

dans la phase (VIII) (*cf.* partie I), nous pouvons même considérer cette phase (VIII) comme la première étape de la fusion de la phase cristalline (IX) du TBBA.

Références

- CHARVOLIN, J. & DELOCHE, B. (1976). *J. Phys. Colloq.* **C3**, 69–72.
- COMÈS, R., LAMBERT, M. & GUINIER, A. (1968). *Solid State Commun.* **6**, 715–719.
- COMÈS, R., LAMBERT, M. & GUINIER, A. (1970). *Acta Cryst.* **A26**, 244–254.
- COTRAIT, M., DESTRADE, C. & GASPAROUX, H. (1975). *Acta Cryst.* **B31**, 2704–2706.
- DELOCHE, B., CHARVOLIN, J., LIEBERT, L. & STREZELECKI, L. (1975). *J. Phys. Colloq.* **C1**, 21–26.
- DESCAMPS, M. & COULON, G. (1976). *Solid State Commun.* **20**, 379–383.
- DOUCET, J., LEVELUT, A. M. & LAMBERT, M. (1973). *Mol. Cryst. Liq. Cryst.* **24**, 317–329.
- DOUCET, J., LEVELUT, A. M. & LAMBERT, M. (1974). *Phys. Rev. Lett.* **32**(6), 301–303.
- DOUCET, J., MORNON, J.-P., CHEVALIER, R. & LIFCHITZ, A. (1977). *Acta Cryst.* **B33**, 1701–1710.
- GUINIER, A. (1964). *Théorie et Technique de la Radio-cristallographie*, p. 492. Paris: Dunod.
- HERVET, H., VOLINO, F., DIANOUX, A. J. & LECHNER, R. E. (1974). *J. Phys. Radium*, **35**, L151–L155.
- KRIGBAUM, W. R. & BARBER, P. G. (1971). *Acta Cryst.* **B27**, 1884–1891.
- KRIGBAUM, W. R. & TAGA, T. (1974). *Mol. Cryst. Liq. Cryst.* **28**, 85–98.
- LEVELUT, A. M. (1976). *J. Phys. Colloq.* **C3**, 51–54.
- LEVELUT, A. M., DOUCET, J. & LAMBERT, M. (1974). *J. Phys. Radium*, **35**, 773–779.
- LEVELUT, A. M. & LAMBERT, M. (1971). *C.R. Acad. Sci. Paris, Sér. B*, **272**, 1018–1021.
- LUZ, Z. & MEIBOOM, S. (1974). *J. Chem. Phys.* **61**(5), 1758–1765.
- TAYLOR, T. R., ARORA, S. L. & FERGASON, J. L. (1970). *Phys. Rev. Lett.* **25**(11), 722–726.
- URBACH, W. & BILLARD, J. (1972). *C.R. Acad. Sci. Paris*, **274**, 1287–1290.
- VRIES, A. DE (1974). *J. Chem. Phys.* **61**(6), 2367–2371.

Acta Cryst. (1977). **B33**, 1716–1724

Molecular Compounds and Complexes.

X.* The Crystal Structure of the π -Molecular Compound Benzo[*c*]phenanthrene–2,3-Dichloro-5,6-dicyanobenzoquinone

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The influence of π -molecular compound formation on the deviations from planarity of the overcrowded aromatic molecule benzo[*c*]phenanthrene has been studied by determining the crystal structure of benzo[*c*]phenanthrene–2,3-dichloro-5,6-dicyanobenzoquinone [$a = 10.953(2)$, $b = 16.090(3)$, $c = 13.827(3)$ Å, $\beta = 122.63(1)^\circ$; space group $P2_1/c$; $Z = 4$]. The structure was solved by direct methods and refined to $R = 0.065$ for 3385 observed reflexions. Stacks with alternating donor and acceptor molecules extend in the c direction. The acceptor molecule takes on two orientations, with population ratio $\sim 4:1$. Comparison of the structures of the benzo[*c*]phenanthrene molecule here and in its pure crystals shows that it is significantly less distorted from planarity in the present molecular compound, but that bond lengths and angles remain practically unchanged. The diminished distortion from planarity may be due to the donor–acceptor interaction.

1. Introduction

Most crystallographic studies of π -molecular compounds have been made on systems in which the donor

and acceptor moieties are essentially rigid, planar molecules. Comparison of the molecular geometries (especially bond lengths and angles) of the components in the crystalline molecular compound with those found in the structures of the pure components has consistently shown virtually no change upon molecular-compound formation. This is not surprising since the forces required to alter these geometrical features are

* Part IX: Herbstein, Kaftory & Regev (1976).

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larger than those involved in molecular-compound formation.

In the large majority of the π -molecular compounds studied to date there is some form of infinite stack of alternating donor and acceptor molecules, strongly suggesting the presence of a principal component of the charge-transfer forces perpendicular to the molecular planes. For some non-planar donors (*e.g.* hexahelicene, phenothiazine, dibenzo[*g,p*]chrysene* and benzo[*c*]phenanthrene) this component may be sufficient to induce a change in the conformation of the molecule, in particular in its deviations from planarity.

