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

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Abstract

Crystals of the title compound, $C_{12}H_4N_4.C_{13}H_9N$, are monoclinic, $P2_1$, with two units of the complex in a unit cell having $a = 7{\cdot}803\,(1)$, $b = 18{\cdot}878\,(2)$, $c = 6{\cdot}883\,(1)$ Å and $\beta = 100{\cdot}55\,(2)°$. The structure was solved from three-dimensional precession diffractometer data by using Patterson search methods, and was refined to a conventional $R = 0{\cdot}056$ and weighted $r = 0{\cdot}044$. Almost parallel TCNQ and 7,8-benzoquinoline molecules are alternately stacked along the c axis. The layer-like arrangement of the complex is compared with that found in the (1:1) TCNQ:*o*-phenanthroline crystalline molecular compound [Goldberg & Shmueli (1977). *Acta Cryst.* B**33**, 2189–2197]. The differences between the packing modes of the two closely related compounds appear to be due mainly to a different relative contribution of the dipole–dipole interaction to the stabilization of the structures. A rigid-body anisotropic constrained refinement was carried out which converged to $R = 0{\cdot}061$ and weighted $r = 0{\cdot}051$. The results of the constrained refinement along with results of energy-profile calculations indicate that the (large) thermal parameters of 7,8-benzoquinoline describe genuine motion, unlike those of the related *o*-phenanthroline in the above-mentioned structure.

Introduction

Structural studies of crystalline molecular compounds are associated with problems concerning important stabilizing interactions, their effects on the molecular geometry, unequal dynamic behaviour of the constituent molecules and their degree of order in the crystalline state. These and related questions form the basis of the programme of studies, in which compounds involving 7,7,8,8-tetracyanoquinodimethane (TCNQ) have so far been investigated (Goldberg & Shmueli, 1973; Shaanan, Shmueli & Rabinovich, 1976), being carried out in this laboratory.

Our study of the TCNQ:1,10-phenanthroline (PHT) compound (Goldberg & Shmueli, 1977, hereafter GS) showed that the highly polar PHT molecule is disordered and, moreover, the rather frequently observed mixed-stack arrangement of donor and acceptor

* Part VIII: Goldberg & Shmueli (1977).
† A preliminary report on this work was presented at the Fourth European Crystallographic Meeting, Oxford (Shaanan & Shmueli, 1977).

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molecules gives way to an arrangement of well separated donor–acceptor pairs. The TCNQ:7,8-benzoquinoline (BQ) compound was thought to be of interest because of the close similarity between the isoelectronic BQ and PHT which, however, differ in their electronic structures in that BQ results by replacing one N atom of PHT with a C—H group.

We describe in this paper the crystal and molecular structure of the TCNQ:BQ compound, as determined from precession diffractometer data. This structure is also compared with that of TCNQ:PHT with respect to packing arrangements and the possible interactions that may explain the structural differences and similarities found in these two molecular compounds.

Experimental

Equimolar solutions of commercial TCNQ and BQ in ethyl acetate were mixed and dark-violet crystals were obtained after slow evaporation.

Microanalysis confirmed the 1:1 ratio of TCNQ to BQ in the crystals.

Unit-cell dimensions were determined with the aid of precession and (calibrated) Weissenberg photographs. Their values, given below, are based on their least-squares fit to 16 reflections. The density of the crystals was measured by the flotation method.

Crystal data

$C_{12}H_4N_4.C_{13}H_9N$, $M_r = 383{\cdot}4$, monoclinic, $a = 7{\cdot}803\,(1)$, $b = 18{\cdot}878\,(2)$, $c = 6{\cdot}883\,(1)$ Å, $\beta = 100{\cdot}55\,(2)°$, $V = 996{\cdot}9$ Å^3, $d_m = 1{\cdot}281$, $Z = 2$, $d_c = 1{\cdot}277$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·085 mm^{-1}. Systematic absences: $0k0$: $k = 2n + 1$.

The possible space groups are $P2_1$ and $P2_1/m$, the former being confirmed by the structure determination.

