

Structure and Packing Arrangement of Molecular Compounds. X.† 9,10-Diazaphenanthrene–2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2 : 1)‡

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Abstract

Crystals of the title compound, $2C_{12}H_8N_2 \cdot C_8Cl_2N_2O_2$, $M_r = 587.4$, are monoclinic, space group $P2_1/a$, with four units of the complex in a unit cell of dimensions: $a = 13.022$ (8), $b = 11.521$ (8), $c = 18.386$ (8) Å, $\beta = 97.36$ (4)°; $V = 2735.7$ Å³, $D_c = 1.305$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.28$ mm⁻¹. The structure was solved from four-circle diffractometer data by direct methods and was refined to a conventional $R = 0.045$ and a weighted $r_w = 0.041$ for 1738 observations. The structure consists of sheets of 'dimerized' donors (diazaphenanthrene) which alternate with relatively flat layers of the acceptor (dichlorodicyanobenzoquinone) molecules. Each acceptor is thus enclosed in a 'vise' formed by two nearly coplanar donors, the mean molecular planes of donors and acceptor being nearly *perpendicular*. The existence of a significant attractive donor–acceptor interaction is suggested by short contacts (2.85–2.92 Å) between the N atoms of the donors and the quinoid ring of the acceptor. The charge-transfer interaction is probably of the $n-\pi^*$ type. A remarkable similarity of the packing arrangement of the diazaphenanthrene layers to that found in uncomplexed diazaphenanthrene has been observed. This, rather unique, packing arrangement is illustrated in detail.

Introduction

The packing arrangement of molecular compounds, consisting of nearly planar organic molecules in their

neutral ground state, is often associated with a charge-transfer interaction of the $\pi-\pi^*$ type (Prout & Wright, 1968; Herbstein, 1971; André, Bieber & Gautier, 1976) which is responsible, in part, for the formation of infinite stacks of alternating and almost parallel donor and acceptor molecules. There are a small number of cases where very significant deviations from parallelism were reported [e.g. TCNQ:naphthalene (Shaanan, Shmueli & Rabinovich, 1976), TCNQ:*p*-terphenyl (Lisensky, Johnson & Levy, 1976)] but these can be regarded as perturbations of the usual pattern, induced by packing requirements of other intra- and intermolecular interactions.

The most frequently observed composition of such compounds is a 1:1 ratio of their constituent molecules, while in compounds with an ionic ground state – in particular in the extensively studied TCNQ salts (e.g. André *et al.*, 1976) – the occurrence of a one-donor-to-two-acceptor composition is commonplace. Much less frequent is the two-donor-to-one-acceptor ratio [e.g. (8-hydroxyquinoline)₂(chloranil) (Prout & Wheeler, 1967), (tetramethylbenzidine)₂(chloranil) (Yakushi, Ikemoto & Kuroda, 1971)] which is usually due to specific donor–donor interactions that cause their 'dimerization'. The above compounds, however, preserve their donor–acceptor parallelism and can still be referred to as π -molecular compounds (Herbstein, 1971).

Another aspect of molecular complexes, which ought to be mentioned in this introduction, is the rarely observed similarity relationship between crystal structures of such complexes and those of their constituent molecules. Where such a relationship exists, it is probably due to strong interactions which are present in the uncomplexed species and persist in the molecular compound in which this species appears. The similarity of the hydrogen-bonded thymine layers in thymine crystal (Ozeki, Sakabe & Tanaka, 1969) and in the thymine–*p*-benzoquinone compound (Sakurai, 1969) illustrates this point.

† Part IX: Shaanan & Shmueli (1980).

‡ A preliminary report on this work was presented at the Eleventh International Congress of Crystallography, Warsaw (Colapietro, Shaanan & Shmueli, 1978).

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The title compound, the structure of which has been briefly described elsewhere (Shaanan, Shmueli & Colapietro, 1978), is a two-donor-to-one-acceptor molecular compound which crystallizes in a rather unique packing mode. It will be seen from what follows that the mean planes of adjacent donor (9,10-diazaphenanthrene, also known as benzo[*c*]cinnoline, hereafter BC) and acceptor (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, hereafter DDQ) molecules are mutually nearly perpendicular, thus precluding a π - π^* donor-acceptor interaction. Furthermore, the cross-hatched pattern of dipolarly coupled BC 'dimers', found in the uncomplexed species (van der Meer, 1972), persists to a remarkable extent in the BC:DDQ compound thus providing another example of packing invariance. This is, however, conditioned by weaker interactions than those present in thymine and its *p*-benzoquinone compound (Ozeki *et al.*, 1969; Sakurai, 1969).