The π -molecular compound of benzo[*c*]phenanthrene (BP) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) is an attractive model system for examining the effect of molecular-compound formation on the degree of distortion of a non-planar component. The structure of the donor has been studied (Herbstein & Schmidt, 1954; Hirshfeld, Sandler & Schmidt, 1963) and thus provides a standard geometry for comparison with that found in the molecular compound.

2. Experimental

Crystals of the 1:1 molecular compound suitable for X-ray studies were grown by vapour diffusion of *n*-pentane into a chloroform solution of approximately equimolar quantities of the two components (Stout & Jensen, 1968). The crystals were dark, opaque prisms elongated along *c*.

The space group ($P2_1/c$) and approximate cell dimensions were obtained from photographs. With the appropriate transformation they conform to those previously reported in the non-standard space group $B2_1/c$ (Herbstein, 1971). More accurate cell dimensions (Table 1) were obtained from a least-squares fit of four-circle diffractometer measurements of 2θ values at 20°C for 15 reflexions with $47.5^\circ \leq 2\theta \leq 50.73^\circ$ (Mo $K\alpha$).

A prism $0.18 \times 0.34 \times 0.50$ mm was mounted on a Syntex $P\bar{I}$ autodiffractometer with *c* nearly parallel to

* Also called tetrabenzonaphthalene.

Table 1. *Crystal data*

Benzo[<i>c</i>]phenanthrene-2,3-dichloro-5,6-dicyano- <i>p</i> -benzoquinone (BP-DDQ), $C_{18}H_{12} \cdot C_8N_2O_2Cl_2$	
Monoclinic	FW 455.01
Space group $P2_1/c$	M.p. 137–140°C
$a = 10.953$ (2) Å	$Z = 4$
$b = 16.090$ (3)	$D_m = 1.454$ g cm ⁻³
$c = 13.827$ (3)	$D_x = 1.471$
$\beta = 122.63$ (1)°	$F(000) = 928$
$V = 2052.19$ Å ³	$\mu(\text{Cu } K\alpha) = 30.7$ cm ⁻¹
$\lambda(\text{Mo } K\alpha) = 0.70926$ Å	

the φ axis of the diffractometer. Intensities were measured with graphite-monochromatized Cu $K\alpha$ radiation and the θ - 2θ scanning technique. The variable scanning speed employed ranged from 2 to 24° min⁻¹, according to a rapid prescan of the peak intensity of the current reflexion. A total average decrease of 4% in the intensities of the four monitor reflexions was taken into account in the data reduction.

The intensities of 3852 unique reflexions (about 85% of the Cu sphere) were measured for $\sin \theta/\lambda < 0.60$ Å⁻¹; 3153 of these, whose measured intensity was more than $2.5\sigma(I)$, were considered observed. Corrections were made for Lorentz and polarization factors and for absorption (Coppens, Leiserowitz & Rabinovich, 1965). The last correction was made after nine cycles of refinement. Intensities were assigned variances $\sigma^2(I)$, according to counting statistics and a factor to account for instrumental instability, *i.e.* $\sigma^2(I) = [\sigma_c^2(I) + (0.03I)^2]$, where $\sigma_c^2(I)$ is the variance based on counting statistics.

3. Structure determination and refinement

3.1. Solution of the structure

The intensities were placed on an approximately absolute scale by Wilson's (1942) method, and normalized structure factor magnitudes (E) were derived. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). From 326 reflexions with $|E| > 1.68$, 16 sets of signs for 322 reflexions were obtained. The set chosen for calculation of the E map was that with the highest absolute figure of merit (1.028) and the lowest residual (34.17). The resulting map gave a clear view of the entire structure except in the region of the $-\text{C}\equiv\text{N}$ groups, where only weak and diffuse peaks appeared. The four atoms in these two groups were added on the basis of chemical considerations.

3.2. Refinement

The structure was refined in the block-diagonal approximation, the blocks corresponding to the two molecular moieties. First, coordinates of non-hydrogen atoms and an overall temperature factor were refined for reflexions with $\sin \theta/\lambda < 0.4$ Å⁻¹. Individual isotropic temperature factors were then introduced ($\sin \theta/\lambda < 0.5$ Å⁻¹). At this stage the $\text{C}\equiv\text{N}$ bonds were very short (0.95 Å). Suspecting that this was an anomaly of the refinement we shifted the two N atoms to positions calculated on the basis of more reasonable $\text{C}\equiv\text{N}$ lengths. Two additional cycles resulted in a shortening of the $\text{C}\equiv\text{N}$ lengths to the value obtained previously. Anisotropic temperature factors were then introduced ($\sin \theta/\lambda < 0.52$ Å⁻¹). Expected H positions were calculated and were included in the following

