(6)–H(6)	1·04 (4)				

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

Table 9. *Comparison of bond distances observed in TCNQ and in several mixed-stack complexes with theoretically predicted values*

The numbering of the atoms refers to Fig. 4. Unless otherwise specified, bond distances are corrected for libration.

	C(1')–C(11')	C(1')–C(2') (average)	C(2')–C(4')	Reference
TCNQ	1·346 Å	1·488 Å	1·347 Å	Long, Sparks & Trueblood (1965)
TCNQ–anthracene	1·35	1·46	1·37	Williams & Wallwork (1968)
TCNQ–hexamethyl-benzene*	1·358	1·462	1·391	Colton & Henn (1970)
TCNQ–phenazine	1·341	1·442	1·365	Present paper
TCNQ–dibenzo-*p*-dioxin	1·346	1·436	1·363	Goldberg & Shmueli (1973*a*)
Average	1·348	1·450	1·372	
Theoretical	1·356	1·453	1·371	Lowitz (1967)
	1·350	1·457	1·361	Jonkman & Kommandeur (1972)

* Uncorrected.

thermal parameters. The librational motion of phena-
zine is appreciable about its long axis and the plane-
normal and is smaller about the N---N line, possibly
owing to the inhibition of the latter type of motion by
short contacts between stacked molecules.

The thermal parameters of the heavy atoms of
TCNQ can also be explained in terms of rigid-body ten-
sors. Separate calculations were made for the whole
molecule [$\langle(\Delta U_{ij})^2\rangle^{1/2}=0\cdot0040$ Å^2] and for the central
eight-atom portion [$\langle(\Delta U_{ij})^2\rangle^{1/2}=0\cdot0030$ Å^2]. The re-
sults indicate, as is usually observed, the partial non-
rigidity of the cyano groups of TCNQ. The transla-
tional motion is nearly isotropic, the directions of the
principal axes being only slightly affected by consider-
ing the quinonoid part rather than the whole molecule.
The librational motion of TCNQ appears to be con-
fined to the long molecular axis with which a large
amplitude (6·0°) of libration is associated. The very
small amplitude of motion about l_2 (Table 6) and the
zero amplitude of libration about the short molecular

axis appear to be, at first sight, rather meaningless.
However, a careful consideration of the molecular ar-
rangement leads to a qualitative conclusion that the
motion about these two directions should, in fact, be
very limited. This is also supported by intermolecular
potential calculations now in progress at this lab-
oratory.

Examination of the thermal parameters of TCNQ
shows that the out-of-plane vibration amplitude of
N(8'), which overlaps the peripheral ring of phenazine,
is considerably smaller than the corresponding vibra-
tion of the 'free' TCNQ nitrogen, N(6') (Fig. 3).

Molecular geometry

The phenazine molecule is essentially planar, the maxi-
mal deviation, of a non-hydrogen atom from its best
plane being 0·012 Å. In TCNQ, the above is true for
the quinonoid part, while the cyano groups deviate in
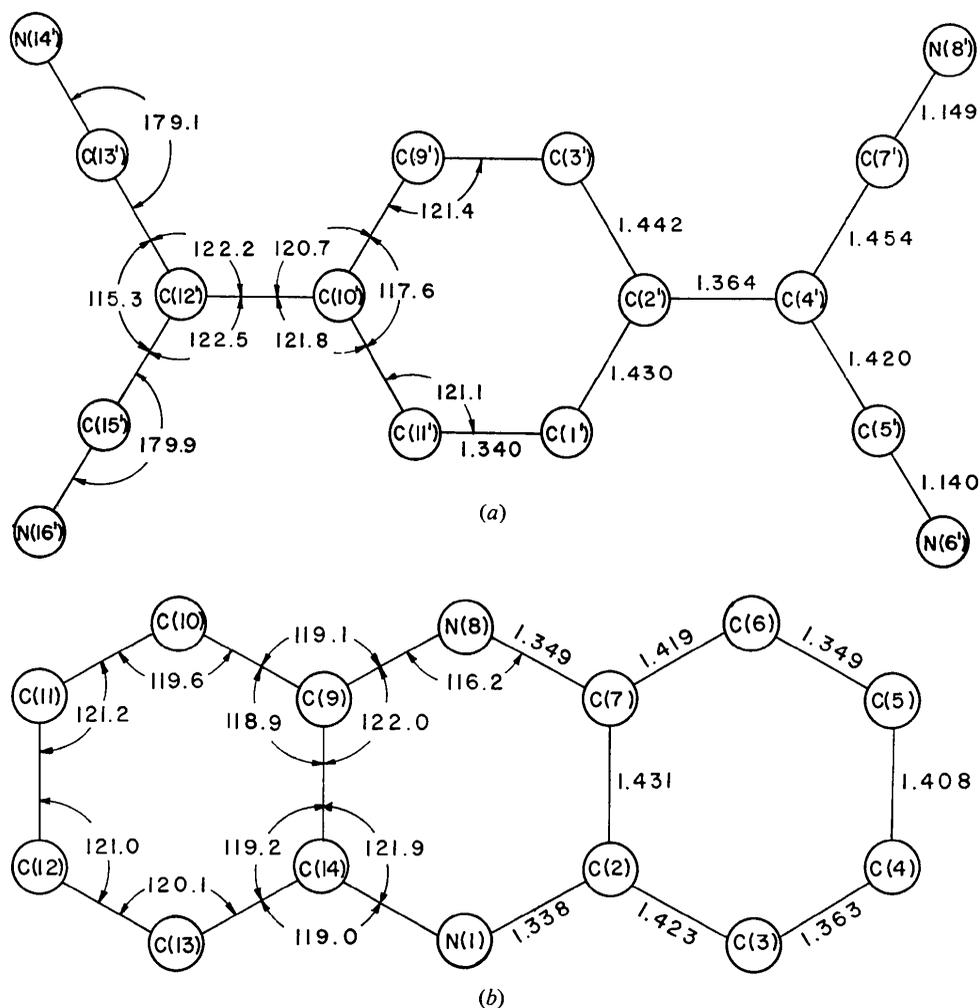opposite directions from the quinonoid best plane. The

