

Structure and Packing Arrangement of Molecular Compounds. VII.* 7,7,8,8-Tetracyanoquinodimethane–Naphthalene (1:1)†

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Crystals of the (1:1) 7,7,8,8-tetracyanoquinodimethane–naphthalene compound are triclinic, with one unit of the complex in a unit cell of dimensions $a = 8.216(1)$, $b = 7.807(1)$, $c = 7.873(1)$ Å and $\alpha = 120.34(1)$, $\beta = 92.22(1)$, $\gamma = 96.63(1)^\circ$. The structure was solved from three-dimensional precession diffractometer data, with Patterson methods, and was refined to a conventional $R = 0.062$ and weighted $r = 0.038$. TCNQ and naphthalene are alternately stacked along the [001] direction; however, their best planes deviate very significantly from the parallel arrangement so frequently observed in (1:1) compounds consisting of planar molecules and forming mixed stacks. The molecular geometries of TCNQ and naphthalene agree very well with those observed in the uncomplexed molecules. Both molecules are well ordered and the observed packing arrangement appears to be conditioned mainly by van der Waals and dipole–dipole interactions. Calculated energy profiles indicate that the observed librational motion of the molecules reflects usual packing restrictions.

Introduction

The present study of a crystalline charge-transfer complex formed by 7,7,8,8-tetracyanoquinodimethane (TCNQ) and naphthalene is part of a programme pursued in this laboratory which aims at contributing to the understanding of the various interactions stabilizing such complexes and determining their dynamics (e.g. Goldberg & Shmueli, 1973*a,b*; Shmueli & Goldberg, 1973; Goldberg, 1975).

Naphthalene, as a donor, was thought to be interesting for several reasons. This molecule is one of the most extensively studied aromatics and is part of several molecular compounds, the structures of which have been published (with pyromellitic dianhydride: Boeyens & Herbstein, 1965; with tetracyanoethylene: Williams & Wallwork, 1968; with tetracyanobenzene: Kumakura, Iwasaki & Saito, 1967). In all the examples referred to, naphthalene was found to be disordered and no accurate information on the structure of naphthalene in a solid charge-transfer compound has so far been available. Furthermore, naphthalene is smaller than the donors to TCNQ previously investigated (in crystalline donor–acceptor complexes) and thus a TCNQ–naphthalene compound may lend itself more readily to an interpretation of its electronic and dynamic properties.

The purpose of the present paper is to describe the crystal and molecular structure of a TCNQ–naphtha-

lene compound, as determined from data which were collected by a novel counting technique, precession diffractometry.

Experimental

Dark-violet crystals of the complex were prepared by slow evaporation of a mixture of equimolar solutions of (commercial) TCNQ and naphthalene in acetonitrile. A major difficulty, during the initial stages of the work, was a tendency of the crystals to deteriorate when exposed to room atmosphere for several days. This deterioration, which manifested itself by the formation of a yellow deposit on the surface of the crystal, did not occur when crystals were kept in a refrigerator or in a sealed glass capillary. Difficulties in obtaining stable specimens of this complex were also reported by Tickle & Prout (1973).

The density of the crystals was measured by flotation, with freshly prepared specimens. Unit-cell dimensions were determined first with the aid of Weissenberg and precession photographs and subsequently (and more accurately) from diffractometer measurements. They were also rechecked in detail after the data collection was completed and no significant changes were noted. The unit-cell dimensions shown below were derived from counter data.

Crystal data

(C₁₀H₈)(C₁₂H₄N₄), M.W. 332.3; triclinic, $a = 8.216(1)$, $b = 7.807(1)$, $c = 7.873(1)$ Å; $\alpha = 120.34(1)$, $\beta = 92.22(1)$, $\gamma = 96.63(1)^\circ$; $V = 430.2$ Å³; $D_m = 1.28$, $Z = 1$, $D_c = 1.282$ g cm⁻³; space group $P\bar{1}$ or $P1$; $\mu(\text{Mo } K\alpha) = 0.8$ cm⁻¹.

Intensity data were collected with the aid of a computer-controlled precession diffractometer sup-

* Part VI: Goldberg (1975).

