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The Crystal and Molecular Structure of Inner Triple-Layered Paracyclophanequinone

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(Received April 25, 1986)

Synopsis. The molecular structure of inner quinone isomer of two triple-layered paracyclophanequinones has been determined by means of X-ray diffraction. $C_{26}H_{24}O_2$, M 368.5, orthorhombic, space group *Pbcn*, a=12.923(1), b=11.507(1), c=12.550(1) Å, V=1866.2(3) Å^3, Z=4. The structure was solved by the direct method. Anisotropic refinement by the block-diagonal least-squares procedure gave R=0.042 for non-zero reflections. The molecule has a two-fold symmetry. The benzoquinone moiety is sandwiched by two donor benzene rings, and the two-fold axis passes through the O=C···C=O bonds of the twisted benzoquinone moiety. The outer benzene rings take a boat-form and the central benzoquinone ring is twisted.

Three isomeric triple-layered and two isomeric quadruple-layered charge-transfer cyclophanes containing benzoquinone and dimethoxybenzene moieties have been synthesized together with two quadruple-layered paracyclophanes and interesting charge-transfer spectra related to their structures, e.g. number of layers and relative donor-acceptor orientation, have been reported.1) Two isomeric triple-layered paracyclophanequinones also showed a structural relationship corresponding to the position of quinone group in their CT spectra.2)

Experimental

Yellow prismatic crystals were recrystallized from a solution of benzene-hexane mixed solvent. The crystal used had dimensions of ca. 0.15×0.23×0.20 mm. A Rigaku automated, four-circle diffractometer combined with rotating-anode X-ray generator was used at the Institute for Protein Research, Osaka University. Ni-filtered Cu$K\alpha$ radiation (λ=1.54178 Å) was used.

Intensity data were collected by the θ—2θ scan technique: the 2θ scan rate was 16° min^{-1} and the scan width from $\{2\theta(\alpha_1)-1.0\}$ to $\{2\theta(\alpha_2)+1.0\}$°. Backgrounds were measured ca. 1 s at both ends of a scan. Three standard reflections were measured after every 57 reflections, which showed no intensity decrease during the data collection. In total, 1307 reflections out of 1567($2\theta<118°$), were observed ($|F_o|>3\sigma(F_o)$). Usual Lorentz and polarization corrections were applied but absorption correction was ignored[μ(Cu)=6.3 cm^{-1}].

Structure Solution and Refinement

The structure was solved by the direct method (*MULTAN*),4) and refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).5) The function minimized was $\sum w(\Delta F)^2$. All the hydrogen atoms were located on a difference Fourier map, which were included in the refinement with isotropic temperature factors. The R value converged to 0.042. The weighting schemes used at the final stage were $w=\{\sigma^2(F_o)-0.096|F_o|+0.005|F_o|^2\}^{-1}$ for $|F_o|>0$ and w=0.667 for $|F_o|=0$, where σ is the standard deviation obtained by the counting statistics. The final atomic parameters are given in Table 1.††

Table 1. Final Atomic Coordinates of Non-Hydrogen Atoms with Equivalent Isotropic Temperature Factors6)

Atom	x	y	z	B_{eq}/Å^2
O(1)	0.50000	0.44109(14)	0.25000	3.9
O(2)	0.50000	−0.01366(14)	0.25000	4.3
C(1)	0.59996(13)	0.33588(16)	0.42624(14)	3.7
C(2)	0.52320(14)	0.31909(16)	0.52302(13)	3.8
C(3)	0.42039(13)	0.27061(14)	0.48638(12)	3.0
C(4)	0.34967(12)	0.33880(14)	0.43081(13)	3.0
C(5)	0.27872(12)	0.28866(14)	0.36215(13)	3.1
C(6)	0.27561(11)	0.16862(14)	0.34701(13)	3.0
C(7)	0.33271(12)	0.10106(14)	0.41754(13)	3.2
C(8)	0.40369(13)	0.15099(14)	0.48626(13)	3.2
C(9)	0.23218(13)	0.11955(15)	0.24473(14)	3.7
C(10)	0.32077(13)	0.09249(16)	0.16281(13)	3.7
C(11)	0.41796(11)	0.15743(14)	0.19172(12)	2.7
C(12)	0.43766(11)	0.27001(14)	0.16987(12)	2.7
C(13)	0.50000	0.33463(19)	0.25000	2.7
C(14)	0.50000	0.09285(19)	0.25000	2.9

Atomic scattering factors were taken from International Tables for X-Ray Crystallography.7) Computations were done mainly on an NEAC 2200—500 computer at the Computation Center, Osaka University, and at the final stage an ACOS 850 computer was used at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Figure 1 shows a perspective view8) of the molecule. Selected bond distances and bond angles are given in Fig. 2.

