The Crystal and Molecular Structure of Perylene-2,5-Dibromo-3,6-dichloro-*p*-benzoquinone Complex

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Crystals of the 1 : 1 molecular complex of perylene–2,5-dibromo-3,6-dichloro-*p*-benzoquinone are triclinic, with $a=8.669$, $b=9.697$, $c=7.321$ Å, $\alpha=103.20$, $\beta=110.92$, $\gamma=64.60°$, space group $P\bar{1}$, $Z=1$. The structure has been determined from diffractometer data by the heavy atom method and refined using the full-matrix least-squares method to R 0.069 for 2241 independent reflections. Stacks, with alternating donor and acceptor molecules, extend along the **c** direction. The acceptor molecule assumes two orientations, with a population ratio 1 : 1. A small degree of correlative change in the C–C bond lengths has been found in the perylene molecule on complex formation. The geometry of the quinonoid skeleton of the acceptor is similar to those of the anils and their complexes.

Perylene is a characteristic electron donor among polycyclic aromatic hydrocarbons. The perylene-iodine possesses the lowest electrical resistivity among hydrocarbon-iodine complexes.[1] And the perylene-antimony pentachloride is highly conductive in complexes which include antimony pentachloride as an electron acceptor.[2] Recently, perylene and 7,7,8,8-tetracyanoquinodimethane (TCNQ) were found to form a new type of complex, composed of three perylene molecules and one TCNQ moiety.[3,4] It is very rare in TCNQ complexes that more than two molecules of donor adduct to an acceptor molecule.

Tetrahalobenzoquinones are very useful electron acceptors, forming mainly π-π type donor-acceptor complexes. Their high electron affinity often gives complexes of ionic ground states.[5]

In this paper, the crystal structure of the 1 : 1 complex of perylene and 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (BCQ) will be reported.

Experimental

Dark blue prismatic crystals of perylene-BCQ complex have been grown in a toluene solution. The crystal ($2.0\times0.5\times0.2$ mm^3) was mounted with the c axis parallel to the ϕ axis of a Rigaku four-circle automated diffractometer. The cell parameters and intensity data were obtained with LiF-monochromatized Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). The intensities of the 2916 unique reflections were collected by the 2θ-ω scan technique with a scan speed of 1° min^{-1} in 2θ in the range $2\theta\leq60°$, 2241 reflections ($F_o\geq3\sigma(F)$) were used in the calculations. The scan range for each reflection was $(1+0.45\tan\theta)°$, and the background measurements were made 15 s at the extremeties of the scan range. Four reflections were monitored every 50 measurements and the fluctuations in the intensities of the monitored reflections were within ±2 %. Lorentz and polarization corrections were made, but no absorption correction was applied.

Crystal Data. $C_{20}H_{12}\cdot C_6Br_2Cl_2O_2$, $F.W.=587.1$; Triclinic, $a=8.669(3)$, $b=9.697(3)$, $c=7.321(3)$ Å, $\alpha=103.20(2)$, $\beta=110.92(2)$, $\gamma=64.60(1)°$, $V=517.2$ Å^3; $D_m=1.87$, $D_x=1.885$ g cm^{-3}, $Z=1$, $\mu(\text{Mo }K\alpha)=43.9$ cm^{-1}, $F(000)=288$. Space group $P\bar{1}$.

The density was measured by the flotation method in an aqueous solution of K_2HgI_4. Structure determination was conducted assuming the space group $P\bar{1}$, and the possibility of $P1$ was excluded at the refinement step.

Structure Determination

The structure was solved by the heavy atom method. Several block-diagonal, least-squares calculation cycles for non-hydrogen atoms gave convergence at a residual index $R=0.176$. At this stage, the electron densities about the Br and Cl atoms, both in the Fourier and difference Fourier maps, suggested the existence of orientational disorder in the BCQ molecule. Subsequent full-matrix, least-squares refinements were performed with two sets of Br and Cl atoms positionally overlapping, based on the assumption that the two kinds of overlapping halogen atoms had equal probability of occupancy (0.5 : 0.5). The anomalous dispersion corrections for the Br and Cl atoms, reduced the value of R to 0.074. The positional parameters of the six hydrogen atoms attached to perylene, were estimated, assuming a C–H bond distance of 1.08 Å. The next refinement including the hydrogen atoms with an isotropic temperature factor of 4.5 Å^2 converged at $R=0.069$. In the final cycle, the average parameter shift/e.s.d. for non-hydrogen atoms was 0.26.