The purpose of this paper is to describe the structure of BC:DDQ and its determination and to illustrate the above-mentioned features of the packing arrangement.

Experimental

Red crystals of the compound were obtained by slow evaporation of a mixture of solutions of commercial BC and DDQ in ethyl acetate. The 2:1 BC:DDQ composition of the crystals was established by elemental analysis [%C 64.1 (65.4); %H 2.75 (2.76); %O 5.77 (5.45); %N 14.77 (14.30); %Cl 12.67 (12.07); values in parentheses refer to calculated percentages].

Unit-cell dimensions and crystal symmetry were determined with the aid of Weissenberg and precession photographs and were redetermined from diffractometer measurements. The latter are taken as the final values shown above. Intensity data for BC:DDQ were collected on a Syntex P_2_1 diffractometer using graphite-monochromatized Mo radiation. The diffractometer was operated in the ω scan mode, the scanning speed being varied from 0.025 to 0.49° s⁻¹. Altogether, 5995 reflections were measured within a quadrant of the copper sphere but only 1752 independent ones, with $I > 3\sigma$, could be secured for subsequent work. The ratio $\langle F_o^2(h+l=\text{odd}) \rangle / \langle F_o^2(h+l=\text{even}) \rangle$ is 0.23 within the observed data set, indicating that the paucity of observed reflections is due, in part, to a pseudo *B*-centring. No systematic trend was present in the intensities of three monitoring reflections which were scanned at intervals of 200 reflections. The data were not corrected for absorption and extinction.

Intensity-data collection was performed at the Laboratory of Structural Chemistry at Monterotondo and the structure determination and refinement were carried out with the aid of a CDC-6600 computer at the Tel-Aviv University.

Structure determination and refinement

The first attempt at a solution of the phase problem with the aid of the *MULTAN74* system failed, presumably because of the unusually low *B* value (1.4 Å²) which resulted from an automatic application of this procedure. Overall scale and temperature factors were then evaluated with the aid of a local Wilson-plot routine and were used in a repeated application of *MULTAN74*. The latter run proved to be successful and the structure was subjected to a conventional refinement. The H atoms of the two BC molecules were inserted at chemically reasonable positions during the initial stage of the anisotropic refinement and only their positional parameters were allowed to vary. The atom-block diagonal approximation was used during the initial stages while in the few final cycles a three-block diagonal approximation was employed, where each of the blocks contained all the intramolecular derivative products pertaining to a molecule. After each of these final cycles the **T**, **L** and **S** tensors of both BC molecules were evaluated and were used, along with the hydrogen coordinates, in the calculation of anisotropic vibration tensors of the H atoms. The isotropic vibration parameter of each H atom was then taken as one third of the trace of its calculated anisotropic vibration tensor and was kept fixed in the next cycle. This appears to be a proper way of estimating isotropic thermal parameters of H atoms when these cannot be refined due, for example, to a low ratio of observations to parameters. Fourteen reflections which were probably affected by extinction were excluded from the refinement during its final stages. The final difference map was found to be featureless. The final discrepancy indices, calculated for 427 parameters, are $R = 0.045$, $r_w = 0.041$ and $\langle w\Delta^2 \rangle_{n-m}^{1/2} = 1.67$, where $\Delta = F_o - K|F_c|$, $R = \sum |\Delta| / \sum F_o$, $r_w = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$ and $\langle w\Delta^2 \rangle_{n-m}^{1/2} = [\sum w\Delta^2 / (n-m)]^{1/2}$ with $n = 1738$ and $m = 427$. Relativistic Hartree-Fock atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for the heavy atoms and those of Stewart, Davidson & Simpson (1965) were used for hydrogen. The final atomic coordinates* and the equivalent isotropic vibration parameters are shown in Table 1.

Description of the structure

Molecular geometry

The asymmetric unit of BC:DDQ (2:1) contains three molecules: two BC and one DDQ and can thus be

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36253 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

chosen as one unit of the complex. Best-plane projections of the three molecules, including 50% probability ellipsoids, are shown in Fig. 1. The bond distances and angles, given in Table 2, show a generally fair agreement between chemically equivalent distances as well as a close similarity of the molecular geometries of BC and DDQ as observed in this work to those

Table 1. *Final atomic coordinates and equivalent isotropic vibration parameters U_{eq} (\AA^2)*