Intensity data were collected with the aid of a two-circle precession diffractometer (see Shaanan, Shmueli & Rabinovich, 1976) using a crystal of approximate dimensions 0·4 × 0·3 × 0·3 mm. 6462 intensities were measured with graphite-monochromatized Mo $K\alpha$ radiation, each reflection being scanned along the precession-arc circle, *i.e.* the circle which controls the orientation of the appropriate Laue cone. The intensity record comprises 24 layers, made up of four sets perpendicular to the [100], [010], [110] and [210] directions. The first set consists of three layers (0–2) and the others consist of seven layers each (0–6). The standard deviation of the net intensity I, in counts per second, was calculated as

$$\sigma(I) = [I_p + (B_r + B_l)(t_p/t_b)^2 + (0{\cdot}03I_p)^2]^{1/2},$$

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 scan times, respectively. Reduction of intensities to structure amplitudes was performed with the aid of Lorentz and polarization factors. The Lorentz factor was of the form given by Buerger (1964) for a single encounter of a reciprocal-lattice point with the sphere of reflection.

The reduced intensities were cross-scaled using 2583 common and symmetry-related reflections. The final discrepancy factor for these reflections is $R = \sum |\langle F_o^2\rangle - F_{oi}^2|/\sum F_{oi}^2 = 0{\cdot}034$. This process yielded 2034 independent reflections, including 792 unobserved reflections,* which were subsequently employed in the structure determination.

All the calculations were carried out with the aid of a CDC-6600 computer at the Tel-Aviv University Computation Centre.

Structure determination and refinement

Our first attempt to solve the phase problem for TCNQ:BQ was a routine application of the *MULTAN* 74 system (Main, Woolfson, Lessinger, Germain & Declercq, 1974). This procedure gave several sets of phases with reasonably high figures of merit, but none of the E maps based on these sets proved to be informative and some of them contained hexagonal arrays of peaks, as have sometimes been observed previously (Thiessen & Busing, 1974; Lai & Marsh, 1974). We then proceeded to Patterson search techniques and employed the method of Braun, Hornstra & Leenhouts (1969) for this purpose. The best result of the orientation search indicated that the inertial systems of TCNQ and BQ are very similarly oriented. A subsequent translation search placed the centres of gravity of the two molecules at very close positions and it was found from simple packing considerations that BQ had to be rotated through 180° about its plane normal and displaced through $\frac{1}{2}\mathbf{c}$ with respect to the position which was indicated. The initial value of R for this model was 0·25 (with 70 reflections), which decreased to 0·135 after three cycles of rigid-body refinement. During this calculation, the inertial system of BQ was rotated through ~15° about the plane normal with respect to the inertial system of TCNQ, thus leading to an overlap diagram similar to that found for TCNQ:PHT (see below).

Subsequent conventional refinement of the above model started with an atom-per-block scheme and was concluded with four cycles of anisotropic refinement in which the parameters of each molecule corresponded to a full block about the diagonal of the matrix of normal equations.

The y coordinate of C(1) in the BQ molecule was kept fixed throughout the refinement because of the polar-axis indeterminacy. Since the ratio of the number of

* Reflections for which $F_o^2 \leq 3\sigma(F_o^2)$ were considered as unobserved.

Table 1. *Atomic positional* ($\times 10^4$) *parameters after the conventional refinement*

The e.s.d.'s are given in parentheses in units of the last decimal place. The numbering of the atoms is shown in Fig. 3.

TCNQ

	x	y	z
C(1′)	2051 (7)	3234 (4)	8204 (6)
C(2′)	3898 (6)	3252 (4)	8298 (5)
C(3′)	4800 (6)	2567 (4)	8434 (6)
C(4′)	4781 (7)	3870 (4)	8252 (6)
C(5′)	3938 (8)	4547 (4)	8196 (7)
N(6′)	3241 (7)	5071 (4)	8143 (7)
C(7′)	6621 (8)	3894 (4)	8185 (6)
N(8′)	8053 (6)	3908 (3)	8075 (6)
C(9′)	3937 (7)	1963 (4)	8425 (6)
C(10′)	2046 (6)	1933 (4)	8241 (6)
C(11′)	1173 (6)	2622 (4)	8156 (6)
C(12′)	1157 (7)	1319 (4)	8146 (6)
C(13′)	2003 (8)	649 (4)	8226 (8)
N(14′)	2663 (7)	102 (3)	8290 (7)
C(15′)	−706 (8)	1307 (4)	7905 (7)
N(16′)	−2203 (7)	1279 (4)	7659 (7)
H(1′)	1343	3724	8167
H(3′)	6173	2550	8407
H(9′)	4652	1474	8483
H(11′)	−205	2636	8137