The final difference map showed maxima about 1.3 e Å^{-3} and only around the halogen atoms. This may be due to systematic error arising from the Br and Cl atoms being located at almost the same positions.

The quantity minimized in the refinement was $\sum w(|F_o|-k|F_c|)^2$, $w=1.0$. The numerical calculations were carried out on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo with UNICS program[6] and XRAY system.[7] The atomic scattering factors and anomalous dispersion factors were taken from "International Tables for X-Ray Crystallography" (1974).[8] The final atomic parameters are shown in Tables 1 and 2 and the F_o-F_c data is kept as Document No. 7918 at the Bulletin.

Results and Discussion

Figure 1 shows the molecular packing in the crystal and the numbering of the atoms. Each molecule occupies a center of symmetry. As is common to π-π complexes, the donor and the acceptor molecules alternately stack in a plane-to-plane manner along the c axis, forming columns. The molecular overlapping

Table 1. The final atomic parameters ($\times 10^4$) for non-hydrogen atoms
The anisotropic thermal parameters are of the form:
$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)*	2945(10)	1339(8)	3028(10)	104(6)	95(6)	148(9)	−43(5)	49(4)	−39(4)
Cl(1)*	3866(19)	−2295(19)	2248(22)	442(36)	548(37)	541(46)	199(27)	90(31)	295(32)
Br(2)*	3899(3)	−2310(2)	2304(3)	91(3)	88(2)	169(4)	−6(2)	15(3)	31(2)
Cl(2)*	2686(24)	1590(18)	3249(23)	81(11)	51(8)	126(15)	−17(7)	68(8)	−49(7)
O	−889(7)	3034(6)	600(9)	156(11)	72(7)	274(16)	−27(7)	48(10)	7(8)
C(1)	1320(9)	556(8)	1395(10)	104(11)	83(9)	151(15)	−39(8)	32(10)	1(9)
C(2)	1728(8)	−950(8)	1050(10)	96(11)	89(9)	127(13)	−19(8)	24(9)	20(8)
C(3)	−493(9)	1657(8)	317(10)	106(11)	78(9)	157(14)	−27(8)	31(10)	10(9)
C(4)	−2744(11)	4179(8)	4339(13)	152(15)	67(9)	235(20)	−4(9)	33(14)	17(10)
C(5)	−3830(10)	3544(9)	2992(13)	135(14)	89(10)	232(20)	3(9)	36(13)	34(11)
C(6)	−3335(10)	1950(8)	2690(11)	125(13)	95(9)	167(16)	−28(9)	32(11)	14(10)
C(7)	−1699(8)	976(7)	3825(10)	93(10)	81(8)	140(13)	−24(7)	43(10)	11(8)
C(8)	−1156(9)	−700(7)	3526(10)	105(11)	78(8)	137(14)	−33(8)	42(10)	−3(8)
C(9)	−2215(10)	−1412(8)	2162(11)	128(13)	93(9)	196(17)	−48(9)	32(12)	−2(10)
C(10)	−1681(11)	−3007(9)	1889(12)	183(16)	116(11)	209(19)	−81(11)	27(14)	−11(12)
C(11)	−70(11)	−3919(8)	3036(13)	197(17)	68(9)	242(21)	−53(10)	68(15)	−20(11)
C(12)	1055(10)	−3250(8)	4441(11)	148(13)	65(8)	194(17)	−30(8)	48(12)	4(9)
C(13)	546(9)	−1634(7)	4732(10)	101(10)	78(8)	133(13)	−27(7)	35(9)	7(8)

*Br(1) and Cl(1) are located at the same positions of Cl(2) and Br(2) respectively.

Table 2. The final positional parameters of hydrogen ($\times 10^3$)
Isotropic thermal parameter B=4.5 Å^2.