The value of U_{eq} for a heavy atom was taken as one third of the trace of its refined anisotropic vibration tensor, transformed to a Cartesian system. The average e.s.d.'s of vibration tensor components are 0.0035, 0.0036 and 0.0034 \AA^2 for BC(A), BC(B) and DDQ respectively. The isotropic vibration parameters of the H atoms were estimated as described in the text.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
<i>(a) BC(A)</i>				
C(1A)	0.3190 (4)	0.4421 (5)	0.6091 (3)	0.0532
C(2A)	0.2392 (5)	0.5109 (5)	0.6236 (3)	0.0634
C(3A)	0.1813 (5)	0.5729 (5)	0.5682 (4)	0.0708
C(4A)	0.2023 (4)	0.5661 (5)	0.4975 (3)	0.0610
N(5A)	0.3007 (3)	0.4941 (3)	0.4091 (2)	0.0500
N(6A)	0.3751 (3)	0.4328 (3)	0.3890 (2)	0.0488
C(7A)	0.5184 (4)	0.3074 (4)	0.4130 (3)	0.0514
C(8A)	0.5845 (4)	0.2422 (5)	0.4592 (4)	0.0696
C(9A)	0.5720 (5)	0.2370 (5)	0.5335 (4)	0.0691
C(10A)	0.4955 (5)	0.2967 (4)	0.5603 (3)	0.0581
C(11A)	0.4263 (4)	0.3654 (4)	0.5140 (3)	0.0401
C(12A)	0.3446 (4)	0.4321 (4)	0.5367 (2)	0.0357
C(13A)	0.2844 (4)	0.4959 (4)	0.4817 (3)	0.0404
C(14A)	0.4387 (4)	0.3696 (4)	0.4399 (3)	0.0396
H(1A)	0.360 (3)	0.395 (3)	0.643 (2)	0.0582
H(2A)	0.229 (3)	0.520 (4)	0.670 (2)	0.0762
H(3A)	0.123 (4)	0.613 (4)	0.576 (3)	0.0826
H(4A)	0.164 (3)	0.606 (4)	0.459 (2)	0.0741
H(7A)	0.524 (3)	0.315 (3)	0.361 (2)	0.0667
H(8A)	0.637 (4)	0.195 (4)	0.439 (2)	0.0862
H(9A)	0.620 (4)	0.195 (4)	0.569 (3)	0.0904
H(10A)	0.488 (3)	0.295 (3)	0.611 (2)	0.0632
<i>(b) BC(B)</i>				
C(1B)	0.6819 (4)	0.9422 (5)	-0.1026 (3)	0.0523
C(2B)	0.7627 (5)	1.0051 (5)	-0.1198 (3)	0.0635
C(3B)	0.8278 (5)	1.0620 (5)	-0.0655 (4)	0.0709
C(4B)	0.8116 (4)	1.0561 (5)	0.0062 (3)	0.0611
N(5B)	0.7159 (3)	0.9869 (3)	0.0983 (2)	0.0535
N(6B)	0.6412 (3)	0.9294 (3)	0.1204 (2)	0.0501
C(7B)	0.4895 (5)	0.8154 (5)	0.0998 (3)	0.0566
C(8B)	0.4170 (5)	0.7575 (5)	0.0540 (4)	0.0677
C(9B)	0.4228 (5)	0.7542 (5)	-0.0211 (4)	0.0704
C(10B)	0.5005 (5)	0.8087 (4)	-0.0500 (3)	0.0569
C(11B)	0.5774 (4)	0.8701 (4)	-0.0044 (3)	0.0388
C(12B)	0.6607 (4)	0.9324 (4)	-0.0288 (2)	0.0395
C(13B)	0.7279 (4)	0.9914 (4)	0.0242 (3)	0.0419
C(14B)	0.5701 (4)	0.8718 (4)	0.0712 (3)	0.0399
H(1B)	0.634 (3)	0.903 (4)	-0.133 (2)	0.0604
H(2B)	0.769 (3)	1.017 (4)	-0.171 (2)	0.0833
H(3B)	0.889 (4)	1.096 (4)	-0.078 (3)	0.0845
H(4B)	0.852 (4)	1.093 (4)	0.039 (2)	0.0738
H(7B)	0.486 (4)	0.826 (4)	0.144 (2)	0.0683
H(8B)	0.369 (4)	0.722 (4)	0.075 (3)	0.0853
H(9B)	0.368 (4)	0.717 (4)	-0.054 (2)	0.0911
H(10B)	0.503 (3)	0.806 (3)	-0.101 (2)	0.0655