Fig. 4. Molecular geometry of (a) TCNQ and (b) phenazine. The bond distances (Å) and bond angles shown are uncorrected
for libration.

smaller deviation pertains to the cyano group C(7')–N(8'), which overlaps a peripheral ring of phenazine (Table 7) and is slightly but significantly bent towards this ring.

The molecular geometry of the two constituents of the complex is shown in Table 8 and in Fig. 4.

Bond distances in the quinonoid part of TCNQ are close to those found in the TCNQ–dibenzo-*p*-dioxin (Goldberg & Shmueli, 1973*a*) and in the structure of TCNQ (Long, Sparks & Trueblood, 1965). Table 9 shows the bond distances for several TCNQ compounds, together with those theoretically predicted for the neutral TCNQ species. The cyano groups are excluded from this comparison, since their dimensions appear to be somewhat less reliable owing to their well documented independent motion. Except for the somewhat longer quinonoid bond found in the TCNQ–hexamethylbenzene complex, the observed and predicted (Lowitz, 1967; Jonkman & Kommandeur, 1972) bond distances of the quinonoid group agree rather well within the listed compounds.

The reliability of the libration corrections of the bond distances in TCNQ (Table 8) is difficult to assess because of the possible inaccuracy in the rigid-body motion analysis.

The phenazine molecule has an approximate *mm* symmetry, as the discrepancy in any pair of chemically equivalent bond distances does not exceed 1.5σ, σ being the standard deviation of the difference between these bond lengths. Molecular dimensions of phenazine, in the present compound, are very close to those observed in the uncomplexed molecule (Herbstein & Schmidt, 1955). The geometries of benzene rings in phenazine (present paper), phenazine (Herbstein & Schmidt,

1955), *N*-methylphenazinium (Fritchie, 1966) and *N,N'*-dimethyldihydrophenazine (Goldberg & Shmueli, 1973*b*) are quite similar. The dimensions of the central ring, on the other hand, appear to depend on the state of hybridization of the nitrogen atom. Thus, average uncorrected C–N bond distances are 1·344 Å in phenazine, 1·345 Å in phenazine crystal (Herbstein & Schmidt, 1955), 1·361 Å in the orientationally disordered *N*-methylphenazinium (Fritchie, 1966) and 1·386 Å in *N,N'*-dimethyldihydrophenazine (Goldberg & Shmueli, 1973*b*).

Discussion

The mixed stacks present in the structures of TCNQ–phenazine (I), TCNQ–dibenzo-*p*-dioxin (II) (Goldberg & Shmueli, 1973*a*) and TCNQ–anthracene (III) (Williams & Wallwork, 1968) differ in several respects. The differences between the three structures, reflected in the unlike environments of the stacks and in the observed patterns of thermal motion, were discussed in part II of this series (Goldberg & Shmueli, 1973*a*). In the present discussion, some intrastack structural features will be considered. Common to I, II and III is the face-to-face stacking mode frequently observed in π-molecular compounds. Structurally, they differ in the repeating distance along the stack and in the interplanar spacings and hence in the molecular overlapping modes of the constituent molecules, as shown below:

	I	II	III
Repeating distance	8·57 Å	7·04 Å	7·00 Å
Interplanar spacing	3·38	3·46	3·50
Offset along l	1·85	0·51	~0
Offset along m	1·89	0·48	~0

where the centre of the donor is offset from above the centre of the acceptor in the directions of the long (l) and short (m) axes of the acceptor.