BQ

	x	y	z
C(1)	3483 (8)	1722	3464 (7)
C(2)	2998 (11)	986 (5)	3442 (8)
C(3)	1239 (16)	815 (5)	3178 (10)
C(4)	−3 (10)	1306 (5)	2985 (8)
C(5)	−859 (7)	2573 (6)	2887 (7)
C(6)	−374 (9)	3280 (5)	2876 (8)
C(7)	1885 (11)	4211 (4)	3032 (8)
C(8)	3582 (14)	4359 (4)	3152 (9)
C(9)	4804 (9)	3815 (5)	3381 (8)
N(10)	4388 (6)	3133 (4)	3423 (5)
C(11)	2650 (8)	2952 (4)	3255 (6)
C(12)	2211 (7)	2216 (4)	3262 (6)
C(13)	423 (8)	2032 (5)	3044 (6)
C(14)	1340 (9)	3482 (4)	3048 (6)
H(1)	4836	1876	3627
H(2)	3957	574	3447
H(3)	870	266	3106
H(4)	−1318	1140	2998
H(5)	−2196	2431	2883
H(6)	−1334	3683	2951
H(7)	953	4629	3085
H(8)	4007	4903	3247
H(9)	6136	3953	3379

observations (1234) to the number of parameters (271) is rather low, the positional parameters of the H atoms were estimated from chemical considerations and their isotropic thermal parameters were taken as $\frac{1}{3}$ of the trace of U of the C atoms to which they are bonded. None of the H atom parameters were refined; however, all were adjusted after each stage of the refinement. One strong reflection, probably affected by extinction, and seven moderately weak low-angle reflections, which were apparently inaccurately measured, were excluded from the calculation during its final stages.

The final discrepancy factors are: conventional $R = 0{\cdot}056$, weighted $r = 0{\cdot}044$ and $\langle w\Delta^2\rangle^{1/2}_{n-m} = 2{\cdot}57$, with $n = 1234$ and $m = 271$. The weighting scheme, used in the final cycles, was $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and (F_o^2) was obtained from the equation above.

Atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964) for C and N, and from Stewart, Davidson & Simpson (1965) for H.

The final positional parameters* of the TCNQ:BQ structure are given in Table 1.

* Lists of structure factors and thermal parameters and detailed results of the constrained refinement have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34402 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Constrained refinement

The anisotropic thermal parameters, obtained for the BQ molecule in the above conventional refinement, are rather large and qualitatively similar to those of PHT in the thermally disordered TCNQ:PHT compound (GS) [*cf.* Fig. 1(*b*) and (*d*)]. Rigid-body-motion analysis of these parameters also indicates that the BQ molecule has the largest libration amplitude associated with its plane normal. Although such behaviour is often encountered in molecular compounds and can hardly be described as unusual, the similarity between BQ and PHT in their structurally related (see below) TCNQ compounds behoves one to test further whether or not the observed thermal motion of BQ is genuine.

The final difference map, calculated after the conventional refinement of TCNQ:BQ, is rather clean ($\Delta\rho_{max} \sim 0{\cdot}09$ e Å^{-3}). This, however, is not necessarily conclusive evidence, since false thermal parameters may have been used and consequently the electron density may have been incorrectly smeared out, thus leading to a clean $\Delta\rho$ map. Of course, this might be so if the motion were strongly anharmonic or if the barrier separating the energies of the preferred orientations were very low (*cf.* Shmueli & Goldberg, 1973). If, on the other hand, such orientations were well separated by a sizeable barrier, the difference density might well show some indications of such a situation (Herbstein, 1971; Shmueli & Goldberg, 1974).