† A preliminary report on this work was presented at the annual meeting of the Israel Crystallography Society, Haifa, 11 May 1975.

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plied by Yeda Ltd (Israel). The operation of this instrument, developed by one of us (D. R.), can be qualitatively understood in terms of the cone-axis method (Buerger, 1964) where the diffracted beams are recorded by a scintillation counter rather than by a photographic film. The instrument is set for recording a given diffracted beam by first orienting the Laue cone to which this beam belongs (usual precession motion) and then by bringing the counter to an appropriate azimuthal orientation on the cone-axis circle examined. Intensity measurements can be made for each of the two possible orientations of the Laue cone (Buerger, 1964) for each reflexion. A detailed description of the instrument will be published elsewhere (Rabinovich, 1976) along with an outline of the computer programs for the least-squares fit of cell parameters, calculation of angular settings and intensity data reduction to structure amplitudes.

A crystal of approximate dimensions $0.5 \times 0.4 \times 0.25$ mm was sealed in a thin-walled glass capillary and was used in intensity data collection. 6576 intensities were measured* with graphite-monochromatized Mo $K\alpha$ radiation and were converted to structure amplitudes by Lorentz and polarization corrections. The intensity record comprises sixteen layers made up of four sets of four layers (0th, 1st, 2nd and 3rd layers) perpendicular to the [100], [010], [110] and $[\bar{1}\bar{1}0]$ directions. No absorption or extinction corrections were applied. The Lorentz factors are the same as those given by Buerger (1964) for a single encounter of a reciprocal lattice point with the sphere of reflexion during a precession motion. Polarization corrections for unpolarized radiation were employed.†

The standard deviation of the net intensity I , in counts per second, was calculated as $\sigma(I) = [I_p + (B_r + B_l)(t_p/t_b)^2 + (0.03 I_p)^2]^{1/2}$, where I_p , B_r , B_l and t_p/t_b are peak count, right background count, left background count and the ratio of peak to (total) background scanning times respectively.

The observations were averaged over experimentally equivalent and symmetry-equivalent reflexions and were brought to a common scale with the aid of a least-squares procedure, using 1294 reflexions which appeared in more than one layer. Altogether 1881 independent reflexions, including 173 reflexions of which the net intensity was negative and which were excluded from the calculation, were available for study. The averaged data set comprises 95% of possible independent reflexions within the copper sphere.

Most computer programs used in the determination, refinement and description of the structure have

* Each reflexion was measured twice, for the two possible orientations of the Laue cone.

† Test calculations using Azaroff's formula (1955) for the polarization correction of monochromatized diffracted intensity, which was in the meantime adapted to the geometry of the precession diffractometer, showed deviations amounting to a few tenths of a percent of F_o in the angular range and for the wavelength employed.

been mentioned elsewhere (Goldberg & Shmueli, 1971).

Determination and refinement of the structure

Since both TCNQ and naphthalene are centrosymmetric molecules and there is one unit of the complex in the unit cell, the assumption of $P\bar{1}$ seemed plausible. This assumption was further supported by the results of an $N(z)$ test (Howells, Phillips & Rogers, 1950) and by the distribution of normalized structure amplitudes and their functions.