Atom	x	y	z
H(4)	−284(14)	532(12)	450(15)
H(5)	−506(14)	427(12)	192(15)
H(6)	−424(14)	144(12)	169(15)
H(9)	−335(13)	−80(12)	91(15)
H(10)	−243(14)	−352(12)	92(15)
H(11)	23(14)	−501(12)	286(15)

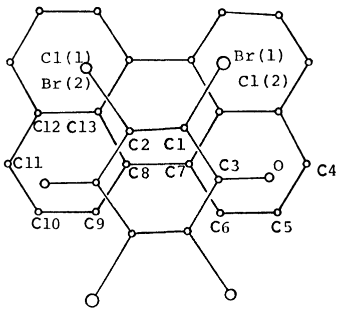

Fig. 2. Two overlapping molecules, viewed along normal to least-squares plane of a perylene molecule.

manner of BCQ onto perylene, shown in Fig. 2, is the same as that in the perylene-fluoranil complex.[9] The perylene and the BCQ molecules are planar within standard deviations except for the halogen atoms. The shifts of Br(1) (0.074 Å) and Cl(2) (0.151 Å) from the least-squares BCQ plane are nine and eight times as large as the e.s.d.'s, but the existence of disorder qualifies the significance of these values. The equations of the least-squares planes of the perylene and the BCQ molecules (calculated without hydrogen and halogen atoms) are

$$0.7345X + 0.0132Y - 0.6784Z = -3.270 \quad \text{and}$$

$$0.6752X + 0.0292Y - 0.7370Z = 0.0 \quad \text{respectively,}$$

where X, Y, and Z are orthogonal coordinates (in Å) given by the following equation.

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^* \\ 0 & 0 & c\sin\beta\sin\alpha^* \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

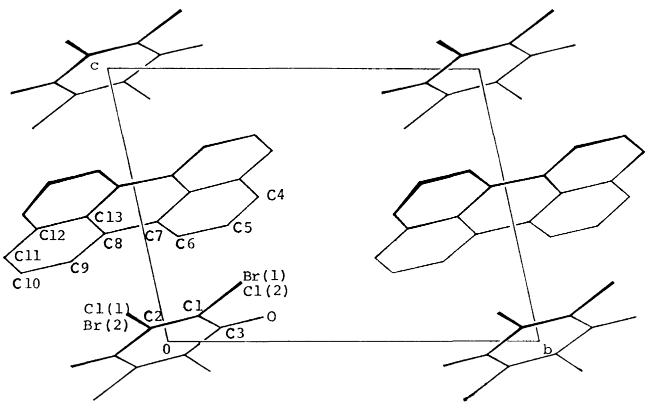

Fig. 1. Projection of the molecular arrangement onto the (100) plane.

The mean separation between the two planes (in the region of overlap) is 3.35 Å and the angle between the plane normals is 4.9°. The values are larger than those of the perylene-fluoranil complex (3.23 Å, 1.8°),[9] which may be explained in terms of the difference between the van der Waals radii of the halogen atoms. The minimum interatomic distances between the overlapping molecules are 3.334 Å for O′–C(10), 3.350 Å for C(3′)–C(9), 3.371 Å for C(3′)–C(8), 3.376 Å for C(3)–C(6), 3.378 Å for C(3)–C(7), and 3.395 Å for O–C(5).

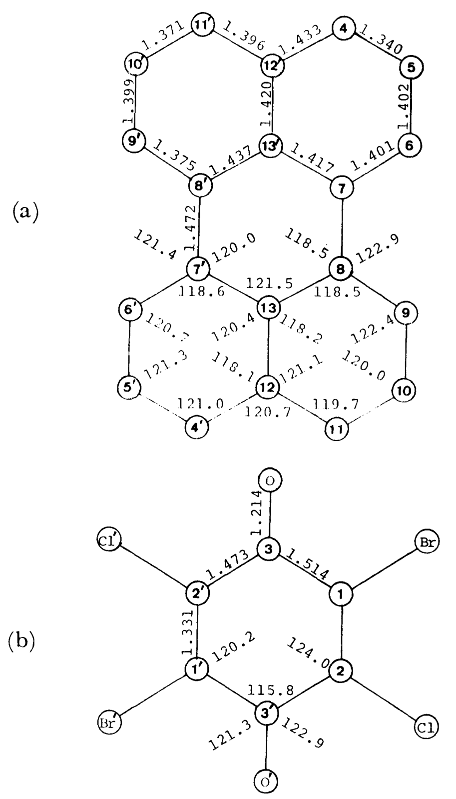

Fig. 3. Bond lengths (Å) and bond angles (°).
(a) Perylene; mean e.s.d.'s are 0.011 Å and 0.7° respectively.
(b) BCQ (quinonoid skeleton); mean e.s.d.'s are 0.010 Å and 0.7° respectively.