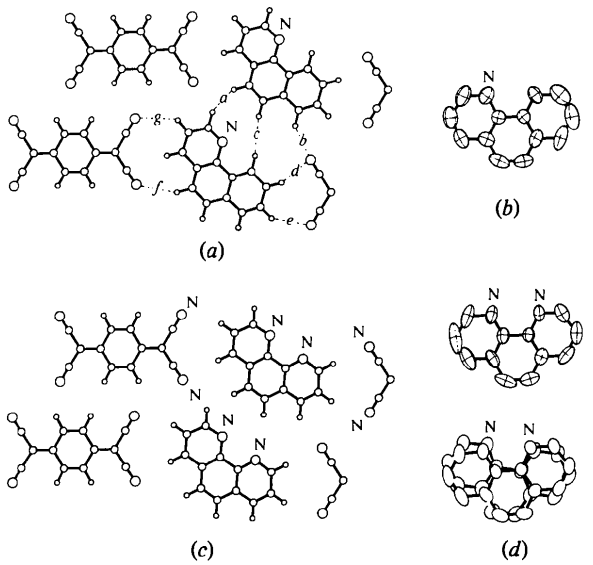

Fig. 1. Layer-like arrangements and thermal ellipsoids in TCNQ:BQ and TCNQ:PHT (GS) structures. (*a*) A layer in the TCNQ:BQ compound viewed along the TCNQ plane normal. The intralayer distances indicated are: $a = 2{\cdot}11$, $b = 2{\cdot}56$, $c = 2{\cdot}69$, $d = 2{\cdot}79$, $e = 2{\cdot}86$, $f = 2{\cdot}95$ and $g = 2{\cdot}98$ Å. (*b*) BQ showing 50% probability thermal ellipsoids. (*c*) A layer in TCNQ:PHT viewed along the TCNQ plane normal. (*d*) 50% probability thermal ellipsoids of PHT after the conventional refinement (upper drawing) and after the constrained refinement (*cf.* GS) (lower drawing).

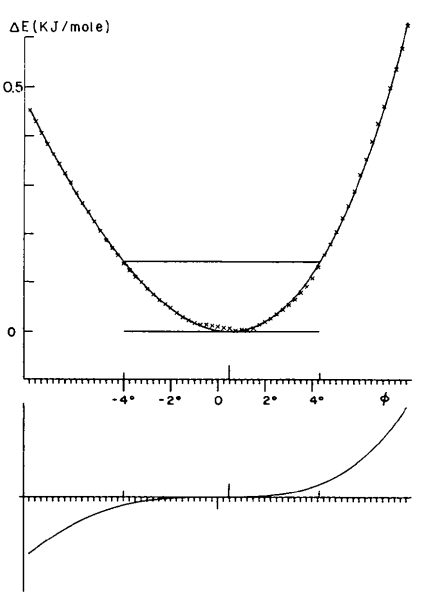

Fig. 2. Energy profile corresponding to a rotation of the BQ molecule about its plane normal. The smooth curve in the upper graph is a fourth-degree polynomial, fitted to the calculated energy values (denoted by ×), while the lower graph is a sum of the cubic and quartic terms of the polynomial (Shmueli & Kroon, 1974). The horizontal line above the minimum is drawn at the height kT.

Table 2. *Summary of the constrained refinement*

The angular and positional parameters ($\boldsymbol{\varphi}, \boldsymbol{\rho}$) are referred to the axes of a Cartesian working system defined by three unit vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$ and $\hat{\mathbf{e}}_3$, parallel to $\mathbf{a}$, $\mathbf{b}^*$ and $\mathbf{a} \times \mathbf{b}^*$, respectively. The angles φ_x, φ_y, φ_z denote rotations in the positive sense of the input molecules about the axes of the working system, and the components of the vector $\boldsymbol{\rho}$ denote the coordinates of the centres of gravity of the molecules in this system. The components of the **T**, **L**, **S** tensors of each molecule, as well as the components of the vibration tensors **U** of the conventionally refined atoms, are referred to the working system. The unit vectors $\mathbf{m}_i$, $\mathbf{l}_i$ and $\mathbf{t}_i$, $i = 1, 2, 3$, correspond to the principal axes of the tensors of inertia, libration and translation respectively of the rigid group considered.

(*a*) Input

TCNQ and BQ

(1) Fractional coordinates of TCNQ and BQ as given in Table 1

(2) Angular and positional parameters:

$$\varphi_x = \varphi_y = \varphi_z = 0°; \quad \rho_x = \rho_y = \rho_z = 0 \text{ Å}$$

(3) Isotropic U_o's of H atoms not refined

(*b*) Final discrepancy indices (m = number of parameters)

Conventional $R = 0{\cdot}056$, $r = 0{\cdot}044$, $m = 271$, $\langle w\Delta^2\rangle^{1/2} = 2{\cdot}57$

Constrained $R = 0{\cdot}061$, $r = 0{\cdot}051$, $m = 100$, $\langle w\Delta^2\rangle^{1/2} = 2{\cdot}76$

