

Molecular Compounds and Complexes.

XI.* The Crystal Structure of the π -Molecular Compound Phenanthrene–2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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We have studied the crystal structure of the π -molecular compound phenanthrene–2,3-dichloro-5,6-dicyano-*p*-benzoquinone (PH–DDQ) to compare the component arrangement in the mixed stacks with that found in benzo[*c*]phenanthrene–DDQ [Bernstein, Regev & Herbstein, *Acta Cryst.* (1977), B33, 1716–1724]. PH–DDQ is orthorhombic, $a = 16.101$ (2), $b = 7.244$ (3), $c = 15.544$ (3) Å, space group $Pca2_1$, $Z = 4$. The structure was solved by direct methods and refined to $R = 0.056$ using 1632 unique reflections. The structure is of the well known mixed-stack type, with the stack axis along **b**. The crystal structures of PH–DDQ and BPH–DDQ are quite different in the mutual arrangement of the components. Dimensions of the component molecules do not differ significantly from those obtained in other analyses but appear to be the most accurate currently available. Both component molecules are slightly but significantly non-planar, presumably due to packing effects.

1. Introduction

In the crystal structure of benzo[*c*]phenanthrene–2,3-dichloro-5,6-dicyano-*p*-benzoquinone (BPH–DDQ) (Bernstein, Regev & Herbstein, 1977), the DDQ molecules are positioned above and below ‘phenanthrene’ portions of the BPH molecules, with alignment of polar carbonyl groups above polarizable ‘benzene’ rings. Such an arrangement, which is common but not universal in appropriate π -molecular compounds (Prout & Wallwork, 1966), might also be anticipated in phenanthrene–DDQ (PH–DDQ). However, the results of the present crystal structure analysis show that this is not so, contrary to our expectations.

2. Experimental

Black prismatic needles, elongated along [010] and of excellent diffraction quality, were obtained from xylene. Crystal data in Table 1 extend (and correct) preliminary results (Herbstein, Kaftory & Regev, 1976). Intensities of 1671 reflections were measured with a Stoe Weissenberg diffractometer (Mo $K\alpha$ radiation, graphite monochromator) and reduced to a set of structure factors by standard methods (absorption

correction not applied). This set of structure factors (set 1) was used for structure solution and refinement ($R = 0.087$) but the results had certain unsatisfactory features, such as the occurrence of apparently significant differences between symmetry-related bond lengths within the molecules. Intensities were therefore remeasured (Mo $K\alpha$, graphite monochromator) on a computer-controlled precession diffractometer (DIFFREX) developed by one of us (DR) and described briefly by Shaanan, Shmueli & Rabinovich (1976). A crystal, $\sim 0.3 \times 0.3 \times 0.4$ mm, was mounted with **b** along the dial axis of the diffractometer. Intensities of 4081 reflections were measured (17 layers, five normal to [100], five normal to [001] and seven normal to [101]). After correction of all measurements for background, Lorentz and polarization factors, symmetry-equivalent reflections were averaged and the various layers brought to a common scale by a least-squares

Table 1. *Crystal data for PH–DDQ (cell dimensions were measured on a Weissenberg diffractometer)*

$C_{14}H_{10} \cdot C_8N_2O_2Cl_2$, FW 405.21, m.p. 188 °C	
Orthorhombic, space group $Pca2_1$ * (No. 29)	
$a = 16.101$ (2) Å	$D_m = 1.50$ g cm ⁻³
$b = 7.244$ (3)	$D_x = 1.485$, for $Z = 4$
$c = 15.544$ (3)	$F(000) = 824$
$V = 1813.0$ Å ³	$\mu(\text{Mo } K\alpha) = 3.87$ cm ⁻¹
$\lambda(\text{Mo } K\alpha) = 0.71069$ Å	

* Part X: Bernstein, Regev & Herbstein (1977).