The structure was determined with the aid of a three-dimensional Patterson synthesis and projections of the Patterson function on the (100), (010) and (001) planes. The projections indicated that the orientations of the molecular planes are roughly similar and, accordingly, a model of parallel TCNQ and naphthalene molecules was fitted to the three-dimensional map. The best fit was obtained for a vector set corresponding to donor and acceptor having their long axes inclined at about 30° to each other and approximately parallel plane normals. Naphthalene and TCNQ were inserted with their centres at $(0,0,0)$ and $(0,0,\frac{1}{2})$ respectively. This trial structure led to a rather high R value, $R=0.55$, which decreased slowly but steadily down to $R=0.16$ in 12 cycles of overall isotropic refinement, based on 450 reflexions with $\sin \theta/\lambda \leq 0.4$. It is probable, in retrospect, that the unexpected non-parallel arrangement of the plane normals of TCNQ and naphthalene was responsible for the poorly convergent initial refinement. Full-matrix refinement of the positional and individual isotropic thermal parameters of the heavy atoms reduced the discrepancy index to $R=0.128$. Anisotropic refinement of the heavy-atom coordinates and vibration tensors, resulted in $R=0.098$ while the addition of hydrogen atoms, with adjustable coordinates and isotropic thermal parameters led to the final discrepancy index $R=0.062$. During the last two stages of the refinement, the parameters of each molecule were kept in a separate block of the matrix of normal equations. The initial positions of the hydrogens were deduced from chemical considerations. The weights were taken as $w = (aK^2 + bF_o^2/4w_o)^{-1}$, where K is the scale factor and w_o is an experimental weighting parameter, defined as $w_o(I) = I^2/\sigma^2(I) = F_o^4/\sigma^2(F_o^2)$, assigned to each reflexion during the processing of the data. The values of the constants were $a=1$ and $b=0$ in isotropic refinement rounds and $a=0$ and $b=1$ in all subsequent calculations.

The final discrepancy indices, $R = \sum |F_o - K|F_c| / \sum F_o$ and $r = [\sum w(F_o - K|F_c|)^2 / \sum wF_o^2]^{1/2}$, are $R=0.062$ and $r=0.038$ for 1700 observed reflexions. The final value of $[\sum w(F_o - KF_c)^2 / (n-m)]^{1/2}$, with $n=1700$ and $m=142$, is 1.67.

Eight strong reflexions (with indices: 102, 110, 002 012, 211, 031, 100 and 111) which were probably affected by extinction were excluded from the calculations during the intermediate and final stages.

Atomic scattering factor tables were taken from Hanson, Herman, Lea & Skillman (1964) for carbon and nitrogen and from Stewart, Davidson & Simpson (1965) for hydrogen atoms.

The final positional and thermal parameters of naphthalene and TCNQ, together with their estimated standard deviations, are presented in Table 1.*

Packing arrangement

Naphthalene and TCNQ are situated with their molecular centres of symmetry on crystallographic centres at (0, 0, 0) and (0, 0, $\frac{1}{2}$) respectively, thus forming stacks in which the constituent molecules are alternating along the *c* axis. A projection of the structure down the *c* axis is shown in Fig. 1. It is interesting to note that the cyano groups of TCNQ are arranged in nearly exactly planar layers, parallel to the *bc* plane, and that each group is surrounded within the layer by antiparallel neighbours. A projection of such a layer, on a plane perpendicular to the *a* axis, is shown in Fig. 2. The closely spaced dipoles in the (011) planes are indicative of the significance of dipole-dipole interaction in this structure. This favourable packing arrangement of the C–N dipoles of TCNQ is not usually achieved because of the sizeable donors so far studied (*cf.* TCNQ–phenazine, Goldberg & Shmueli,

1973*b*). It is also seen from Fig. 1 that the long axes of the constituent molecules form an angle of about 15°, in projection. As shown below, the non-parallel arrangement of the molecular axial systems is in fact complete. Another view of the structure is displayed in Fig. 3, which shows a parallel projection of three stacks viewed along the short axis of a naphthalene molecule. This view again confirms the non-parallel arrangement of the molecular systems and shows that naphthalene's nearest neighbours in adjacent stacks are the bulkier TCNQ molecules. The intermolecular

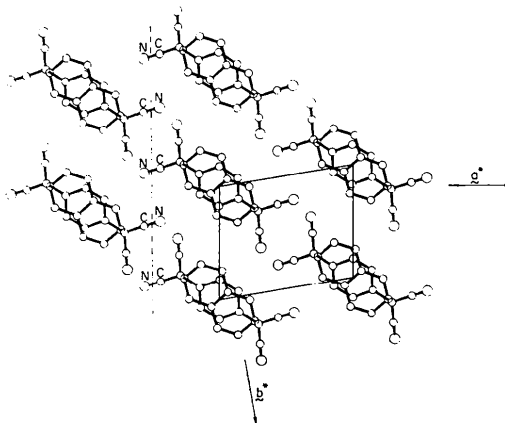


Fig. 1. Projection of the structure along the *c* axis. The dashed line passing through the C≡N groups corresponds to the layer of dipoles, illustrated in Fig. 2.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31674 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positional and thermal parameters