(*c*) Results

Positional parameters

TCNQ

	x	y	z
$\boldsymbol{\varphi}$ (°)	−0·0025 (0·03)	0·0033 (0·04)	0·0031 (0·02)
$\boldsymbol{\rho}$ (Å)	−0·0004 (0·001)	0·0	−0·0007 (0·0008)

BQ

	x	y	z
$\boldsymbol{\varphi}$ (°)	0·030 (0·04)	0·064 (0·05)	−0·099 (0·05)
$\boldsymbol{\rho}$ (Å)	−0·003 (0·002)	−0·009 (0·003)	−0·0004 (0·0008)

(*d*) Eigenvalues and eigenvectors of **T** and **L** for TCNQ (quinonoid part) and BQ

Values in parentheses refer to conventional rigid-body-motion analyses. The actual interaxial angles, rather than their cosines, are given.

	R.m.s. amplitudes		$\mathbf{m}_1$	$\mathbf{m}_2$	$\mathbf{m}_3$
(1) TCNQ					
	6·35 (6·20)°	$\mathbf{l}_1$	171 (3)°	92 (92)°	82 (92)°
L	2·74 (2·72)	$\mathbf{l}_2$	92 (89)	2 (18)	90 (108)
	2·23 (2·23)	$\mathbf{l}_3$	98 (88)	90 (72)	172 (18)
	0·25 (0·25) Å	$\mathbf{t}_1$	12 (10) Å	81 (81) Å	98 (96) Å
T	0·20 (0·19)	$\mathbf{t}_2$	78 (80)	129 (127)	41 (38)
	0·18 (0·18)	$\mathbf{t}_3$	88 (87)	140 (142)	130 (128)
(2) BQ					
	5·81 (5·77)°	$\mathbf{l}_1$	99 (93)°	83 (87)°	12 (175)°
L	4·85 (4·63)	$\mathbf{l}_2$	170 (176)	87 (92)	100 (87)
	2·86 (2·86)	$\mathbf{l}_3$	86 (92)	7 (4)	84 (87)
	0·25 (0·26) Å	$\mathbf{t}_1$	18 (17) Å	72 (71) Å	90 (92) Å
T	0·23 (0·23)	$\mathbf{t}_2$	72 (72)	160 (150)	82 (66)
	0·19 (0·19)	$\mathbf{t}_3$	87 (84)	98 (113)	171 (156)

Calculation of energy profiles for rotation of BQ about the principal axes of its tensor of inertia (*cf.* Shmueli & Kroon, 1974) appears to indicate that the motion of BQ in this crystal is genuine and harmonic. The profiles have single minima, corresponding fairly well to the observed structure, and nearly parabolic shapes in the neighbourhood of these minima. The result pertaining to rotation about the plane normal is shown in Fig. 2.

This, in itself, is a favourable indication of order; however, the r.m.s. discrepancy in the conventional (Schomaker & Trueblood, 1968) rigid-body-motion analysis was rather high (about 2·5 times the average standard deviation of the observed U^{ij}'s), and we therefore decided to perform a constrained refinement of the structure, mainly in order to see whether or not the rigid-body-motion parameters, fitted directly to the experimental data, provide the same picture of the average motion of BQ as that given by the conventional **TLS** analysis. The calculation was performed as described by Shmueli & Goldberg (1974). The input to and the results of the constrained refinement are shown in Table 2. It should be pointed out that the working system chosen was based on **a**, **b*** and **a** × **b*** rather than on the inertial axes of the first molecule input, since this choice enabled us to deal conveniently with the y-axis indeterminacy of the polar space group.

It can be seen from Table 2 that the constrained refinement converged to an R value which is close to that obtained from the conventional refinement, in spite of the fact that the number of parameters was decreased by a factor of 2·7. The extent and anisotropy of the rigid-body motion of both molecules are closely similar to those indicated earlier by the conventional **TLS** analysis. It is also evident that the positional parameters underwent barely significant changes, and thus the constrained refinement has served its purpose and provided additional support for the ordered structure of TCNQ : BQ.†