cycles (observed reflexions and the unobserved for which $F_c > kF_o$ on the previous cycle). In the last three cycles the three strongest reflexions (020, 110 and $\bar{1}14$) were given zero weight because of extinction. The temperature factors of H[BP C(1)] and H[BP C(12)] were fixed at 0.04 \AA^2 as the previous cycles had yielded excessively large shifts for them. The final R is 0.065 ($R_w = 0.028$) for the 3385 observed reflexions and those for which $F_c > kF_o$. For all the reflexions (3852, including unobserved) $R = 0.068$. The goodness-of-fit is 3.17 , suggesting that the weighting scheme was not ideal. The function minimized was $\sum w(|kF_o|^2 - |F_c|^2)^2$, where $w = 1.0/\sigma^2(F_o^2)$. Scattering factors were taken from *In-*

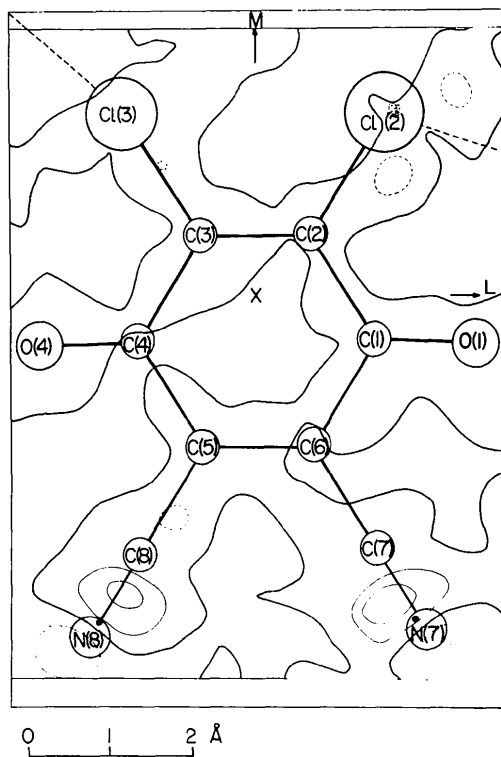
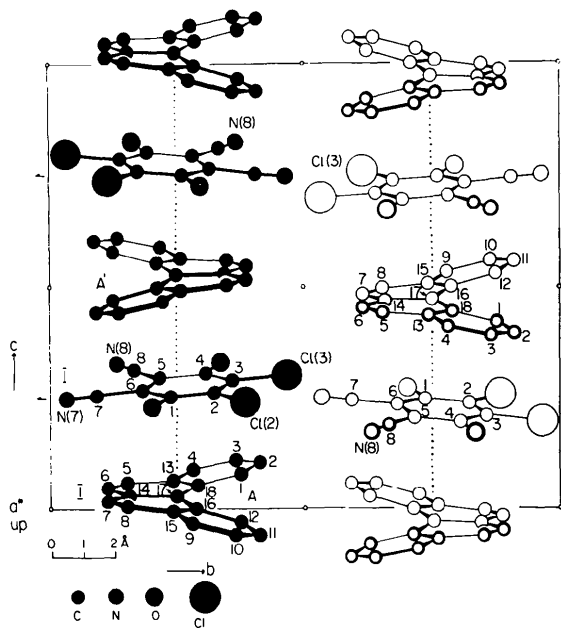
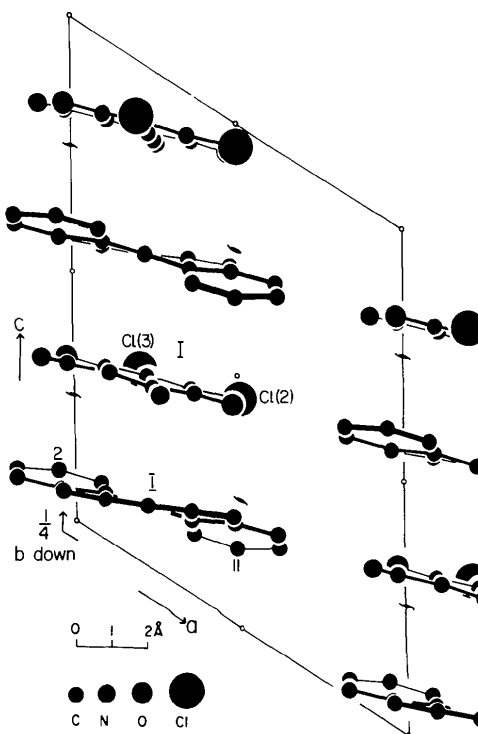


Fig. 1. Difference map in the DDQ plane, contours at intervals of 1 e \AA^{-3} . The heavy line shows the zero contour and the broken line the 0.5 e \AA^{-3} contour; other contours are at intervals of 1 e \AA^{-3} (dotted lines show negative regions). The coordinate system from the best-plane calculation (§4.2.2) is shown together with the principal orientation of the DDQ molecule (the structure factors used in the difference synthesis were calculated on the basis of this model). The peaks between C and N atoms of the CN groups are ascribed to Cl atoms of the minor orientation. The positions to which the N atoms refined when disorder was ignored are shown by dots in N(7) and N(8). The dashed line from Cl(3) goes up to H[BP C(5)]ⁱⁱⁱ and that from Cl(2) goes down to H[BP C(4)]^{iv} (symmetry codes of molecules are given in Table 3).