The fractional coordinates of heavy atoms were multiplied by 10^4 and those of hydrogens by 10^3 . The estimated standard deviations are given in parentheses in units of the last decimal place for all the parameters. The anisotropic temperature factor is of the form:

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

where h_i and a^i , $i=1,2,3$, are reflexion indices and reciprocal unit-cell edges respectively. The isotropic vibration parameters of the hydrogen atoms appear in the column of U^{11} . All thermal parameters are given in $\text{\AA}^2 \times 10^4$.

Naphthalene	<i>x</i>	<i>y</i>	<i>z</i>	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{31}
C(1)	2274 (3)	482 (4)	618 (2)	725 (14)	1040 (16)	672 (9)	241 (12)	470 (10)	51 (9)
C(2)	2633 (3)	2401 (4)	1021 (2)	806 (16)	1042 (18)	714 (10)	-157 (14)	401 (11)	-54 (10)
C(7)	-1379 (4)	-3398 (3)	-889 (3)	1234 (22)	739 (14)	801 (11)	11 (15)	390 (11)	127 (12)
C(8)	193 (3)	-2498 (3)	-361 (2)	1042 (18)	767 (13)	724 (9)	293 (12)	439 (9)	200 (10)
C(9)	624 (2)	-520 (2)	64 (2)	674 (11)	631 (10)	498 (6)	146 (8)	313 (6)	69 (7)
H(1)	303 (2)	-26 (2)	65 (2)	791 (55)					
H(2)	381 (3)	303 (3)	136 (2)	1139 (67)					
H(7)	-169 (3)	-479 (3)	-119 (2)	1215 (74)					
H(8)	118 (3)	-315 (3)	-26 (2)	1175 (69)					
TCNQ									
C(1')	1426 (2)	-442 (2)	5637 (2)	470 (9)	574 (9)	635 (7)	144 (7)	390 (7)	38 (7)
C(2')	1475 (2)	1373 (2)	5581 (2)	502 (9)	503 (8)	518 (6)	152 (7)	313 (6)	90 (6)
C(3')	-23 (2)	1736 (2)	4905 (2)	548 (9)	509 (8)	630 (7)	162 (7)	377 (7)	82 (6)
C(4')	2909 (2)	2722 (2)	6165 (2)	496 (9)	563 (9)	618 (7)	149 (7)	370 (7)	79 (6)
C(5')	4396 (2)	2428 (2)	6915 (2)	536 (10)	663 (10)	879 (9)	55 (8)	510 (8)	26 (8)
N(6')	5583 (2)	2234 (2)	7552 (2)	603 (10)	1081 (12)	1430 (12)	57 (9)	894 (10)	-76 (9)
C(7')	3007 (2)	4537 (2)	6115 (2)	516 (9)	586 (9)	685 (7)	104 (7)	357 (7)	46 (6)
N(8')	3106 (2)	5991 (2)	6091 (2)	810 (11)	649 (9)	1020 (9)	134 (7)	512 (7)	59 (7)
H(1')	240 (2)	-67 (2)	610 (2)	602 (40)					
H(3')	0 (2)	294 (2)	486 (2)	585 (39)					

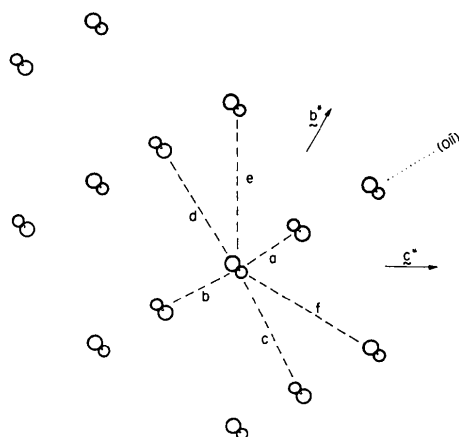


Fig. 2. Arrangement of $C\equiv N$ dipoles in the layer indicated in Fig. 1. Large and small circles denote nitrogen and carbon atoms respectively. The distances between the centres of the dipoles, indicated in the figure, are: $a=3.57$, $b=4.24$, $c=6.68$, $d=6.94$, $e=7.81$ and $f=7.87$ Å.

intrastack contact distances are appreciably longer* than those usually found in crystals of molecular compounds of the charge-transfer type.