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* From structure analysis.

procedure. The 1806 independent structure factors so obtained were designated set 2. The atomic parameters derived from set 1 were used as the starting point for further refinement using set 2; convergence was reached at $R = 0.056$ for 1632 reflections [174 reflections with $F_o < \sigma(F_o)$ were excluded; the structure factors were assigned experimental weights]. All details of the structure described below are based on set 2.

3. Structure solution and refinement

3.1. Solution

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) using 305 E 's greater than 1.3; intensity statistics showed clearly that the space group was $Pca2_1$, and not $Pcam$. The set of phases with the highest figure of merit (1.04) and lowest residual (37.26) was chosen for calculation of an E map, which showed all 14 atoms of the DDQ molecule and 12 of the 14 non-hydrogen atoms of the PH molecule.

3.2. Refinement

The structure was refined by least squares, using G. M. Sheldrick's *SHELX 76* program package. Convergence was obtained at $R = 0.056$ for 1632 observed reflections. Anisotropic temperature factors were used for the heavy atoms; H positions were refined but not their isotropic temperature factors ($U_{iso} = 0.057 \text{ \AA}^2$).

Complex atomic scattering factors were taken from Tables 2.2A and 2.3.1 of *International Tables for X-ray Crystallography* (1974). Electron density difference maps, based on the final parameters, were calculated in the planes of the two molecules. There were no features on these maps greater than 0.4 e \AA^{-3} .

Atomic coordinates are given in Table 2.* The numbering of atoms and rings in the phenanthrene molecule follows that used by Kay, Okaya & Cox (1971).

4. Results

4.1. Crystal structure

An *ORTEP* stereoview of the structure down [010] is shown in Fig. 1. The two components are arranged in mixed stacks extending along the b axis. Each stack is of the single-unit type (Herbstein, 1971). The phenanthrene and DDQ best planes are inclined to the b axis by 68.1 and 70° respectively. The unit cell contains four stacks related by the space-group symmetry elements. Each stack is surrounded by six stacks forming a quasi-hexagonal close-packed ar-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32984 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final fractional coordinates for non-hydrogen ($\times 10^4$) and hydrogen ($\times 10^3$) atoms; e.s.d.'s in parentheses are in units of the least significant digits

Hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

	x	y	z		x	y	z
PH				PH			
C(1)	6523 (4)	4852 (8)	-521 (6)	H(7)	708 (3)	850 (7)	391 (4)
C(2)	5709 (5)	4783 (8)	-766 (6)	H(8)	807 (4)	746 (7)	287 (5)
C(3)	5100 (4)	5310 (9)	-189 (6)	H(9)	841 (4)	623 (7)	157 (4)
C(4)	5284 (3)	5932 (7)	620 (0)	H(10)	799 (3)	514 (7)	10 (4)
C(5)	5784 (4)	7383 (7)	2351 (6)				
C(6)	6048 (5)	8025 (8)	3132 (6)	DDQ			
C(7)	6896 (5)	8087 (8)	3350 (6)	C(1)	6974 (3)	835 (6)	706 (5)
C(8)	7475 (5)	7494 (7)	2763 (6)	C(2)	6117 (3)	653 (6)	364 (6)
C(9)	7832 (4)	6191 (7)	1330 (6)	C(3)	5443 (3)	1048 (6)	848 (5)
C(10)	7603 (4)	5561 (7)	551 (7)	C(4)	5526 (4)	1788 (7)	1744 (6)
C(11)	6742 (3)	5478 (6)	302 (5)	C(5)	6396 (3)	1965 (6)	2083 (6)
C(12)	6124 (3)	6038 (6)	895 (5)	C(6)	7059 (4)	1517 (6)	1613 (5)
C(13)	6356 (3)	6732 (6)	1733 (5)	C(7)	6466 (4)	2637 (7)	2965 (6)
C(14)	7227 (3)	6807 (7)	1951 (5)	C(8)	7893 (4)	1717 (8)	1934 (6)
H(1)	694 (3)	454 (7)	-94 (4)	N(7)	6541 (4)	3146 (7)	3646 (6)
H(2)	558 (4)	439 (7)	-133 (4)	N(8)	8543 (3)	1906 (7)	2216 (6)
H(3)	457 (4)	524 (7)	-35 (4)	O(1)	7589 (2)	408 (5)	291 (5)
H(4)	482 (4)	637 (6)	109 (4)	O(4)	4935 (3)	2278 (5)	2165 (5)
H(5)	523 (4)	741 (7)	214 (4)	Cl(2)	6037 (1)	-140 (2)	-672 (4)
H(6)	565 (4)	846 (7)	346 (4)	Cl(3)	4450 (1)	742 (2)	491 (4)