According to Briegleb (1964) the charge-transfer energy is an approximately linear function of the difference ΔE between the ionization potential of the donor and the electron affinity of the acceptor for a series of complexes having the same acceptor. As shown by Wallwork (1961), a similarly regular dependence of the interplanar separation on measured ionization potentials of some donors exists in *s*-trinitrobenzene and chloranil complexes, indicating that compounds with higher charge-transfer energies have smaller intermolecular separations. In order to get an idea of how this correlation applies to mixed-stack TCNQ complexes an all valence electron calculation, employing Slater-type orbitals in an iterative extended Hückel procedure (Rein, Clarke & Harris, 1970), was performed for TCNQ and for a series of donors, most of which belong to known TCNQ complexes. The donor ionization potential and the electron affinity of the acceptor were replaced by the calculated energies of the highest occupied donor and lowest unoccupied acceptor molecular orbitals respectively. Fig. 5 shows
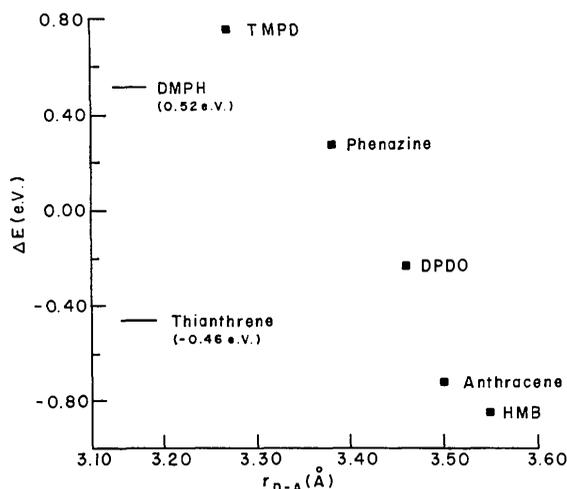

Fig. 5. Dependence of ΔE (see text) on the donor–acceptor interplanar distance r_{D-A}, for a series of donors which form mixed-stack complexes with TCNQ. The r_{D-A} values are taken from the relevant papers. Abbreviations: TMPD, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; DMPH, *N,N'*-dimethyldihydrophenazine, DPDO, diphenylene dioxide (or dibenzo-*p*-dioxin); HMB, hexamethylbenzene.

the dependence of ΔE on the perpendicular donor–acceptor separations, observed in the corresponding structures. It must be pointed out that the values of ΔE for particular donors may be somewhat inaccurate since the iteration on charge in an extended Hückel-type calculation does not affect properly the energies of the empty orbitals. This expected discrepancy in the calculation is probably reflected in the slightly positive ΔE for phenazine whereas the TCNQ–phenazine complex probably has a mainly no-bond ground state.

It is seen from Fig. 5 that a regular and roughly linear behaviour of ΔE is found in the range of observed interplanar separations. The ΔE values for DMPH and for thianthrene are marked separately since in neither case is it possible to define the interplanar separation as both molecules are folded. Whereas rather short ($< 3\cdot3$ Å) distances were observed between stacked DMPH and TCNQ (Goldberg & Shmueli, 1973b) the TCNQ complex with thianthrene has not been reported to exist in the solid.

Calculations of the orbital overlap, employing coefficients of the highest occupied orbitals of the donors and those of the lowest vacant orbital of the acceptor, show that the observed structures of I, II and III correspond fairly closely to the positions of maximum orbital overlap. This is in accord with Mulliken's overlap and orientation principle (Mulliken, 1956) insofar as the long molecular axes are kept parallel and the observed interplanar distances are maintained constant. A detailed description of the calculations and of the results will be presented elsewhere (Goldberg & Shmueli, 1973c).

In the present as well as in other attempts at rationalizing the observed structures of molecular complexes (e.g. Kuroda, Amano, Ikemoto & Akamatu, 1967; Chesnut & Moseley, 1969) many factors determining the lattice energy are left out from the calculation and yet the agreement between predicted and observed structures is usually encouraging. It appears that the question why approximate methods sometimes work so well is a difficult one to answer (Löwdin, 1968). However, in view of the fact that anthracene, dibenzo-p-dioxin and phenazine (in particular the latter two) have very similar shapes although different packing arrangements are observed for their TCNQ complexes, it is possible that charge-transfer interactions are of major importance in the formation of the relevant structures.

Calculations were performed on the CDC 6600 computer at the Tel-Aviv University Computation Centre.

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