(a)



(b)

Fig. 2. (a) Projection of structure on the (100) plane. The two reference molecules (coordinates in Table 2) are designated (i) (the symmetry code is in Table 3). The two enantiomers of BP are designated *A* and *A'*. (b) Projection of part of the structure on (010).

Table 2. Final fractional coordinates ($\times 10^4$, for H $\times 10^3$)

E.s.d.'s in parentheses are in units of the least significant digits. H atoms are numbered according to the C atoms to which they are bonded.

	x	y	z
BP			
C(1)	756 (4)	3748 (2)	1097 (3)
C(2)	-535 (5)	4115 (3)	789 (4)
C(3)	-1796 (4)	3651 (3)	298 (4)
C(4)	1747 (4)	2814 (3)	162 (4)
C(5)	-384 (4)	1538 (3)	421 (4)
C(6)	876 (5)	1144 (3)	829 (4)
C(7)	3511 (5)	1141 (3)	1679 (4)
C(8)	4776 (4)	1533 (3)	2069 (4)
C(9)	6127 (4)	2804 (3)	2253 (4)
C(10)	6181 (4)	2620 (3)	2053 (4)
C(11)	4901 (5)	4089 (3)	1056 (4)
C(12)	3622 (4)	3724 (2)	1230 (3)
C(13)	-435 (4)	2422 (3)	475 (3)
C(14)	2195 (4)	1588 (2)	1239 (3)
C(15)	4814 (4)	2410 (3)	1954 (3)
C(16)	3523 (4)	2884 (2)	1479 (3)
C(17)	2186 (4)	2472 (2)	1208 (3)
C(18)	861 (4)	2893 (2)	912 (3)
H[BP C(1)]	162 (5)	404 (3)	154 (4)
H[BP C(2)]	-63 (7)	473 (4)	93 (5)
H[BP C(3)]	-256 (6)	386 (4)	14 (5)
H[BP C(4)]	-261 (7)	243 (4)	-17 (5)
H[BP C(5)]	-119 (6)	125 (4)	10 (4)
H[BP C(6)]	98 (7)	54 (4)	88 (5)
H[BP C(7)]	343 (6)	51 (4)	170 (5)
H[BP C(8)]	559 (6)	129 (4)	237 (5)
H[BP C(9)]	689 (7)	248 (4)	262 (5)
H[BP C(10)]	701 (8)	391 (4)	222 (6)
H[BP C(11)]	493 (6)	473 (4)	123 (5)
H[BP C(12)]	280 (5)	401 (3)	81 (4)
DDQ			
C(1)	3648 (4)	2351 (3)	4058 (4)
C(2)	3472 (5)	3246 (3)	4098 (4)
C(3)	2209 (5)	3594 (3)	3822 (4)
C(4)	897 (4)	3076 (3)	3445 (4)
C(5)	1060 (4)	2170 (3)	3393 (4)
C(6)	2327 (4)	1825 (3)	3666 (3)
C(7)	2498 (5)	933 (4)	3611 (4)
C(8)	-249 (5)	1641 (4)	3033 (4)
Cl(2)	4987 (2)	3853 (1)	4521 (1)
Cl(3)	1979 (2)	4663 (1)	3847 (1)
N(7)	2548	340	3558*
N(8)	-1047	1309	2829*
O(1)	4781 (3)	2018 (2)	4319 (3)
O(4)	-248 (3)	3373 (2)	3188 (3)

* Parameters of the N atoms were obtained from the refinement of the disordered structure and have no chemical meaning.

4. Results and discussion

4.1. Crystal structure

The projections on the (100) and (010) planes (Fig. 2) show the two components arranged in an alternating

array in mixed stacks. The angle between the plane of the DDQ molecule and the reference plane of BP (see §4.2 for definition) is 6.2° ; because of the non-planarity of BP the exact value of this angle has little physical significance. The component molecules lie approximately in $\{\bar{1}14\}$ planes; the reflexions from these planes are very strong and are accompanied by intense diffuse scattering. The unit cell contains two stacks which are related to one another by the twofold screw axis; the stacks are approximately hexagonally close-packed (Fig. 3). Shorter intermolecular distances are listed in Table 3 and some of these are shown in Fig. 3.