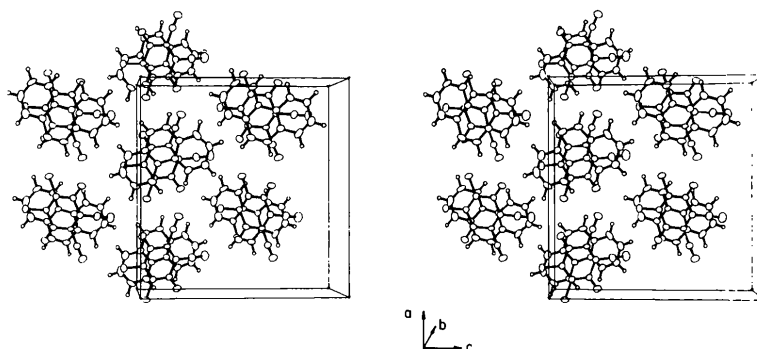


Fig. 1. ORTEP (Johnson, 1965) stereoview of unit cell, looking down [010]. The reference PH and DDQ molecules are in the central stack, surrounded by six other stacks.

rangement. Short intermolecular distances within the stack and between stacks are listed in Table 3.

The stacks related by a glide planes are shifted with respect to one another along [010], whereas those related by c glide planes change their mutual orientation. Therefore the structure cannot be described in terms of alternating sheets, as found in the structure of BPH-DDQ. We note the relatively short distance of 3.13 Å between the Cl and O atoms of DDQ molecules in adjacent stacks (Table 3), the C=O and C-Cl vectors being nearly collinear. It is not clear whether this should be considered a van der Waals approach, as Rudman (1971) has suggested for a similar situation

in tetrachlorophthalic anhydride, or whether some attractive interaction is involved, as Kaftory (1978) has proposed for α -N-(*p*-tolyl)tetrachlorophthalimide [$d(\text{Cl}\cdots\text{O}) = 2.99$ Å].

The overlap diagrams of a DDQ molecule below a phenanthrene molecule in a stack (Fig. 2a) and the DDQ molecule above the phenanthrene (Fig. 2b) are quite different, and neither shows any resemblance to the overlap diagrams found for BPH-DDQ. The 'interplanar distance' between the reference* DDQ molecule and the reference* phenanthrene molecule is 3.43 Å, and that between the reference phenanthrene and the DDQ molecule translated by $+b$ is 3.38 Å; the two distances are sensibly equal [because the planes are not quite parallel, these distances were calculated from atoms of the DDQ molecule most nearly above and below the centre of mass of the phenanthrene molecule].

Table 3. Intermolecular distances (Å) (distances greater than 3.5 Å between non-hydrogen atoms are excluded)

(a) Donor-acceptor distances along a stack

PH C(4) ^l ...DDQ C(4) ^l	3.495	PH C(9) ^l ...DDQ C(8) ^l	3.375
PH C(1) ^l ...DDQ C(2) ^l	3.402	PH C(13) ^l ...DDQ C(5) ^l	3.497
PH C(11) ^l ...DDQ C(1) ^l	3.442	PH C(12) ^l ...DDQ C(4) ^l	3.485
PH C(10) ^l ...DDQ C(6) ^l	3.474		