All these features of the packing structure of the TCNQ-naphthalene molecular compound is stabilized mainly by van der Waals and dipole-dipole interactions and the role played by charge-transfer interactions in the formation of the final structure is probably minor.

Rigid-body motion

The anisotropic vibration parameters of the heavy-atom skeletons of TCNQ and naphthalene (Table 1) were analysed in terms of the rigid-body tensors of

* All the intrastack distances shorter than 3.6 Å are: $C(9)\cdots C(4')$ 3.39, $C(10)\cdots C(3')$ 3.53 and $C(2)\cdots N(8')$ 3.50 Å. There are also nine contacts, involving C and N, lying between 3.6 and 3.7 Å. Due to the non-parallel arrangement, the intrastack interplanar distance cannot be defined.

Table 2. Results of rigid-body-motion analysis

All the tensors are referred to the axial systems of the tensors of inertia defined below, \mathbf{l}_i and \mathbf{t}_i are unit vectors along the principal axes of the libration tensor \mathbf{L} and the translation tensor \mathbf{T} respectively.

(a) Naphthalene

Tensor of inertia:	Eigenvalues	Eigenvectors†
	127 (at.wt Å ²)	\mathbf{l} 4.671 5.517 -1.499
	348	\mathbf{m} 6.534 -5.395 2.615
	475	\mathbf{n} 1.732 1.193 -7.273

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

Tensor	11	12	13	22	23	33
\mathbf{L} (rad ²)	719 (215)	47 (44)	232 (79)	512 (63)	1 (47)	1198 (45)
\mathbf{T} (Å ²)	7178 (140)	170 (132)	252 (156)	5476 (186)	619 (189)	4513 (377)

R.m.s. amplitudes

Principal axes‡

\mathbf{L}	6.52°	\mathbf{l}_1	-0.37629	-0.02334	-0.92621
	4.58	\mathbf{l}_2	-0.87445	-0.32142	0.36336
	4.04	\mathbf{l}_3	-0.30618	0.94665	0.10054
\mathbf{T}	0.269 Å	\mathbf{t}_1	0.98284	0.13809	0.12233
	0.239	\mathbf{t}_2	0.17713	-0.89161	-0.41672
	0.205	\mathbf{t}_3	0.05152	0.43123	-0.90077

R.m.s. discrepancy in U^{ij} 0.0042 Å²
 $[\sum(U_{obs}^{ij} - U_{calc}^{ij})^2 / \sum(U_{obs}^{ij})^2]^{1/2}$ 0.052

(b) TCNQ

Tensor of inertia:	Eigenvalues	Eigenvectors†
	404 (at.wt Å ²)	\mathbf{l} 6.197 3.888 -0.649
	1835	\mathbf{m} 4.478 -6.759 4.607
	2239	\mathbf{n} 3.010 -0.410 -6.352

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

Tensor	11	12	13	22	23	33
\mathbf{L} (rad ²)	1164 (82)	-130 (10)	71 (18)	150 (21)	-31 (12)	132 (11)
\mathbf{T} (Å ²)	5763 (100)	1 (98)	-432 (104)	3424 (140)	-223 (141)	4530 (163)

R.m.s. amplitudes

Principal axes‡

\mathbf{L}	6.24°	\mathbf{l}_1	0.98953	-0.12610	0.07018
	2.23	\mathbf{l}_2	0.14161	0.75476	-0.64053
	1.88	\mathbf{l}_3	0.02780	0.64376	0.76472
\mathbf{T}	0.243 Å	\mathbf{t}_1	-0.95218	-0.02771	0.30429
	0.211	\mathbf{t}_2	-0.30339	0.20389	-0.93080
	0.184	\mathbf{t}_3	-0.03625	-0.97860	-0.20254

R.m.s. discrepancy in U^{ij} 0.0039 Å²
 $[\sum(U_{obs}^{ij} - U_{calc}^{ij})^2 / \sum(U_{obs}^{ij})^2]^{1/2}$ 0.067

† Referred to the reciprocal base vectors \mathbf{a}^* , \mathbf{b}^* , and \mathbf{c}^* .