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
<i>(c) DDQ</i>				
C(1)	0.1745 (4)	0.5782 (4)	0.2767 (2)	0.0426
C(2)	0.1360 (4)	0.4556 (4)	0.2683 (2)	0.0441
C(3)	0.1946 (4)	0.3710 (4)	0.2484 (2)	0.0409
C(4)	0.3028 (4)	0.3899 (4)	0.2333 (2)	0.0443
C(5)	0.3401 (4)	0.5132 (4)	0.2402 (2)	0.0363
C(6)	0.2806 (4)	0.5988 (4)	0.2594 (2)	0.0358
C(7)	0.3175 (4)	0.7172 (5)	0.2629 (3)	0.0510
C(8)	0.4444 (5)	0.5300 (5)	0.2252 (3)	0.0554
Cl(2)	0.0118 (1)	0.4364 (1)	0.2844 (1)	0.0713
Cl(3)	0.1515 (1)	0.2304 (1)	0.2377 (1)	0.0701
N(7)	0.3434 (4)	0.8100 (4)	0.2644 (3)	0.0789
N(8)	0.5279 (4)	0.5445 (5)	0.2151 (2)	0.0798
O(1)	0.1232 (3)	0.6561 (3)	0.2968 (2)	0.0581
O(4)	0.3578 (3)	0.3128 (3)	0.2158 (2)	0.0682

reported for the uncomplexed BC (van der Meer, 1972) and DDQ (Zanotti, Bardi & Del Pra, 1980). The molecular dimensions of BC also agree rather well with those found in its tetracyanoethylene complex (Shmueli & Mayorchik, 1981) of similar structure and donor-acceptor composition to the present one. Best-plane calculations (*cf.* Table 3) show that the BC molecules are nearly planar with a few possibly significant deviations from their best planes. The general trend of these deviations can be described as a slight folding of the two molecules about their long axes. The deviations of DDQ atoms from the best plane of the quinoid ring are much more significant and it is interesting to point out that they follow a similar pattern to that observed in the uncomplexed DDQ (Zanotti *et al.*, 1980). It thus appears that the lack of planarity in DDQ as a whole is caused mainly by intramolecular interactions. The disparity of DDQ's environments in its (present) complexed and uncomplexed states supports this impression.

Packing arrangement

The overall view of the structure is presented in Fig. 2(a). It is seen that a nearly flat layer of DDQ molecules is enclosed between two crystallographically independent layers of the BC's, and the crystal structure can thus be described as a sequence of molecular layers, $\dots BC(A)-DDQ-BC(B)-DDQ\dots$, perpendicular to the e^* direction. Fig. 3 displays a more detailed view of the interlayer association. Each DDQ molecule is enclosed between two nearly coplanar BC's which have their mean planes nearly perpendicular to the mean plane of the acceptor, their long axes being nearly parallel to a line which intersects the C(1)-C(2) and C(4)-C(5) bonds of DDQ.† Both BC's form short

† The angles between the plane normals, relevant to Fig. 3, are: 80.6, 84.4 and 4.5° for BC(A)-DDQ, BC(B)-DDQ and BC(A)-BC(B) respectively.

Table 2. Bond distances (Å) and angles (°) and their standard deviations

The numbering refers to Fig. 1. The C—H bond distances, in BC(A) and BC(B), range from 0.83 to 0.98 Å with an average e.s.d. of 0.05 Å.

DDQ

C(1)—C(2)	1.501 (7)	C(2)—Cl(2)	1.695 (5)
C(2)—C(3)	1.319 (7)	C(3)—Cl(3)	1.717 (4)
C(3)—C(4)	1.488 (7)	C(4)—O(4)	1.210 (6)
C(4)—C(5)	1.502 (7)	C(5)—C(8)	1.433 (8)
C(5)—C(6)	1.329 (7)	C(8)—N(8)	1.139 (8)
C(6)—C(1)	1.476 (7)	C(6)—C(7)	1.445 (7)
C(1)—O(1)	1.204 (6)	C(7)—N(7)	1.120 (8)

	BC(A)	BC(B)
C(1)—C(2)	1.361 (8)	1.348 (9)
C(2)—C(3)	1.385 (8)	1.389 (8)
C(3)—C(4)	1.365 (9)	1.364 (9)
C(4)—C(13)	1.401 (8)	1.394 (8)
C(13)—N(5)	1.379 (6)	1.392 (6)
N(5)—N(6)	1.291 (6)	1.285 (6)
N(6)—C(14)	1.376 (6)	1.380 (6)
C(14)—C(7)	1.402 (7)	1.393 (8)
C(7)—C(8)	1.356 (8)	1.357 (8)
C(8)—C(9)	1.397 (10)	1.393 (10)
C(9)—C(10)	1.355 (9)	1.357 (9)
C(10)—C(11)	1.402 (7)	1.411 (7)
C(11)—C(12)	1.418 (7)	1.420 (7)
C(12)—C(13)	1.405 (6)	1.400 (6)
C(12)—C(1)	1.416 (7)	1.423 (7)
C(11)—C(14)	1.393 (7)	1.405 (7)