PH C(9) ^l ...DDQ O(1) ^y	3.478	PH C(6) ^l ...DDQ C(5) ^y	3.335
PH C(14) ^l ...DDQ C(6) ^y	3.463	PH C(6) ^l ...DDQ C(8) ^y	3.418
PH C(8) ^l ...DDQ C(6) ^y	3.484	PH C(5) ^l ...DDQ C(4) ^y	3.354
PH C(8) ^l ...DDQ C(8) ^y	3.387	PH C(2) ^l ...DDQ C(2) ^y	3.443
PH C(7) ^l ...DDQ C(7) ^y	3.421		

(b) Donor-acceptor distance between stacks

$$\text{PH C}(3)^{\text{l}}\cdots\text{DDQ N}(7)^{\text{vl}} \quad 3.392$$

(c) Acceptor-acceptor distance between stacks

$$\text{DDQ Cl}(3)^{\text{l}}\cdots\text{DDQ O}(1)^{\text{vll}} \quad 3.126$$

Symmetry code

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

4.2. Molecular structure

The estimated standard deviations of bond lengths and angles are as follows: C-C, C-N ~ 0.008 Å, C=O 0.006 Å, C-Cl 0.005 Å; $\angle\text{C-C-C}$, $\angle\text{C-C-N}$, $\angle\text{C-C=O} \sim 0.6^\circ$, $\angle\text{C-C-Cl} \sim 0.5^\circ$.

4.2.1. *Phenanthrene*. The molecular dimensions averaged in terms of assumed molecular symmetry $mm2$ agree well with those found in phenanthrene itself by neutron and X-ray diffraction (Kay *et al.*, 1971) and with values calculated by molecular orbitals (Dewar & Trinajstić, 1971) (Table 4).

The phenanthrene molecule is approximately planar, with some small but significant and systematic deviations (Fig. 3b) from the best plane ($0.0615X + 0.9276Y - 0.3684Z - 4.181$ Å = 0, where X, Y, Z are atomic coordinates in Å in the crystal system of axes). The individual rings are each planar with small r.m.s. deviations (I 0.003 Å, II 0.005 Å, III 0.004 Å). The

* Those molecules whose coordinates are given in Table 2.

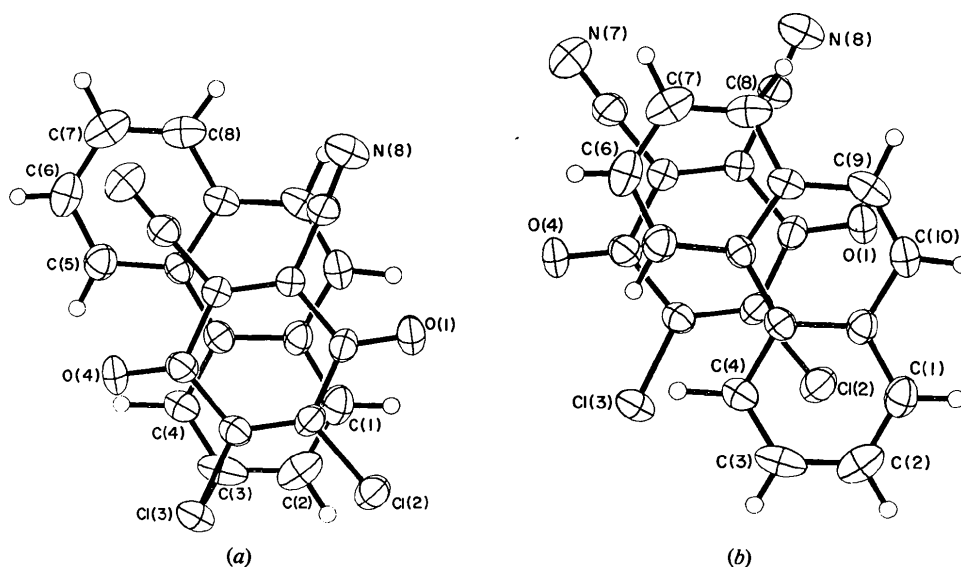


Fig. 2. (a) Overlap diagram of reference PH (below) and DDQ molecules. (b) Overlap diagram of reference PH molecule and DDQ molecule translated by $+b$.

angles between planes I and II, and II and III are both 1.1° .