‡ Referred to the unit vectors \mathbf{l} , \mathbf{m} and \mathbf{n} , defined above.

the two molecules by the method of Cruickshank (1956) with the aid of a program written by one of us (U.S.). The results of this are shown in Table 2.

Although both translational and librational motions of naphthalene exceed those of TCNQ, the two molecules can be regarded as rigid bodies, to the same degree of approximation. The r.m.s. discrepancies between observed and calculated vibration tensors, as well as the appropriate percentage discrepancies (Table 2), indicate a satisfactory agreement of the rigid-body model with the data.

The motion of TCNQ is characterized by a rather large libration about a direction close to the long molecular axis and by smaller (and similar) librations about the other two principal axes of L . Of course some unknown amount of out-of-plane independent wagging motions of the cyano groups may be absorbed in the apparent libration of TCNQ about its long axis. The librational motion of naphthalene about all three principal axes of L is rather large, the greatest amplitude being associated with the plane normal. This is somewhat unusual but such behaviour has been encountered in several related molecular compounds (e.g. Goldberg & Shmueli, 1973*a*). The translational motion of both molecules appears to be normal.

In order to find out to what extent the molecular motion indicated above is compatible with the observed packing arrangement, we evaluated energy profiles corresponding to rotation of TCNQ and naphthalene about their molecular axes. The calculation was performed as described elsewhere (Shmueli & Goldberg, 1973) and the profiles were analysed as indicated by Shmueli & Kroon (1974). The results are given in Table 3 and two profiles, corresponding to the largest librations of TCNQ and naphthalene, are shown in Fig. 4.* All the profiles are nearly parabolic in the neighbourhood of their minima, which are close to the observed molecular orientations about the relevant axes of rotation. The half-widths of the profiles at height kT above their minima are roughly consistent with the extent and anisotropy of the indicated librational motion and, in particular, the large libration of naphthalene about its plane normal appears to be conditioned by usual van der Waals interactions.

Molecular geometry

Planarity of the molecules. Thermal ellipsoid plots of naphthalene and TCNQ are presented in Fig. 5. The deviations of atomic positions from the best molecular planes, displayed in Fig. 5, show that the

* It is recalled that the energy is calculated from Buckingham or Lennard-Jones types of expressions, with published potential function parameters. The upper smooth curve in Fig. 4. is a fourth-degree polynomial, fitted to the calculated energy values while the lower curve is a sum of the cubic and quartic terms of the polynomial (Shmueli & Kroon, 1974). The lower curve thus indicates a probable anharmonic contribution to the potential and should be examined in the neighbourhood of the minimum (say, in the kT range indicated).

carbon skeleton of naphthalene is planar and the same applies to the quinonoid part of TCNQ. This is in agreement with other crystallographic studies in-

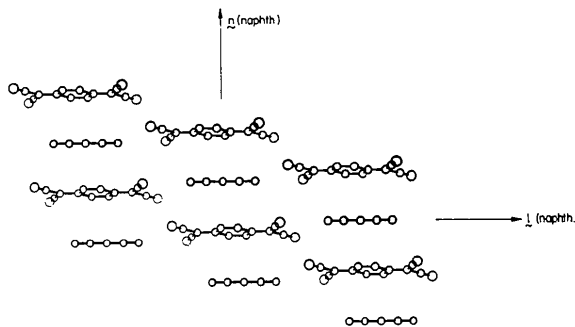


Fig. 3. Projection of the structure down the short axis of the naphthalene molecule.