The overlap diagram is shown in Fig. 4. Chemically identical molecules along a stack are related by the operation of the c glide plane. A particular DDQ molecule is located above one phenanthrene portion of the neighbouring BP molecule; the next DDQ molecule in the stack takes up an analogous position and orientation with respect to the other phenanthrene portion of the BP molecule sandwiched between them, and so on, in alternating fashion, along the stack.

Because the stacks are not shifted with respect to one another along the [001] axis, the structure can also be described in terms of alternating sheets of BP and DDQ molecules. Two views based on this description are shown in Fig. 3. The packing of both BP and DDQ molecules in their respective sheets is rather loose and interstack distances are longer than intrastack dis-

Table 3. Intermolecular distances (Å)

Distances involving N atoms are excluded because of the disorder. Criteria for inclusion in table: $d(\text{C} \cdots \text{C})$, $d(\text{C} \cdots \text{O}) \leq 3.30$; $d(\text{C} \cdots \text{H})$, $d(\text{O} \cdots \text{H}) \leq 2.95$; $d(\text{H} \cdots \text{H}) \leq 2.82$ Å.

(a) Donor-acceptor distances along a stack

BP C(1) \cdots DDQ C(3) ⁱ	3.21	H[BP C(1)] \cdots DDQ Cl(3) ^j	3.16
BP C(8) \cdots DDQ O(1) ⁱ	3.21	DDQ O(4) \cdots BP C(5) ⁱⁱ	3.17
BP C(6) \cdots DDQ C(7) ⁱ	3.27	DDQ C(6) \cdots BP C(12) ⁱⁱ	3.15
BP C(14) \cdots DDQ C(7) ^j	3.29	DDQ O(4) \cdots BP C(6) ⁱⁱ	3.26
H[BP C(1)] \cdots DDQ C(3) ⁱ	2.95	DDQ C(7) \cdots H[BP C(9)] ⁱⁱ	2.87

(b) Donor-acceptor distances between stacks

DDQ O(1) \cdots H[BP C(4)] ^{iv}	2.70	H[BP C(10)] \cdots DDQ O(4) ^{vi}	2.69
DDQ Cl(2) \cdots H[BP C(4)] ^{iv}	3.19		

(c) Donor-donor distances

BP C(9) \cdots BP C(4) ^{iv}	3.53	H[BP C(11)] \cdots H[BP C(7)] ^v	2.73
H[BP C(6)] \cdots H[BP C(6)] ^{vii}	2.82	H[BP C(9)] \cdots H[BP C(4)] ^{iv}	2.81

(d) Acceptor-acceptor distances

DDQ Cl(2) \cdots DDQ Cl(3) ^{viii}	3.71
DDQ Cl(3) \cdots DDQ N(8) ⁱⁱⁱ	3.21

Symmetry code

(i)	x, y, z	(vi)	$1 + x, y, z$
(ii)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	(vii)	$-x, -y, -z$
(iii)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	(viii)	$1 - x, 1 - y, 1 - z$
(iv)	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$	(ix)	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$
(v)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	(x)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

tances; thus a description in terms of stacks is *physically* preferable to that in terms of sheets. In the sheets of DDQ molecules there are short distances of 3.21 Å between chains of molecules along [010] (Fig. 3a); there are two chains per unit cell at $z \sim \frac{1}{4}$ and $z \sim \frac{3}{4}$. Comparison with other structures is made in the discussion (§5).

The diagrams of Fig. 3 are drawn for the principal orientation of the DDQ molecule but the minor orientation can be accommodated without necessitating a large relaxation of molecular positions or orientations. If the reference DDQ molecule (i)* is replaced by a DDQ molecule in the minor orientation (i') but the other molecules are left unchanged then $d[\text{N}(8)^{\text{v}} \cdots \text{N}(8)^{\text{iii}}]$ is 2.7 and $d[\text{N}(8)^{\text{v}} \cdots \text{C}(3)^{\text{viii}}]$ is 2.9 Å.†

4.2. Molecular structure

4.2.1. *Benzo[c]phenanthrene*. Although the molecule (Fig. 5) is clearly non-planar, a mean reference plane may be defined through C(3), C(10), C(14), C(16), C(17) and C(18). The equation of this plane is $0.26398X' - 0.02500Y' - 0.96420Z' + 1.062 \text{ Å} = 0$, where X' , Y' and Z' are coordinates in Å in an orthogonal system, related to the crystal system by the transformation matrix

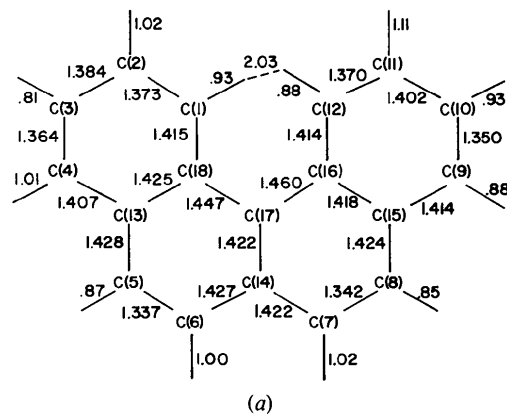
$$\begin{pmatrix} a & 0 & c \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix}.$$