The bond distances and angles of the constituent molecules are shown in Fig. 3, in which the thermal vibrational motion has not been corrected for. The largest difference in the chemically equivalent bonds in the perylene skeleton is 0.037 Å between C(4)–C(12′) and C(11)–C(12) (2.2σ). Thus, in the perylene skeleton, all C–C lengths do not differ from the chemically equivalent bonds within experimental error. The geometry of the perylene molecule is similar to that of perylene itself (α-form)[10] or the complexes.[9,11–14]

Table 3 shows the bond lengths of the perylene skeleton together with six references.[9–14] The seven perylene skeletons show the following trends: (1) the longest bond length, C(7)–C(8), is close to a single bond as expected, and the lengths of C(4)–C(5) and C(10)–C(11) are the shortest within the same skeleton, (2) shortening of the C(7)–C(8) bond is accompanied by elongations of the C(8)–C(13), C(7)–C(13′), C(8)–C(9), and C(6)–C(7) bonds, (3) the chemically equivalent bond lengths slightly deviate from each other when the acceptors on both sides of the perylene are symmetrically situated about the molecular axis through C(12) and C(12′). The deviations become relatively large when the acceptors are not symmetrically situated about the axis.

Figure 3b shows the geometry of the quinonoid skeleton in BCQ. Although it is similar to that of other anils and their complexes,[9,15–30] the positional and thermal parameters of the halogen atoms are little reliable and the lengths of C–X bonds are not standard because of disorder. The bond lengths of C(1)–Br(1), C(2)–Br(2), C(2)–Cl(1), and C(1)–Cl(2) are 1.814, 1.820, 1.786, and 1.870 Å respectively. A similar effect, caused by disorder, was reported for benzo[*c*]phenanthrene and 2,3-dichloro-5,6-dicyanobenzoquinone.[31]

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Table 3. Bond lengths of the perylene skeleton

	Perylene-BCQ	Perylene-TCNE[a]	Perylene-TCNQ[b]	Perylene[c]	Perylene-fluoranil[d]	Perylene-PMDA[e]	Perylene-Ni Thiete[f]
C(4)–C(5)	1.340	1.362	1.364	1.373	1.364	1.366	1.37
C(10)–C(11)	1.371	1.347	1.353	1.366	1.358	1.364	1.34
C(5)–C(6)	1.402	1.430	1.394	1.421	1.401	1.383	1.41
C(9)–C(10)	1.399	1.435	1.403	1.416	1.419	1.407	1.45
C(6)–C(7)	1.401	1.395	1.387	1.391	1.379	1.381	1.35
C(8)–C(9)	1.375	1.429	1.392	1.404	1.380	1.393	1.37
C(4)–C(12′)	1.433	1.391	1.408	1.397	1.415	1.445	1.41
C(11)–C(12)	1.396	1.408	1.425	1.402	1.406	1.366	1.39
C(7)–C(13′)	1.417	1.441	1.432	1.434	1.427	1.407	1.43
C(8)–C(13)	1.437	1.440	1.419	1.417	1.431	1.423	1.42
C(12)–C(13)	1.420	1.413	1.428	1.424	1.434	1.443	1.44
C(7)–C(8)	1.472	1.456	1.464	1.471	1.473	1.493	1.50
σ	0.011	0.01	0.005	0.005	0.005	0.01	0.02

a) Perylene-tetracyanoethylene; Ref. 13. b) Perylene-7,7,8,8-tetracyanoquinodimethane; Ref. 14. c) Ref. 10. d) Ref. 9. e) Perylene-pyromelliticdianhydride; Ref. 11. f) Perylene-bis[*cis*-1,2-bis(perfluoromethyl)ethylene-1,2-dithiolato]nickel; Ref. 12.

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