DDQ

C(1)—C(2)—C(3)	121.8 (4)	C(2)—C(3)—Cl(3)	122.5 (4)
C(2)—C(3)—C(4)	122.7 (4)	C(4)—C(3)—Cl(3)	114.8 (3)
C(3)—C(4)—C(5)	115.2 (4)	O(4)—C(4)—C(3)	123.3 (4)
C(4)—C(5)—C(6)	122.1 (5)	O(4)—C(4)—C(5)	121.5 (5)
C(5)—C(6)—C(1)	122.1 (4)	C(8)—C(5)—C(4)	114.5 (4)
C(6)—C(1)—C(2)	116.0 (4)	C(8)—C(5)—C(6)	123.4 (5)
O(1)—C(1)—C(2)	122.8 (4)	N(8)—C(8)—C(5)	178.3 (5)
O(1)—C(1)—C(6)	121.2 (4)	C(7)—C(6)—C(5)	120.7 (5)
C(1)—C(2)—Cl(2)	114.8 (4)	C(7)—C(6)—C(1)	117.2 (4)
C(3)—C(2)—Cl(2)	123.4 (4)	N(7)—C(7)—C(6)	177.9 (6)

	BC(A)	BC(B)
C(1)—C(2)—C(3)	120.9 (6)	120.5 (6)
C(2)—C(3)—C(4)	120.9 (6)	121.1 (6)
C(3)—C(4)—C(13)	118.8 (5)	118.6 (5)
C(4)—C(13)—C(12)	121.6 (5)	122.2 (5)
C(13)—C(12)—C(1)	117.2 (4)	116.4 (5)
C(12)—C(1)—C(2)	120.6 (5)	121.3 (5)
C(11)—C(12)—C(13)	116.2 (4)	117.4 (4)
C(12)—C(13)—N(5)	123.3 (4)	121.6 (4)
C(13)—N(5)—N(6)	119.9 (4)	120.9 (4)
N(5)—N(6)—C(14)	120.3 (4)	120.9 (4)
N(6)—C(14)—C(11)	123.2 (4)	122.0 (4)
C(14)—C(11)—C(12)	117.0 (4)	117.2 (4)
C(9)—C(10)—C(11)	120.7 (5)	120.5 (5)
C(10)—C(11)—C(14)	117.9 (5)	117.5 (5)
C(11)—C(14)—C(7)	120.7 (4)	121.1 (4)
C(14)—C(7)—C(8)	120.1 (5)	119.5 (5)
C(7)—C(8)—C(9)	119.4 (6)	120.4 (6)
C(8)—C(9)—C(10)	121.2 (5)	120.9 (5)
C(4)—C(13)—N(5)	115.2 (4)	116.2 (4)
N(6)—C(14)—C(7)	116.0 (4)	116.9 (5)
C(10)—C(11)—C(12)	125.1 (5)	125.3 (5)
C(11)—C(12)—C(1)	126.6 (4)	126.2 (4)

contacts with the central part of DDQ *via* their N—N bridges (Fig. 3a) which appear to have their lone-pair lobes pointing at the π system of the acceptor. It is seen that the relevant N...C(carbonyl) contact distances are shorter, by a few tenths of an ångström, than the sum of the corresponding van der Waals radii, and thus strongly suggest an attractive interaction between DDQ and the BC 'vise' in which DDQ is enclosed (Fig. 3b).

The above mode of donor—acceptor association was first reported in the preliminary description of the present structure (Shaanan *et al.*, 1978), and has since been observed in the BC:tetracyanoethylene (2:1) compound (Shmueli & Mayorchik, 1980). This arrangement differs quite radically from the well-known face-to-face packing of molecules with different electron affinities. In the present case this seems to be enabled by intralayer association of dipolarly coupled BC molecules (Fig. 2b) and by the overlap of the exposed N lone-pair lobes of BC with the π system of DDQ.

The structure of the BC(B) layer (not shown) is remarkably similar to that of BC(A) and both layers strikingly resemble the arrangement of BC molecules in the uncomplexed crystal (van der Meer, 1972). These three occurrences of BC 'dimers' differ mainly in the degree of intradimer overlap. While in the uncomplexed BC (Fig. 4c) the N atoms are hidden in the overlap region, in BC(A) and BC(B) (Fig. 4a,b) they are outside this region, thus being able to participate conveniently in interlayer interactions. The mean intradimer interplanar distances are 3.50, 3.53 and 3.49 Å for BC(A), BC(B) and the uncomplexed BC respectively.

Table 3. Deviations of the atoms from the best planes of BC(A), BC(B) and the quinoid ring of DDQ along with their e.s.d.'s

Intra-atomic covariances were used in the calculation of the e.s.d.'s, $\sigma(\Delta)$ (Å), of the atomic deviations Δ (Å) from the best molecular planes (Shmueli, 1981). The deviations and their e.s.d.'s are given in units of 10^{-3} Å.