Discussion

Packing arrangement

The structure consists of mixed donor–acceptor stacks such as are usually observed in molecular compounds of charge-transfer type (Shaanan, Shmueli & Rabinovich, 1976; Herbstein, 1971). The mean interplanar distance within the stack is 3·43 Å, indicating a neutral ground state of the complex‡ (Goldberg & Shmueli, 1973). This arrangement of mixed stacks gives rise to molecular layers which contain alternating rows of BQ and TCNQ held together by several short contacts, as shown in Fig. 1(*a*). The structure of the layers in the present compound resembles that of the layers found in the TCNQ:PHT crystalline compound (GS), as can be seen from comparison of Fig. 1(*a*) and (*c*). However, the most pronounced difference between the two compounds is the manner in which the above-mentioned layers overlap with one another. Thus, in TCNQ:BQ the layers throughout the structure are arranged so that the donor–acceptor overlap propagates continuously along the c axis, resulting in the formation of mixed stacks. On the other hand, in TCNQ:PHT the usual donor–acceptor overlap is confined to a pair of layers only, successive pairs along the c axis being displaced sideways (GS), thus preventing stack formation. It is interesting to note that the contribution of the charge-transfer interaction to the stabilization of the two compounds is indicated to be the same by an iterative extended Hückel all-valence electrons calculation (Rein, Clark & Harris, 1970) performed by us. The coefficients and the energy values of the molecular orbitals obtained for BQ are very close to those of PHT obtained by the same method of calculation (Goldberg, 1975). The resemblance of the charge-transfer interaction in TCNQ:BQ to that in TCNQ:PHT is further supported by the similar donor–acceptor overlap observed in the two compounds (Fig. 3; Fig. 5 in GS). Since the van der Waals interactions in the present structure and in TCNQ:PHT should also be similar, it seems to us that the above-mentioned difference between the arrangement of the layers in the two compounds is due to a different relative contribution of the dipolar interaction to the stabilization of the two structures. Thus, because of the high dipole moment of the PHT molecule (experimental value: $1{\cdot}37 \times 10^{-29}$ Cm; McCllelan, 1963) as compared to that of BQ ($\mu = 5{\cdot}44 \times 10^{-30}$ Cm, as calculated by the iterative extended Hückel method), the contribution of the dipolar interaction among the donor molecules in TCNQ:PHT is greater. It is therefore possible that the

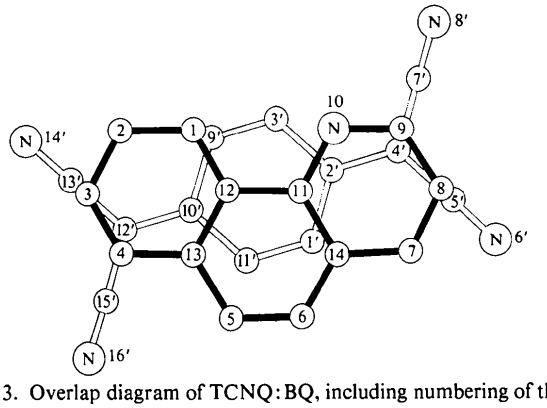

Fig. 3. Overlap diagram of TCNQ:BQ, including numbering of the atoms.

† A lattice-dynamical treatment, by the Born–von Kármán method (Pawley, 1972), of the present structure is in progress and will be reported elsewhere (Shaanan & Shmueli, 1980).

‡ There are two intrastack distances shorter than the mean distance, C(4′)–C(9) = 3·36 Å and C(7′)–C(9) = 3·36 Å, referring to the numbering in Fig. 3. No unacceptably short interstack distances are present in the structure.

dipolar repulsion between the donor molecules along the c axis prevents TCNQ:PHT from crystallizing in the 'usual' mixed-stack arrangement observed in the present structure. The formation of staggered pairs of layers, observed in TCNQ:PHT, does in fact relieve such a repulsive interaction.

Regarding the degree of order in the two related compounds, the more favourable situation in the present structure is probably due in part to the presence of an additional intralayer H···H interaction [*cf.* Fig. 1(*a*) and (*c*)].