The deviations of the C atoms from the plane of ring II show that both rings I and III are bowed slightly upwards; this distortion from planarity is different from that found in crystalline phenanthrene, where rings I and III are twisted in opposite directions (Kay *et al.*, 1971). A detailed comparison is given in Fig. 4.

Table 4. Comparison of bond lengths (\AA) in the phenanthrene molecule, as found in phenanthrene (Kay *et al.*, 1971) and PH-DDQ, and as calculated by molecular orbitals

Experimental values have been averaged on the basis of a molecular twofold axis.

	Kay <i>et al.</i> (1971)*	Present results†	Molecular orbitals‡
C(1)–C(2)	1.374	1.369	1.381
C(2)–C(3)	1.386	1.396	1.412
C(3)–C(4)	1.399	1.368	1.382
C(4)–C(12)	1.412	1.418	1.415
C(1)–C(11)	1.428	1.408	1.416
C(11)–C(12)	1.416	1.430	1.400
C(10)–C(11)	1.450	1.441	1.444
C(9)–C(10)	1.341	1.346	1.361
C(12)–C(13)	1.464	1.445	1.448

* X-ray results, corrected for thermal motion (corrections ~ 0.006 – 0.008 \AA).

† Not corrected for thermal motion [$\sigma(\text{C}–\text{C}) \sim 0.006$ \AA after averaging].

‡ Dewar & Trinajstic (1971).

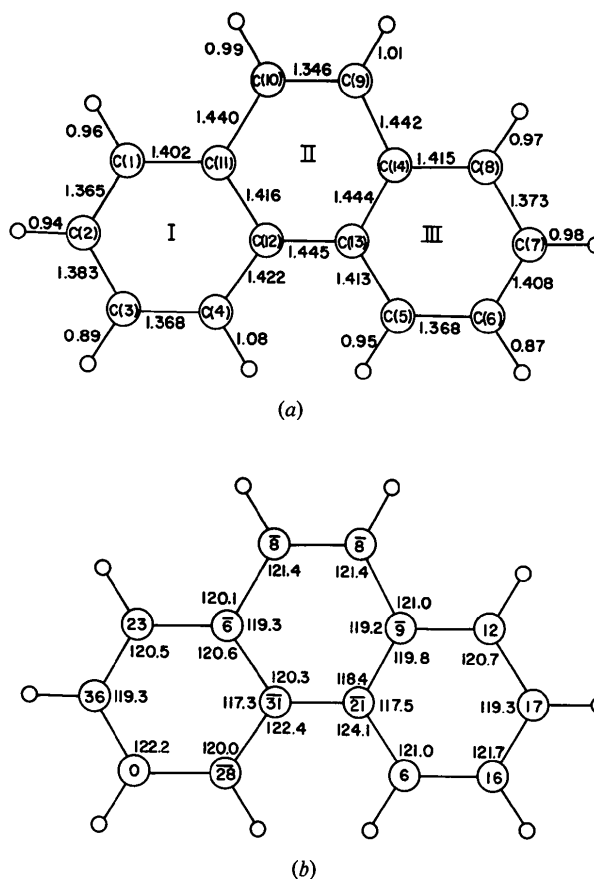


Fig. 3. (a) Numbering of atoms and bond lengths (\AA) in the phenanthrene molecule. (b) Bond angles ($^\circ$) and deviations from planarity (in units of 10^{-3} \AA). The H atoms are given the numbers of the C atoms to which they are bonded.