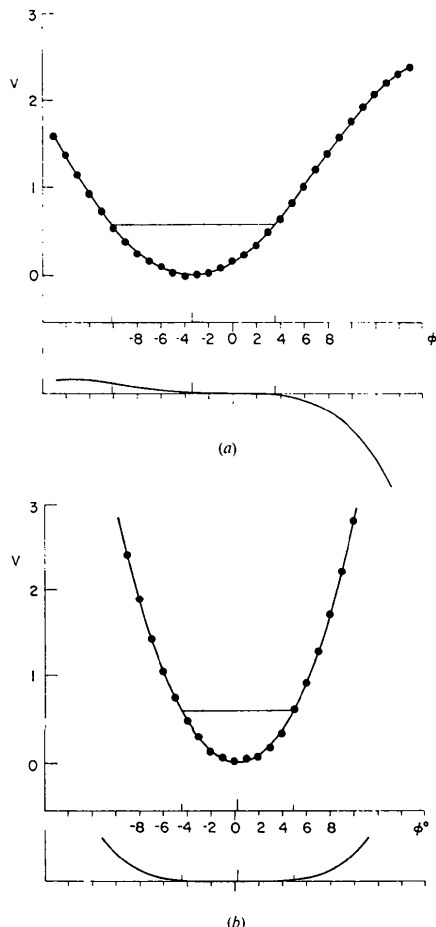
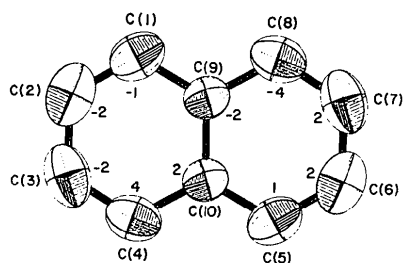
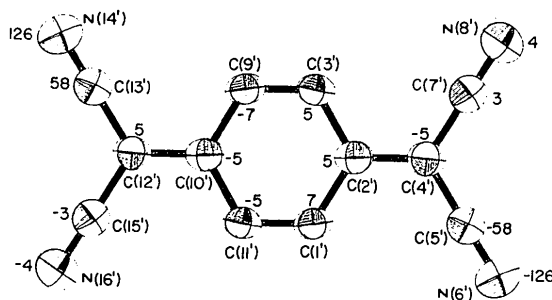


Fig. 4. Energy profiles corresponding to rotation of naphthalene and TCNQ about the plane normal and long axis respectively. The energy is given in kcal mol⁻¹. The horizontal lines above the minima are drawn at the height kT . (a) Naphthalene, (b) TCNQ.

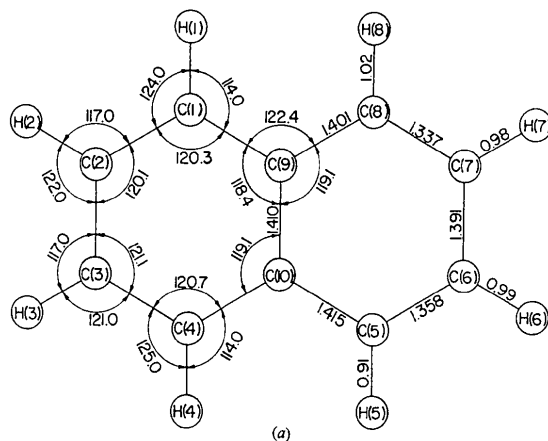


(a)

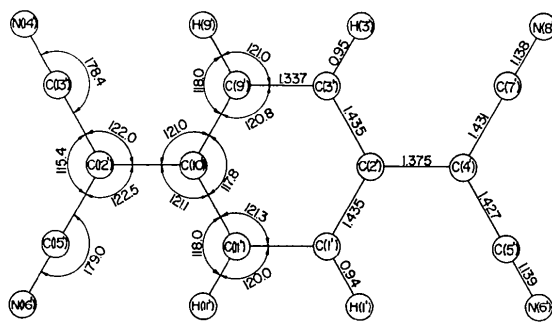


(b)

Fig. 5. Thermal-ellipsoid plots of (a) naphthalene and (b) TCNQ. The deviations of atomic centres, in 10^{-3} Å, from the best planes of naphthalene and TCNQ are shown.