Molecular geometry

The bond distances and angles in TCNQ and BQ are listed in Table 3, along with their estimated standard deviations. The e.s.d.'s are relatively high, which is probably due, in part, to the somewhat low ratio of the numbers of observations and parameters (~4·5) throughout the conventional refinement. Molecular dimensions of TCNQ agree well with those of TCNQ in its crystal (Long, Sparks & Trueblood, 1965) and in its neutral ground-state complexes (Hoekstra, Spoelder & Vos, 1972; André, Bieber & Gautier, 1976; Flandrois & Chasseau, 1977), as indicated in particular by the bond distances C(2′)–C(4′) = 1·36 and C(10′)–C(12′) = 1·35 Å. The quinonoid group of TCNQ is slightly, but significantly, bent (Table 4), while two of the cyano N atoms deviate from the best plane of the quinonoid moiety by as much as 0·21 and 0·33 Å. While the cause for this bending of the cyano groups is not obvious, it should be pointed out that these are the C≡N groups which have the least overlap with BQ (Fig. 3) and, hence, are better exposed to interstack interactions.

The structure of 7,8-benzoquinoline (BQ) has, to our knowledge, been determined for the first time in this study. The molecular geometry of BQ has several features in common with phenanthrene (Kay, Okaya & Cox, 1971) and phenanthroline (Nishigaki, Yoshioka & Nakatsu, 1978), such as, *e.g.*, a long C(11)–C(12) bond, a short C(5)–C(6) bond, and similar dimensions of the pyridine ring to those found in phenanthroline. Since, however, BQ is the least symmetric and least overcrowded of the three molecules, it is not easy to compare all the distances found with those observed in the other analogues. It would be of interest to collect more extensive data from a crystal of uncomplexed BQ and compare its geometry with that found in the present study.

Table 3. *Bond lengths* (Å) *of TCNQ and BQ*

The e.s.d.'s are given in parentheses in units of the last decimal place. The numbering is shown in Fig. 3.

TCNQ		BQ	
C(1′)–C(2′)	1·43 (1)	C(1)–C(2)	1·44 (1)
C(2′)–C(3′)	1·47 (1)	C(1)–C(12)	1·35 (1)
C(2′)–C(4′)	1·36 (1)	C(2)–C(3)	1·39 (2)
C(4′)–C(5′)	1·44 (1)	C(3)–C(4)	1·33 (1)
C(4′)–C(7′)	1·45 (1)	C(4)–C(13)	1·41 (1)
C(5′)–N(6′)	1·13 (1)	C(13)–C(5)	1·42 (1)
C(7′)–N(8′)	1·13 (1)	C(5)–C(6)	1·39 (1)
C(3′)–C(9′)	1·32 (1)	C(6)–C(14)	1·37 (1)
C(9′)–C(10′)	1·46 (1)	C(14)–C(7)	1·44 (1)
C(10′)–C(11′)	1·46 (1)	C(7)–C(8)	1·34 (1)
C(11′)–C(1′)	1·34 (1)	C(8)–C(9)	1·39 (1)
C(10′)–C(12′)	1·35 (1)	C(9)–N(10)	1·33 (1)
C(12′)–C(13′)	1·42 (1)	N(10)–C(11)	1·38 (1)
C(13′)–N(14′)	1·15 (1)	C(11)–C(12)	1·43 (1)
C(12′)–C(15′)	1·43 (1)	C(12)–C(13)	1·42 (1)
C(15′)–N(16′)	1·15 (1)	C(11)–C(14)	1·42 (1)
C(1′)–C(2′)–C(3′)	116·8 (6)	C(1)–C(12)–C(13)	122·1 (7)
C(1′)–C(2′)–C(4′)	121·9 (6)	C(12)–C(1)–C(2)	118·6 (6)
C(2′)–C(1′)–C(11′)	121·7 (6)	C(11)–C(12)–C(13)	117·9 (6)
C(2′)–C(3′)–C(9′)	121·4 (5)	C(11)–C(12)–C(1)	119·9 (5)
C(3′)–C(9′)–C(10′)	122·7 (6)	C(1)–C(2)–C(3)	118·5 (8)
C(3′)–C(2′)–C(4′)	121·3 (5)	C(2)–C(3)–C(4)	122·4 (9)
C(2′)–C(4′)–C(5′)	122·3 (5)	C(3)–C(4)–C(13)	120·8 (8)
C(2′)–C(4′)–C(7′)	122·6 (6)	C(4)–C(13)–C(12)	117·6 (7)
C(7′)–C(4′)–C(5′)	115·0 (6)	C(4)–C(13)–C(5)	122·5 (7)
C(4′)–C(5′)–N(6′)	178·4 (7)	C(12)–C(13)–C(5)	119·9 (7)
C(4′)–C(7′)–N(8′)	177·9 (5)	C(13)–C(5)–C(6)	120·2 (6)
C(9′)–C(10′)–C(11′)	115·1 (6)	C(5)–C(6)–C(14)	121·9 (8)
C(10′)–C(11′)–C(1′)	122·2 (5)	C(6)–C(14)–C(11)	119·0 (7)
C(9′)–C(10′)–C(12′)	122·1 (5)	C(6)–C(14)–C(7)	123·2 (7)
C(11′)–C(10′)–C(12′)	122·1 (5)	C(11)–C(14)–C(7)	117·8 (6)
C(10′)–C(12′)–C(15′)	121·5 (6)	C(14)–C(7)–C(8)	119·2 (7)
C(10′)–C(12′)–C(13′)	122·2 (5)	C(7)–C(8)–C(9)	120·1 (8)
C(12′)–C(15′)–N(16′)	177·5 (7)	C(8)–C(9)–N(10)	123·6 (7)
C(12′)–C(13′)–N(14′)	178·9 (7)	C(9)–N(10)–C(11)	118·5 (6)
		N(10)–C(11)–C(12)	118·1 (6)
		N(10)–C(11)–C(14)	120·8 (7)
		C(14)–C(11)–C(12)	121·1 (6)