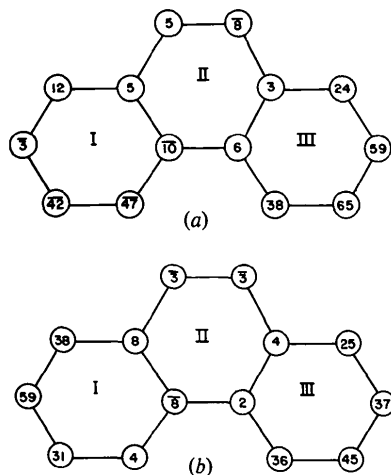


Fig. 4. Comparison of deviations of atoms from the plane of ring II in the phenanthrene molecule (a) in crystalline phenanthrene (Kay *et al.*, 1971) and (b) in PH-DDQ (units of 10^{-3} Å).

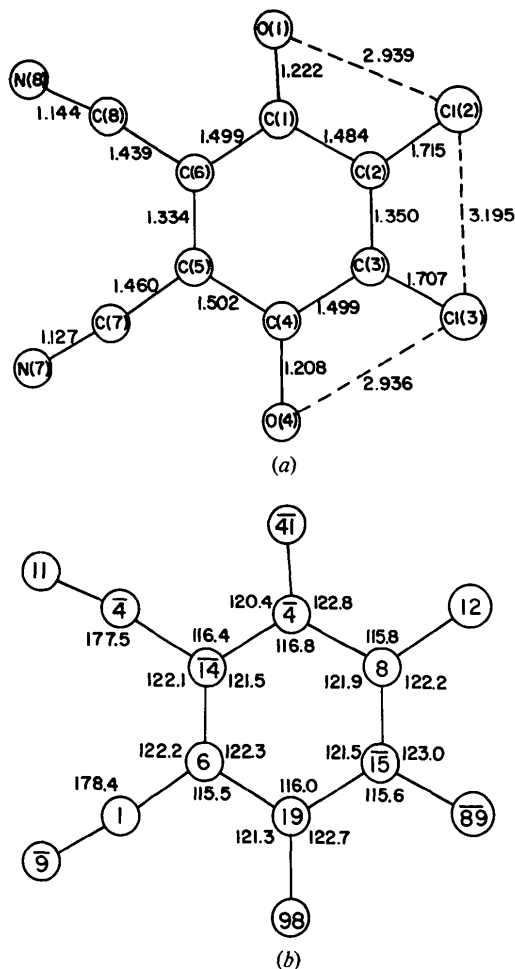


Fig. 5. (a) Numbering of atoms and bond lengths (Å) in the DDQ molecule. (b) Bond angles ($^{\circ}$) and deviations from planarity (in units of 10^{-3} Å).

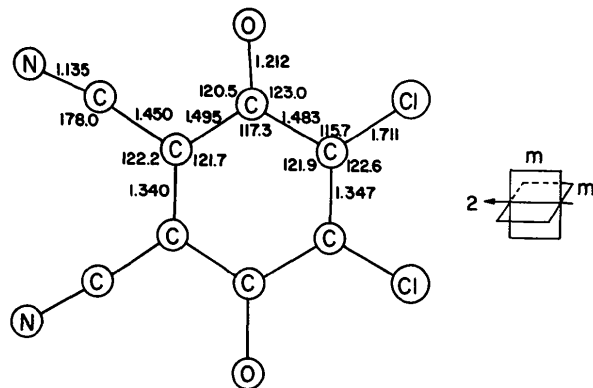


Fig. 6. Standard dimensions for the DDQ molecule, assuming $mm2$ (C_{2v}) symmetry (see text for source of dimensions given).

4.2.2. *DDQ*. The molecular geometry (Fig. 5a and b) conforms rather closely to $mm2$ symmetry, apart from some small deviations from planarity. The ten atoms of the ring and the two cyano groups are not significantly displaced from the plane with equation $0.0331X + 0.9397Y - 0.3404Z - 0.570 \text{ Å} = 0$. However, one Cl and the two O atoms are significantly displaced (Fig. 5b).