(a)



(b)

Fig. 6. Molecular geometry of (a) naphthalene and (b) TCNQ. The bond distances (Å) and bond angles (°) shown are not corrected for libration.

Table 3. Brief summary of energy-profile calculations

A comparison is given of r.m.s. libration amplitudes $L_i^{1/2}$ with half-widths of the energy profiles, $\Delta\phi(i)$, etc., measured at the height kT above the minima. δ denotes the deviation of a minimum from its expected angular position.

(a) Naphthalene		δ	
$L_{11}^{1/2}$	4.86°	$\Delta\phi(l)$	6.35° 2.25°
$L_{22}^{1/2}$	4.10	$\Delta\phi(m)$	4.35 -0.35
$L_{33}^{1/2}$	6.27	$\Delta\phi(n)$	6.85 -3.44

(b) TCNQ		δ	
$L_{11}^{1/2}$	6.18°	$\Delta\phi(l)$	4.68° 0.22°
$L_{22}^{1/2}$	2.22	$\Delta\phi(m)$	2.45 0.69
$L_{33}^{1/2}$	2.08	$\Delta\phi(n)$	2.16 0.58

volving either of the two molecules. However, one of the (independent) cyano groups of TCNQ, C(5')-N(6'), is significantly bent out of the best plane of the quinonoid group and this distortion is ascribed to intermolecular interactions, although it is difficult to say which are mainly responsible for it. A similar distortion of a cyano group was also found in the TCNQ-phenazine compound (Goldberg & Shmueli, 1973b).

Table 4. Bond distances (Å)

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

(a) Naphthalene	Present work	Cruickshank (1957)	Pawley & Yeats (1969)
C(1)-C(2)	1.358 (4) (1.370)	1.353	1.383
C(2)-C(3)	1.392 (4) (1.405)	1.416	1.394
C(1)-C(9)	1.416 (3) (1.428)	1.421	1.415
C(8)-C(9)	1.402 (3) (1.414)	1.419	1.425
C(7)-C(8)	1.338 (4) (1.349)	1.361	1.366
C(9)-C(10)	1.410 (3) (1.424)	1.405	1.415

(b) TCNQ	Present work	Long, Sparks & Trueblood (1965)
C(1)-C(2)	1.435 (2) (1.443)	1.440 (1.446)
C(2)-C(3)	1.435 (2) (1.444)	1.445 (1.450)
C(2)-C(4)	1.375 (2) (1.377)	1.373 (1.374)
C(4)-C(5)	1.427 (2) (1.436)	1.436 (1.441)
C(5)-N(6)	1.139 (3) (1.146)	1.139 (1.141)
C(4)-C(7)	1.431 (3) (1.438)	1.435 (1.440)
C(7)-C(8)	1.138 (3) (1.143)	1.137 (1.139)
C(1)-C(11)	1.337 (2) (1.339)	1.344 (1.346)

Bond distances and angles. Bond distances in the TCNQ molecule [Fig. 6, Table 4(b)] agree remarkably well with those found in the structure of TCNQ (Long, Sparks & Trueblood, 1965), and when compared to the compilation by Hoekstra, Spoelder & Vos (1972) they are indicative of a neutral ground state of the molecule. The quinonoid bond length is also very close to those found in the essentially neutral TCNQ compounds with phenazine and dibenzo-*p*-dioxin (Goldberg & Shmueli, 1973*a,b*). The internal consistency of chemically equivalent bonds in TCNQ is very satisfactory.

The dimensions of the naphthalene molecule are reasonably close to those reported for naphthalene (Cruickshank, 1957) and perdeuteronaphthalene (Pawley & Yeats, 1969). The latter two naphthalene geometries, shown in Table 4, are not corrected for libration and refer to molecules with $\bar{1}$ symmetry. In view of the uncertainty of the libration corrections it is difficult to attach too much significance to the comparison of corrected and/or averaged bond distances of naphthalene in the three structures. Such a comparison may also be complicated by the different anisotropies of librational motion of naphthalene in Cruickshank's and our structure. However, the present determination of the geometry of naphthalene in a molecular compound is consistent with the known picture of incomplete delocalization in this aromatic molecule.

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