Table 4. *Deviations of the TCNQ atoms from the best plane of the quinonoid group*

The values are given in units of 10^{-2} Å. The numbering is shown in Fig. 3.

	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	N(6′)	C(7′)	N(8′)
Δ	−3	0	−2	5	1	−1	19	34
$\sigma(\Delta)$*	0·6	0·5	0·5	0·6	0·6	0·6	0·6	0·6
	C(9′)	C(10′)	C(11′)	C(12′)	C(13′)	N(14′)	C(15′)	N(16′)
Δ	−3	0	−2	5	7	8	12	21
$\sigma(\Delta)$*	0·6	0·6	0·5	0·6	0·6	0·6	0·6	0·6

* Intra-atomic positional covariances were included in the calculation of the standard deviations $\sigma(\Delta)$ of the deviations Δ from the best plane defined by the underlined atoms.

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The Structure of *N*-(*tert*-Butyldithio)succinimide

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Abstract

$C_8H_{13}NO_2S_2$ is monoclinic, $a = 9{\cdot}232\,(4)$, $b = 22{\cdot}518\,(2)$, $c = 10{\cdot}744\,(2)$ Å, $\beta = 93{\cdot}81\,(2)°$, space group $P2_1/c$, $Z = 8$. The structure was solved by the heavy-atom method and refined to $R = 0{\cdot}041$. The angles between the planes C—S—S and S—S—N are 91·1 (86·0)°, and the S—S lengths are both 2·009 Å.

Introduction

The structures of *N,N'*-dithiodisuccinimide and *N*-(*tert*-butyldithio)phthalimide (Mazhar-ul-Haque & Behforouz, 1974, 1979) are known. The structure of this compound was undertaken to see the effect of the *tert*-butyl group on the S—S length and the angle between the planes C—S—S and N—S—S in comparison with those in *N,N'*-dithiodisuccinimide and *N*-(*tert*-butyldithio)phthalimide.

Experimental

Crystal data

$C_8H_{13}NO_2S_2$, $M_r = 219{\cdot}3$, m.p. = 387–388 K, monoclinic, $a = 9{\cdot}232\,(4)$, $b = 22{\cdot}518\,(2)$, $c = 10{\cdot}744\,(2)$ Å, $\beta = 93{\cdot}81\,(2)°$, $U = 2228{\cdot}6$ Å^3, D_m (by flotation) = 1·31, $Z = 8$, $D_c = 1{\cdot}306$ Mg m^{-3}. Space group $P2_1/c$; Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}436$ mm^{-1}, $F(000) = 928$.

A crystal 0·25 × 0·30 × 0·6 mm was used for data collection. The program *SEARCH* was used to obtain 25 reflections, which were then used in *INDEX* to obtain approximate cell dimensions. Accurate cell dimensions with their e.s.d.'s were obtained by least squares from these 25 accurately centred reflections.

The intensities of 3550 independent reflections [θ(Mo $K\alpha$) $\leq 25°$] were measured on an Enraf–Nonius CAD-4 diffractometer controlled by a PDP 8/A computer at a take-off angle of 5° with Mo $K\alpha$

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