BC(A)		BC(B)		DDQ	
	$\Delta[\sigma(\Delta)]$		$\Delta[\sigma(\Delta)]$		$\Delta[\sigma(\Delta)]$
C(1A)	9 (6)	C(1B)	21 (6)	C(1)	-14 (4)
C(2A)	-9 (6)	C(2B)	-1 (6)	C(2)	4 (4)
C(3A)	-23 (5)	C(3B)	-23 (6)	C(3)	9 (4)
C(4A)	-11 (6)	C(4B)	-28 (6)	C(4)	-11 (4)
N(5A)	12 (4)	N(5B)	6 (4)	C(5)	1 (4)
N(6A)	14 (4)	N(6B)	26 (4)	C(6)	11 (4)
C(7A)	-18 (5)	C(7B)	-15 (6)	C(7)	74 (5)
C(8A)	-25 (6)	C(8B)	-29 (6)	C(8)	-16 (5)
C(9A)	-2 (7)	C(9B)	-16 (7)	Cl(2)	55 (2)
C(10A)	16 (6)	C(10B)	9 (6)	Cl(3)	44 (2)
C(11A)	16 (5)	C(11B)	23 (5)	N(7)	153 (5)
C(12A)	17 (5)	C(12B)	19 (5)	N(8)	-57 (5)
C(13A)	4 (5)	C(13B)	-8 (5)	O(1)	-56 (3)
C(14A)	1 (4)	C(14B)	15 (5)	O(4)	-23 (4)

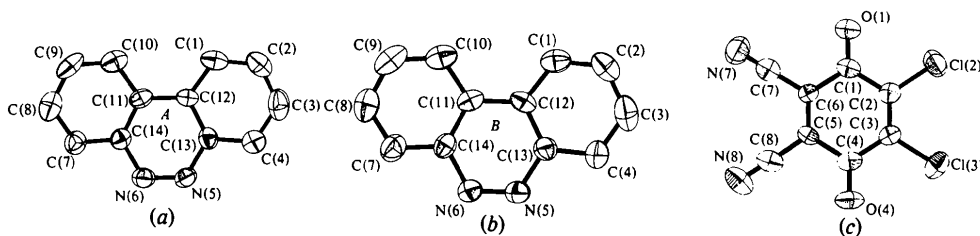


Fig. 1. Projections of the constituent molecules of BC:DDQ onto their best planes, including 50% probability ellipsoids. (a) BC(A), (b) BC(B), (c) DDQ.

The similarity of the packing arrangements of BC in the complexed and uncomplexed states does not apply to the DDQ molecules. A projection of the DDQ layer onto the *ab* plane (Fig. 2c) reveals molecules in orientations which follow the cross-hatched arrangement of the BC's. There are no unacceptably short distances in the DDQ layer, which appears to be stabilized, in part, by dipole-dipole interactions, evident from the Figure.

Some intermolecular distances, relevant to the above description, are summarized in Table 4.

The alternating layers of BC and DDQ, as well as the short C(DDQ)⋯N(BC) distances (Figs. 2 and 3) are probably due, in part, to a charge-transfer interaction which stabilizes this arrangement. The existence of such an interaction is first suggested by the colours of the crystals (BC is bright yellow, the crystals of DDQ are dark yellow while those of BC:DDQ are red and appear orange-red when sufficiently thin) and is also supported by some preliminary observations of emission and absorption spectra of the crystals involved.

Crystals of BC have a strong emission band at $\lambda_{\max} = 480$ nm (de Vries Reilingh, Rettschnick & Hoytink, 1971) which can be readily recorded. This band disappears almost completely in the emission spectrum of BC:DDQ and a new broad band is observed at 610 nm, with intensity appreciably weaker than that of the fluorescence emitted by pure BC (Dodiuk, 1978).

Absorption spectra of powdered BC, DDQ and BC:DDQ were recorded in the 300–750 nm range, using KBr pellets. It was found from several measurements at different concentrations that the absorption spectrum of BC:DDQ contains a new broad band with maximum at about 430 nm and a moderate intensity, as well as some less well defined features at shorter wavelengths.

The above observations call for a careful spectroscopic study, which might define the nature of the charge transfer involved, but leave little doubt as to the probable occurrence of this phenomenon in BC:DDQ crystals. It is seen that the overlap of the π systems of BC and DDQ in crystalline BC:DDQ is nearly minimized and thus a π - π^* interaction between donor

and acceptor seems to be ruled out. A probable alternative is an n - π^* charge-transfer interaction which involves the N lone pairs of BC as n donors. This explanation is consistent with the known ability of azaaromatic molecules to function, potentially, both as n donors and as π donors (Kearns, Gardner & Carmody, 1967; Foster, 1969).