The feature of the molecular structure is that the O(1), C(13), C(14), and O(2) atoms lie on a crystallographic two-fold axis, and the molecule has a two-fold symmetry. Three benzene rings are not in the exact eclipsed position. They are mutually rotated slightly in a helical way (Fig. 3): the C(5)-C(4) and C(12)-C(13) bonds projected onto the least-squares plane of the central benzoquinone ring make an angle of 5.5°, and similarly the C(12)-C(13) and C(3′)-C(4′) bonds form 4.3°. The corresponding angles in XD(Br)X3) are 4.1 and 6.4°, respectively.

The outer benzene rings deformed to a boat form as in [2.2]paracyclophanes.9–12) The bending angle P_1, i.e. the dihedral angle between the plane defined by the

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[††] Tables of anisotropic thermal parameters, coordinates of hydrogen atoms, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8703.

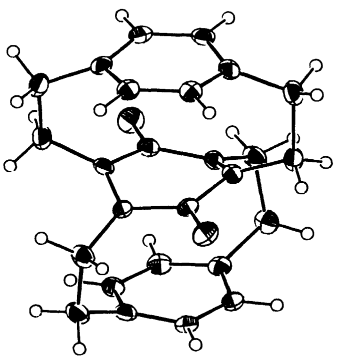


Fig. 1. A perspective view[8] of the molecule. Non-hydrogen atoms are represented as thermal ellipsoids with 30% probability level, and hydrogen atoms as spheres with B=1.0 Å^2.

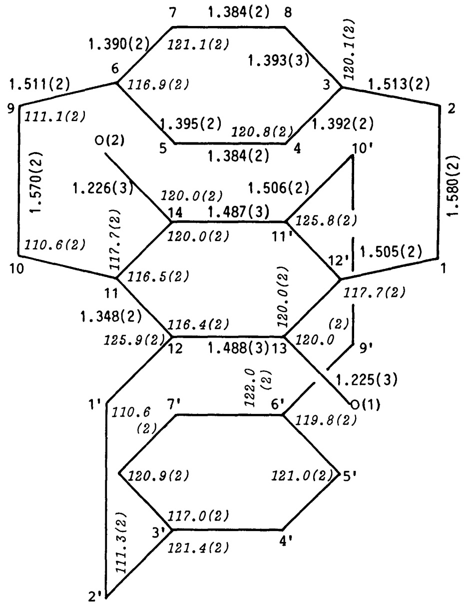
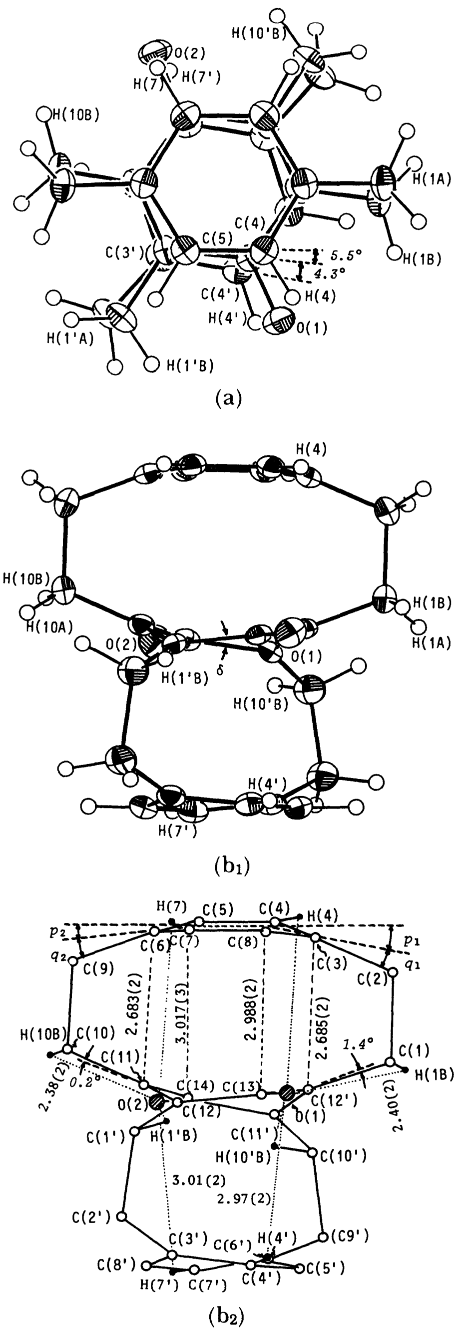


Fig. 2. Selected bond lengths [l/Å] and bond angles [ϕ/°] with estimated standard deviations in parentheses.



(a)

(b_1)

(b_2)

Fig. 3. Projections of the molecules.[8]
(a): Projected along the normal to the mean plane defined by the C(11), C(12), C(13), C(14), C(11′), and C(12′) atoms.
(b_1): Projected along the normal to the plane defined by the C(6), C(11), and C(12′) atoms.
(b_2): Schematic drawing of the (b_1) with nonbonded atomic distances between the outer benzene and central benzoquinone rings [l/Å]. p, q,[3] and other angles [ϕ/°] are also given.