The structure of BP at room temperature has been reported by Hirshfeld, Sandler & Schmidt (1963). As in other charge-transfer molecular compounds, significant differences in bond lengths and angles are not found between the molecules in the BP crystals and in BP-DDQ. Two bonds [C(12)–C(16) and C(2)–C(3)] are 0.023 and 0.030 Å (about 4σ) shorter in the molecular compound, while three angles [C(18)–C(1)–C(2), C(11)–C(12)–C(16) and C(16)–C(15)–C(8)] are larger by 2° (4σ). The non-bonded intramolecular H[BP C(1)]–H[BP C(12)] distance between the overcrowded atoms (2.03 Å) is equal in the two structures.

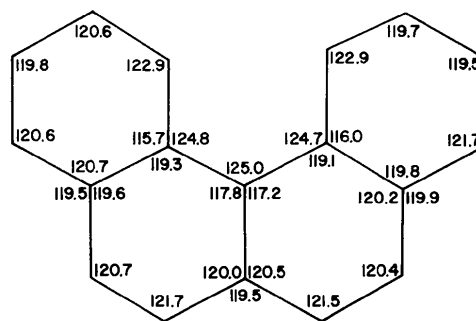
The BP molecule is, however, significantly less distorted from planarity in BP-DDQ than in BP itself. The degree of distortion may be measured by the deviations of atoms from the molecular plane (as defined above) and by the torsion angles about bonds, particularly those through which rings are fused. Most of the deviations from the reference plane in the molecular compound are significantly smaller than those found in BP itself (Fig. 5c); the largest difference is 0.12 Å (17σ

* The molecular identification code is given in Table 3.

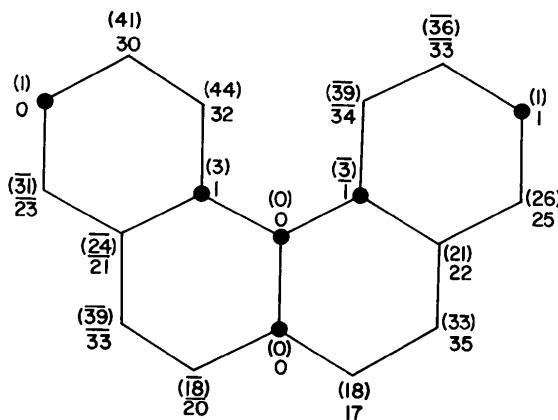
† The numbering of the atoms in the minor orientation is based on the application of a twofold axis *in* the DDQ plane.



(a)



(b)



(c)

Fig. 5. (a) Bond lengths (Å) for BP. E.s.d.'s are $\sim 0.007 \text{ Å}$ ($\sim 0.07 \text{ Å}$ for C–H bonds). (b) Bond angles ($^\circ$) for BP. E.s.d.'s are $\sim 0.4^\circ$. (c) Deviations from planarity (units of 10^{-2} Å) for BP, in BP-DDQ, compared with the deviations for BP [Hirshfeld *et al.* (1963), in parentheses]. The reference plane is defined with respect to the atoms shown as dots.

of bond lengths). Furthermore, the torsion angles (Table 4) approach the values for a hypothetical planar molecule (0 and 180°) more closely in BP-DDQ than in BP itself; the largest change is 4.6° while the r.m.s. deviation from the ideal values for a planar molecule is

The DDQ molecule is essentially planar. The equation of the least-squares plane of the reference molecule, not including $C\equiv N$ groups, is $0.30214X' + 0.07598Y' - 0.95023Z' + 3.908 \text{ \AA} = 0$ (X', Y', Z' have the same meaning as above). Small but significant differences are found in the deviations of the O and Cl atoms from the mean plane of the C atoms in the three similar molecules: chloranil, 2,3-dichlorobenzoquinone (Rees, 1970*a*) and DDQ [however, it should be noted that the largest of these displacements is only 0.085 Å (O of chloranil)]. Rees and van Weperen & Visser suggest that these displacements arise from steric interactions between adjacent non-bonded atoms. Their virtual absence in DDQ suggests that formation of the molecular compound may influence the detailed structure of DDQ, as we have found above for BP. In support of this suggestion we note that chloranil has been found to be planar in its molecular compounds with pyrene (Prout & Tickle, 1973) and with 9-methylanthracene (Tickle & Prout, 1973*b*). However, the second of these results is rendered somewhat uncertain because of disorder in the crystals.