Table 4. Short intermolecular distances (Å) in BC:DDQ and their standard deviations

The first atom in a pair belongs to the reference asymmetric unit (Table 1) while the second is generated by a symmetry operation defined as follows: (i) $-\frac{1}{2} + x, \frac{1}{2} - y, z$, (ii) x, y, z .

C(1)⋯N(6B ¹)	2.853 (6)	C(1)⋯N(5A ¹¹)	2.921 (6)
C(2)⋯N(6B ¹)	3.034 (6)	C(2)⋯N(5A ¹¹)	3.173 (6)
C(3)⋯N(5B ¹)	3.252 (6)	C(4)⋯N(6A ¹¹)	2.940 (5)
C(3)⋯N(6B ¹)	3.301 (6)	C(5)⋯N(5A ¹¹)	3.219 (6)
C(4)⋯N(5B ¹)	2.956 (6)	C(5)⋯N(6A ¹¹)	2.870 (5)
C(5)⋯N(5B ¹)	2.888 (5)	C(6)⋯N(5A ¹¹)	2.985 (6)
C(5)⋯N(6B ¹)	3.245 (6)	C(6)⋯N(6A ¹¹)	3.178 (6)
C(6)⋯N(5B ¹)	3.134 (5)		
C(6)⋯N(6B ¹)	2.957 (5)		

Table 5. A short summary of rigid-body-motion analysis

The r.m.s. amplitudes of librational and translational motion are calculated from the eigenvalues of the translation (T) and libration (L) tensors. The calculation for DDQ is based on its quinonic system only and hence the apparent rigidity. The values of n and m used for evaluating the r.m.s. discrepancies $\langle(\Delta U)^2\rangle_{n-m}^{1/2}$ are $n = 84$, $m = 20$ for BC(A) and BC(B) and $n = 48$, $m = 20$ for the quinonic fragment of DDQ. The translation tensor is referred to an origin which symmetrizes the screw-motion tensor S (not shown).

	DDQ	BC(A)	BC(B)
L	5.45°	4.92°	5.16°
	5.10	3.72	3.68
	3.95	2.99	3.25
T	0.221 Å	0.220 Å	0.220 Å
	0.184	0.178	0.187
	0.103	0.169	0.165
$\langle(\Delta U)^2\rangle_{n-m}^{1/2}$	0.0041 Å ²	0.0050 Å ²	0.0054 Å ²
	$\langle\sigma^2(U^U)\rangle^{1/2}$	0.0034	0.0035

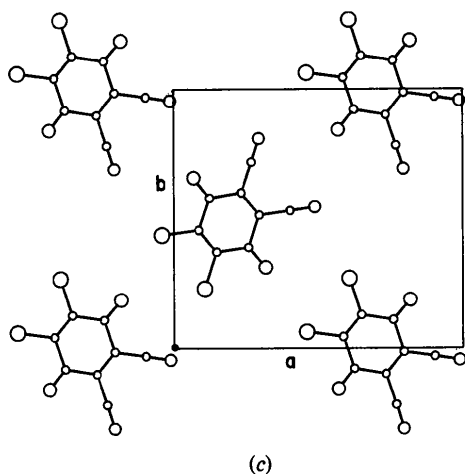
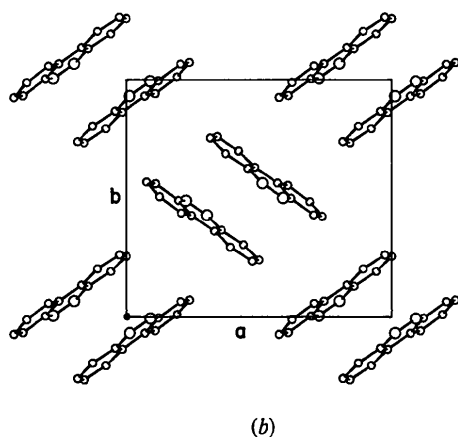
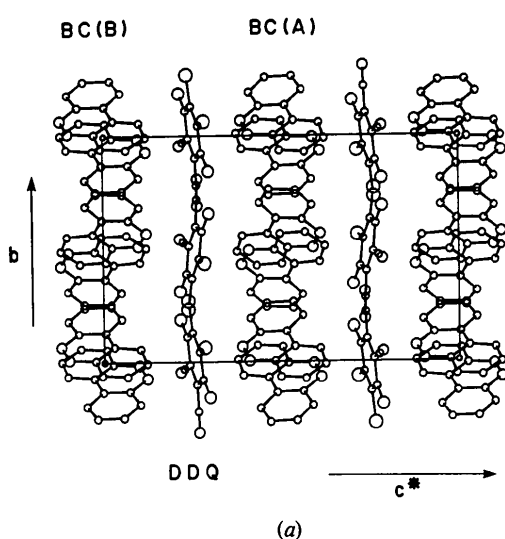


Fig. 2. Packing arrangement in BC:DDQ. (a) Projection of the structure down the a axis, (b) projection of the BC(A) layer from (a) onto the ab plane, (c) projection of the DDQ layer from (a) onto the ab plane. The unit-cell origin is projected in the lower left corner of each of the unit-cell outlines.