Using the dimensions for DDQ obtained here and from BPH-DDQ we can derive a set of standard dimensions for the DDQ molecule (Fig. 6) [$d(\text{C}-\text{Cl})$, $d(\text{C}-\text{CN})$ and $d(\text{C}\equiv\text{N})$ from BPH-DDQ, and corresponding angles, were given zero weight in this averaging because of the disorder in BPH-DDQ].

There is a close resemblance to the values given by Rees (1970b) for various chloro derivatives of *p*-benzoquinone [including chloranil whose structure was determined at 110 K by Weperen & Visser (1972)]. We note particularly that the internal angle at the carbonyl group has a mean value of 117.2° , with corresponding increases in the other intra-ring angles, and that the substituents (Cl and CN) are invariably bent towards the O atoms of the carbonyl groups. There is a further distortion in the unsymmetrically substituted DDQ molecule in that the O atoms are bent away from the Cl atoms towards the cyano groups. The values of $d(\text{C}-\text{CN})$ and $d(\text{C}\equiv\text{N})$ are close to those (1.443 and 1.134 Å respectively) obtained for 1,2,4,5-tetracyanobenzene (Tsuchiya, Marumo & Saito, 1972).

5. Discussion

As the geometries of the components are not appreciably altered on molecular-compound formation there seems little doubt that the ground state of the compound is non-ionic, as in BPH-DDQ. The occurrence of mixed stacks and their quasi-hexagonal mode of arrangement in the crystal are features that are

common to most of the crystalline π -molecular compounds investigated until now. Although the overlap diagrams are quite different in PH-DDQ and BPH-DDQ, the superposition of various dipoles of the DDQ molecule over the polarizable phenanthrene molecule in PH-DDQ nevertheless suggests that dipole-induced dipole interactions play some role in the cohesion of the components. These interactions must, however, be fairly weak because the shorter atom-to-atom distances between adjacent donor and acceptor molecules are close to the sums of the respective van der Waals radii (Table 3) and are about 0.2 Å longer than corresponding distances found in BPH-DDQ; the interplanar distances of 3.4 Å are not particularly short [cf. the values in hexamethylbenzene-chloranil (3.51 Å) (Jones & Marsh, 1962) and tetramethyl-*p*-phenylenediamine-chloranil (3.28 Å, ionic ground state) (de Boer & Vos, 1968)].

Three types of overlap can be discerned among the π -molecular compounds of unsubstituted aromatic hydrocarbons with *p*-benzoquinone derivatives. Overlap of both carbonyl groups with aromatic rings of a particular molecule is found in BPH-DDQ and perylene-fluoranil (Hanson, 1963), which have analogous overlap diagrams. Stepped stacks with overlap of the two carbonyl groups with aromatic rings of successive donor molecules in a stack are found in pyrene-*p*-benzoquinone (Bernstein, Regev, Herbstein, Main, Rizvi, Sasvári & Turcsanyi, 1976), chrysene-fluoranil (Munnoch & Wright, 1975) and pyrene-chloranil (Prout & Tickle, 1973). No such overlap is found in acenaphthene-chloranil (Tickle & Prout, 1973*a*) or 9-methylanthracene-chloranil (Tickle & Prout, 1973*b*). The overlap arrangement in PH-DDQ falls between those found in the second and third of these groups.

Small deviations from planarity have been found for the PH and DDQ molecules in PH-DDQ. Because the analogous effects in phenanthrene, DDQ (in BPH-DDQ), chloranil and 2,3-dichlorobenzoquinone (Rees, 1970*a*) all differ in detail, it seems likely that their cause should be sought in intermolecular interactions (packing forces, which can include charge-transfer forces for the π -molecular compounds) rather than in intramolecular interactions (repulsions between overcrowded adjacent non-bonded atoms).

Thus, in summary, we have been able to show that PH-DDQ and BPH-DDQ are quite different in the mutual arrangement of the components, and have obtained good standard dimensions for the phenanthrene and DDQ molecules.

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