5. Discussion

The molecular dimensions of the component molecules in BP-DDQ leave no doubt that this molecular compound has a non-ionic ground state and thus resembles the molecular compounds of pyrene and perylene with DDQ (Ottenberg, Brandon & Browne, 1964) but not those of DDQ with *N,N,N',N'*-tetramethylphenylenediamine (Foster & Thomson, 1963) or 2,5-diethoxy-*p*-benzoquinone (Hansen, 1968; Gorres & Gurr, 1968). The electron affinity of DDQ is 3.13 eV (Chen & Wentworth, 1975) while the vertical π -ionization potential of BP is 7.62 eV (Brogli & Heilbronner, 1972).

The crystal structure of BP-DDQ shows a number of uncommon (though not entirely novel) features. First the periodicity along the stack axis is $\sim 14 \text{ \AA}$, and the crystallographic repeat unit contains two formula units, related by the *c* glide plane. This structure type with a double-unit periodicity along the stack axis is much less common than the single-unit type [cf. Tables 16 and 20 of Herbstein (1971)]. A similar type of stacking is found in anthracene-1,3,5-trinitrobenzene (Brown, Wallwork & Wilson, 1964) and in 3/2 pyrene-picryl bromide (Herbstein & Kaftory, 1975).

The chains of DDQ molecules along [010] (Fig. 3*a*) and the $N \cdots Cl$ distance of 3.21 Å suggest a weak donor-acceptor interaction (Bent, 1968) between CN and Cl groups, rather similar (also in details of geometry) to that found in 2,4,6-trichlorobenzonitrile (Carter & Britton, 1972). Standard values of van der Waals radii [N 1.5, Cl 1.8 Å (Pauling, 1960)] suggest that the shortening is only 0.09 Å, indicating a rather weak interaction. This could be an underestimate as Witt, Britton & Mahon (1972) have suggested that 1.7 Å may be

a more appropriate value for N. Stronger interactions, but with a linear geometry, have been found in ClCN [$d(N \cdots Cl) = 3.01 \text{ \AA}$ (Heiart & Carpenter, 1956)] and Cl-C \equiv C-CN [$d(N \cdots Cl) = 2.97 \text{ \AA}$ (Bjorvatten, 1968)].

The main feature of the overlap diagram (Fig. 4) is the positioning of the DDQ molecules on the phenanthrene regions of BP; a very similar overlap diagram has been found for perylene-fluoranil (Hanson, 1963), and similar features also appear in the overlap diagrams of perylene-tetracyanoquinodimethane (Tickle & Prout, 1973*a*), and chrysene-TCNQ (Munnoch & Wright, 1974). The predominance of shorter donor-acceptor distances along the stacks (Table 3) suggests a strong interaction in a direction perpendicular to the molecular planes. Indeed these atom-to-atom distances are closer to the interplanar distances in the fluoranil molecular compounds of perylene (3.23 Å; Hanson, 1963), chrysene (3.23 Å; Munnoch & Wright, 1975) and pyrene (3.28 Å; Bernstein & Regev, 1977) than to those in the molecular compounds of chloranil [pyrene-chloranil 3.46 Å (Prout & Tickle, 1973)] or *p*-benzoquinone [pyrene-*p*-benzoquinone 3.49 Å (Bernstein *et al.*, 1976)]. The specific interaction between carbonyl groups and aromatic rings proposed by Prout & Wallwork (1966) is apparent in all these molecular compounds. However, superposition of the acceptor molecule over a phenanthrene portion of the donor does not occur in pyrene-chloranil, pyrene-*p*-benzoquinone or chrysene-fluoranil.

Perhaps the most interesting feature of the present results is the significant reduction in the deformation of the BP and, to a lesser extent, the DDQ molecules that occurs on their incorporation in the molecular compound. A somewhat similar effect has been reported in [3,3]paracyclophane-TCNE (Bernstein & Trueblood, 1971); although there is no significant difference between the bond lengths and angles of [3,3]paracyclophane in its own crystals and those of the TCNE molecular compound, there is a small change in the distance between the parallel planes of the four unsubstituted C atoms of the benzene rings of the paracyclophane molecule. This distance is 3.26 in the pure crystals and 3.20 Å in the molecular compound. The change is about half as large as that in BP-DDQ. Unfortunately details are not available that will permit similar comparisons to be made for 1,12-dimethylbenzo[*c*]phenanthrene and hexahelicene, where crystal structures have been reported both for the pure compounds (Hirshfeld, Sandler & Schmidt, 1963; de Rango, Tsoucaris, Declercq, Germain & Putzeys, 1973) and for their 4-bromo-2,5,7-trinitrofluorenone molecular compounds (Ferguson, Mackay, Pollard & Robertson, 1969).

The BP molecule is chiral and spontaneous resolution into enantiomers occurs on crystallization of benzo[*c*]phenanthrene (space group $P2_12_12_1$; Herbstein & Schmidt, 1954). In BP-DDQ each stack contains

both enantiomers in an alternating array, sandwiched between DDQ molecules (Fig. 2a). A similar situation occurs with hexahelicene, which is spontaneously resolved on crystallization as the pure compound (space group $P2_12_1$; de Rango *et al.*, 1973) but whose molecular compound with 4-bromo-2,5,7-trinitrofluorenone contains both enantiomers (space group $P\bar{1}$; Mackay, Robertson & Sime, 1969).