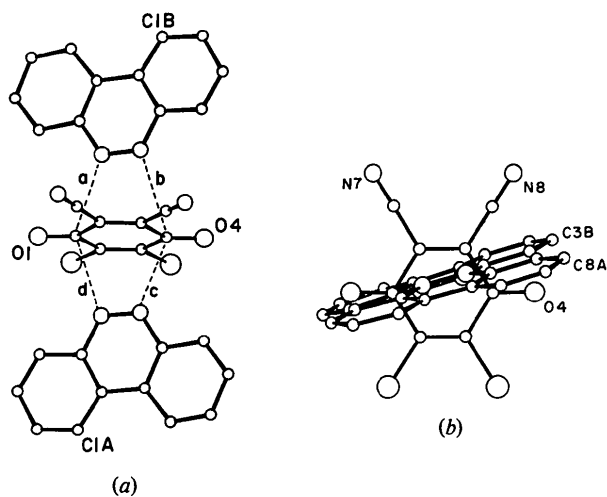


Fig. 3. Two views of the (2:1) BC:DDQ complex. (a) Projection down a direction close to the plane normals of BC(A) and BC(B). The short distances indicated are: $a \equiv C(1) \cdots N(6B) = 2.853$ (6), $b \equiv C(4) \cdots N(5B) = 2.956$ (6), $c \equiv C(4) \cdots N(6A) = 2.940$ (5) and $d \equiv C(1) \cdots N(5A) = 2.921$ (6) Å. (b) Projection of the complex onto the best plane of DDQ.

Thermal motion

The two BC molecules exhibit similar patterns of motional behaviour, as would be expected from the similarity of their environments (*cf.* Fig. 1). These two molecules and, to a smaller extent, the DDQ molecule were shown to behave as approximately rigid bodies, by an analysis of their atomic vibration tensors in terms of the corresponding libration, translation and screw-motion tensors (Schomaker & Trueblood, 1968). A short summary of the results is given in Table 5. The directions of the largest librations of the BC's correspond fairly well to those of their smallest moments of inertia while such correspondence is appreciably worse in the case of DDQ. As for the translation tensors, their principal values are associated, in each case, with directions close to the molecular axes.

We have also tried to supplement the above description of the structure by a calculation of potential-energy profiles corresponding to the rotational and translational motions of the constituent molecules (*cf.* Shmueli & Goldberg, 1973). The calculation shows that all the 18 profiles have nearly parabolic shapes and their minima deviate from their expected positions (*i.e.* from the structure) by less than 1° and less than 0.2 Å for rotation and translation profiles respectively, except for rotations of BC(A) and BC(B) about their long axes, for which deviations of -1.2 and -3.8° have been obtained. The half widths of the profiles, at height kT above their minima, agree reasonably well with the r.m.s. principal translation amplitudes of the three molecules but the agreement is poorer as far as the librations are concerned. It appears that the anisotropy of thermal motion is controlled, to a

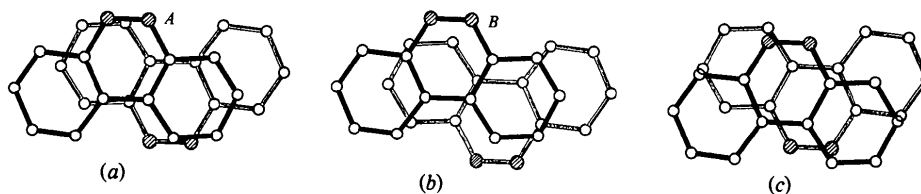


Fig. 4. Overlap diagrams of BC 'dimers' in (a) BC (A) layers, (b) BC (B) layers and (c) uncomplexed BC (van der Meer, 1972).

significant extent, by interactions other than those of the London-van der Waals types, which form the basis of the potential parameters employed in this calculation. Hence, in spite of the apparent harmonic behaviour of the molecular motion it seems that a proper lattice-dynamical study of this interesting compound will require more sophisticated expressions for the interatomic force constants than those usually employed.

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