C(4), C(5), C(7), and C(8) atoms (Plane 1) and that by the C(3), C(4), and C(8) (Plane 2) is 10.5°, and P_2, the dihedral angle between the Plane 1 and the Plane 3 (formed by the C(5), C(6), and C(7) atoms) is 9.9°. These are smaller than the corresponding angles in XD(Br)X [12.0 and 12.1°, respectively],[3] [2.2]paracyclophane [12.6°],[9] and other multi-layered paracyclophanes.[10–12] The C(2)-C(3) bond forms an angle q_1 of 11.9° with the Plane 2, and the C(6)-C(9) an angle q_2 of 11.5° with the Plane 3. These values are almost the same as those of the XD(Br)X and other [2.2]paracyclophanes.

Six C-C bond distances in the outer benzene rings are equal within a range of error [av. 1.390 Å]. The C(4)-C(3)-C(8) and C(5)-C(6)-C(7) angles [117.0(2) and 116.9(2)°], which are the bow and stern of the boat form, are smaller than the other four inner angles which have normal values [from 120.8(2) to 121.1(2)°].

The C_{sp^3}-C_{sp^3} bonds of ethylene bridges, C(1)-C(2) and C(9)-C(10), are 1.580(3) and 1.570(2) Å, which seem slightly shorter than that in [2.2]paracyclophane [1.593 Å].[8] Torsional angles around the C(1)-C(2) [15.5°] and C(9)-C(10) [18.8°] bonds can be compared with those in XD(Br)X [12.5 and 17.6°, respectively].

In the central benzoquinone moiety, the C(11)=C(12)

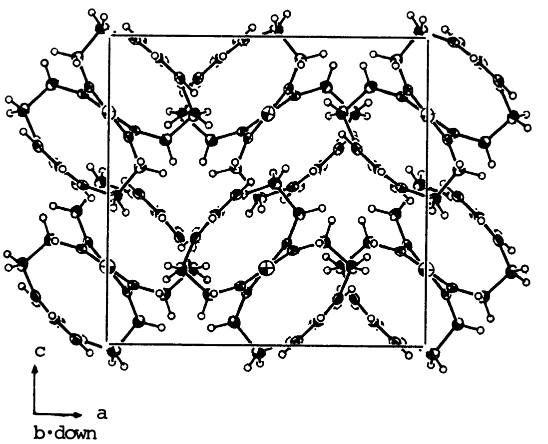


Fig. 4. Crystal structure projected along the b axis.[8]

double bond distance [1.348(2) Å] is slightly longer and the C(12)-C(13)-C(12′) bond angles[120.0(2)°] is smaller than the corresponding bond distances and bond angles in the free benzoquinone molecule,[13] and the rest has normal values. In the benzoquinone moiety, three bond angles around the C(13) and C(14) atoms are all equal [120.0(2)°]. The benzoquinone moiety consists of two planes, one defined by the O(1), C(12), C(13), and C(12′) atoms and the other formed by the rest of atoms. The dihedral angle made by these planes, i.e. the twisting angle δ (Fig. 3(b_1)) is 16.7°, which is much larger than the corresponding angles in triple- and quadruple-layered paracyclophanes [13.6 and 13.4°].[12] Closest nonbonded distances between the benzoquinone moiety and outer layer benzene ring are those observed between the C(6) and C(11) atoms [2.683(2) Å] and between the C(3) and C(12′) [2.685(2) Å], which are shorter than the corresponding distances in XD(Br)X [2.744(7) and 2.754(7) Å] (Fig. 3(b_2)). The C(1)-C(12′) bond bends by 1.4° away from the plane defined by the C(11′), C(12′), and C(13) atoms and the C(10)-C(11) bond by only 0.2° away from the plane made by the C(11), C(12), and C(14). These two angles are much smaller than the corresponding angles in XD(Br)X [6.6 and 4.7°, respectively]. Among the intramolecular nonbonded O···H distances, the O(1)···H(1B) [2.40(2) Å] and O(2)···H(10B) [2.38(2) Å] are closest. Next to these are O(1)···H(4) [2.97(2) Å] and O(2)···H(7) [3.09(2) Å].

The packing of molecules in the crystal is drawn in Fig. 4.[8] The structure of the present crystal is isomorphous with that of XD(Br)X. All of the intermolecular atomic contacts are longer than the van der Waals distances. The closest distance [3.637(2) Å] is observed between the O(1)(x, y, z) and C(9)($0.5-x$, $0.5+y$, z) atoms.

The authors wish to express their deep thanks to Miss Nobuko Kanehisa who helped them at the final stage of the refinement and *ORTEP* drawings.

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