References

- BENT, H. A. (1968). *Chem. Rev.* **68**, 587–648.
- BERNSTEIN, J. & REGEV, H. (1977). In preparation.
- BERNSTEIN, J., REGEV, H., HERBSTEIN, F. H., MAIN, P., RIZVI, S. H., SASVÁRI, K. & TURCSANYI, B. (1976). *Proc. Roy. Soc. A* **347**, 419–434.
- BERNSTEIN, J. & TRUEBLOOD, K. N. (1971). *Acta Cryst.* **B27**, 2078–2089.
- BJORVATTEN, T. (1968). *Acta Chem. Scand.* **22**, 410–420.
- BROGLI, F. & HEILBRONNER, E. (1972). *Angew. Chem. Int. Ed.* **11**, 538–539.
- BROWN, D., WALLWORK, S. C. & WILSON, A. (1964). *Acta Cryst.* **17**, 168–176.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS. A Fortran Crystallographic Least-Squares Program*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CARTER, V. B. & BRITTON, D. (1972). *Acta Cryst.* **B28**, 945–950.
- CHEN, E. C. M. & WENTWORTH, W. E. (1975). *J. Chem. Phys.* **63**, 3183–3191.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- FERGUSON, G., MACKAY, I. R., POLLARD, D. R. & ROBERTSON, J. M. (1969). *Acta Cryst.* **A25**, S132.
- FOSTER, R. & THOMSON, T. J. (1963). *Trans. Faraday Soc.* **59**, 296–300.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GORRES, B. T. & GURR, G. E. (1968). ACA Winter Meeting, Tucson, Ariz. Abstract B9.
- HANSEN, R. L. (1968). *J. Org. Chem.* **33**, 3968–3970.
- HANSON, A. W. (1963). *Acta Cryst.* **16**, 1147–1151.
- HEIART, R. B. & CARPENTER, G. B. (1956). *Acta Cryst.* **9**, 889–895.
- HERBSTEIN, F. H. (1971). *Perspectives in Structural Chemistry*, Vol. IV, edited by J. D. DUNITZ and J. A. IBERS, pp. 166–395. New York: John Wiley.
- HERBSTEIN, F. H. & KAFTORY, M. (1975). *Acta Cryst.* **B31**, 68–75.
- HERBSTEIN, F. H., KAFTORY, M. & REGEV, H. (1976). *J. Appl. Cryst.* **9**, 361–364.
- HERBSTEIN, F. H. & SCHMIDT, G. M. J. (1954). *J. Chem. Soc.* pp. 3302–3313.
- HIRSHFELD, F. L., SANDLER, S. & SCHMIDT, G. M. J. (1963). *J. Chem. Soc.* pp. 2108–2125.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 201. Birmingham: Kynoch Press.
- LARSEN, F. K., LITTLE, R. G. & COPPENS, P. (1975). *Acta Cryst.* **B31**, 430–440.
- MACKAY, I. R., ROBERTSON, J. M. & SIME, J. G. (1969). *Chem. Commun.* pp. 1470–1471.
- MUNNOCH, P. J. & WRIGHT, J. D. (1974). *J. Chem. Soc. Perkin II*, pp. 1397–1400.
- MUNNOCH, P. J. & WRIGHT, J. D. (1975). *J. Chem. Soc. Perkin II*, pp. 1071–1074.
- OTTENBERG, A., BRANDON, R. L. & BROWNE, M. E. (1964). *Nature, Lond.* **201**, 1119–1120.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd edition, p. 260. Ithaca: Cornell Univ. Press.
- PROUT, C. K. & TICKLE, I. J. (1973). *J. Chem. Soc. Perkin II*, pp. 1212–1215.
- PROUT, C. K. & WALLWORK, S. C. (1966). *Acta Cryst.* **21**, 449–450.
- RANGO, C. DE, TSOUCARIS, G., DECLERCQ, J. P., GERMAIN, G. & PUTZEYS, J. P. (1973). *Cryst. Struct. Commun.* **2**, 189–192.
- REES, B. (1970a). *Acta Cryst.* **B26**, 1304–1311.
- REES, B. (1970b). *Acta Cryst.* **B26**, 1311–1316.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 65. New York: Macmillan.
- TICKLE, I. J. & PROUT, C. K. (1973a). *J. Chem. Soc. Perkin II*, pp. 720–723.
- TICKLE, I. J. & PROUT, C. K. (1973b). *J. Chem. Soc. Perkin II*, pp. 731–734.
- WEPEREN, K. J. VAN & VISSER, G. J. (1972). *Acta Cryst.* **B28**, 338–342.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.
- WITT, J. R., BRITTON, D. & MAHON, C. (1972). *Acta Cryst.* **B28**, 950–955.