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Three Dimensional Supramolecules of Triptycene-quinone and Its 6,7-Dimethyl Derivative Formed by Weak Intermolecular π–π Interactions and C-H···O Hydrogen Bonds

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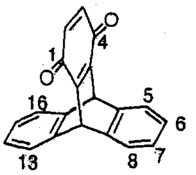
Abstract: The crystal structures of 9,10-dihydro-9,10-[*o*]benzenoanthracene-1,4-dione (TPQ) and its 6,7-dimethyl derivative (6,7-dimethyl-TPQ) were studied. In the latter crystal ribbon-like supramolecules were found to be formed by weak intermolecular π–π interactions between quinone and benzene moieties of the molecules. Similar π–π interaction seems to be present in TPQ. Moreover, the supramolecules were found to be associated each other by C-H···O hydrogen bonds to result in three dimensional supramolecules.

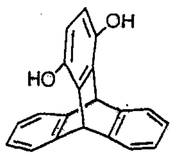
Keywords: Triptycenes, Quinones, Hydrogen bonding, Supramolecular chemistry

Although quinhydrones have been extensively studied for a long time, they have been restricted mostly to the CT complexes built by planar constituents.[1] In our effort to explore CT compounds formed by non-planar quinones and hydroquinoes we found that crystalline binary system of 9,10-dihydro-9,10-[*o*]benzenoanthracene-1,4-dione (triptycene-quinone, TPQ)[2] and 9,10-dihydro-9,10-[*o*]benzenoanthracene-1,4-diol (triptycene-hydroquinone, TPHQ)[2] was one of such candidates, because it exhibited a characteristic color remarkably different from those of TPQ (yellow) and TPHQ (colorless). Furthermore, the color of the binary system (abbreviated as TPQ_xTPHQ_{1-x}, $x >$ ca.0.8) changed from yellow to wine red depending on x.[3] This finding suggests the occurrence of a certain CT interaction in the binary crystals and is interesting enough to be investigated further, since, as pointed out by Iwamura and Makino,[2b] the intermolecular CT interaction between TPQ and TPHQ has been considered to be difficult because of an intramolecular CT interaction between *p*-benzoquinone and dibenzobarrelene moieties. Then, we decided to study the crystal structure of the binary system as well as those of the both components and a few derivatives of TPQ as a basis for the investigation of the origin of the color of TPQ_xTPHQ_{1-x}.

In the course of the present X-ray work it emerged from the examination of the crystal structures of TPQ[4] and its 6,7-dimethyl derivative (6,7-dimethyl-TPQ) that a weak intermolecular π–π interaction was considered to take place between the electron donor (D) and acceptor (A) parts (benzene and quinone moieties, respectively) of each compound. Moreover C-H···O hydrogen bonds appeared to exist in these crystals. In this paper we will report on the intermolecular D···A (π–π) and C-H···O interactions found



TPQ



TPQH

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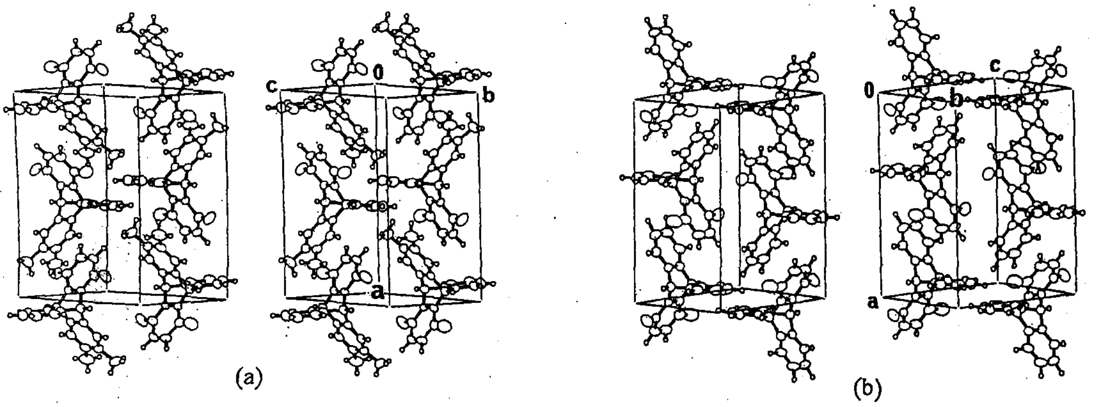
for the two compounds as an important ground for the understanding of the intermolecular π–π interactions in TPQ_xTPHQ_{1-x}.

In the crystal of 6,7-dimethyl-TPQ[5a] there exists a face to face arrangement of the benzene (D) and quinone (A) moieties to result in a ribbon-like structure shown in Fig.1a. It should be noted that the benzene ring bearing methyl groups, which are expected to enhance the donor ability of the benzene moiety, is located parallel to the quinone moiety and that the inter plane distance (d)[6] is ca.3.41 Å. The value of d indicates the contribution of a weak intermolecular D···A (π–π) interactions[7] and the ribbon-like structure is considered to be one dimensional supramolecule formed by the weak D···A interaction. Similar ribbon-like arrangement exsists also in TPQ (see, Fig.1b).[5b,8] In this case, however, the value of d (ca.3.58 Å) is longer than that of 6,7-dimethyl-TPQ, but comparable to those reported for some well-known D···A complexes such as hexamethylbenzene–chloranil,[9] anthracene–TCNQ[10] and hexamethylbenzene–1,2,4,5-tetracyanobenzene[11] (the values of inter plane distances are 3.50, 3.50 and 3.54 Å, respectively). Therfore, one may expect a significant contribution of the π–π interaction to the formation of the ribbon-like structure of TPQ.

The crystal structure of triptycene is completely different from that of TPQ in spite of the similarity between their molecular structures.[12] The crystal structure of TPHQ[13] has a strong resemblance to that of TPQ, but the ribbon-like supramolecule is not formed. The absence of the supramolecular structures in the crystals of triptycene and TPHQ is consistent with the lack of excellent A part such as *p*-benzoquinone in these molecules.

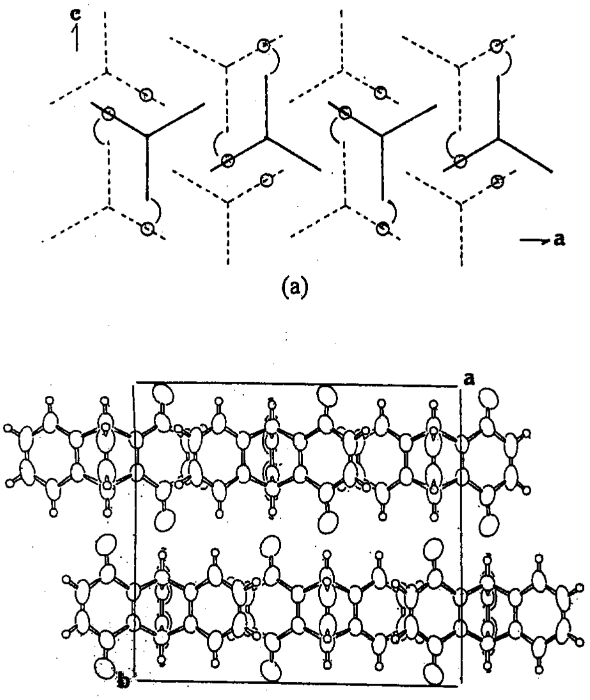


(a)

(b)

Fig.1 Stereo view of the ribbon-like structure (one dimensional supramolecule).
(a): 6,7-dimethyl-TPQ; (b): TPQ.

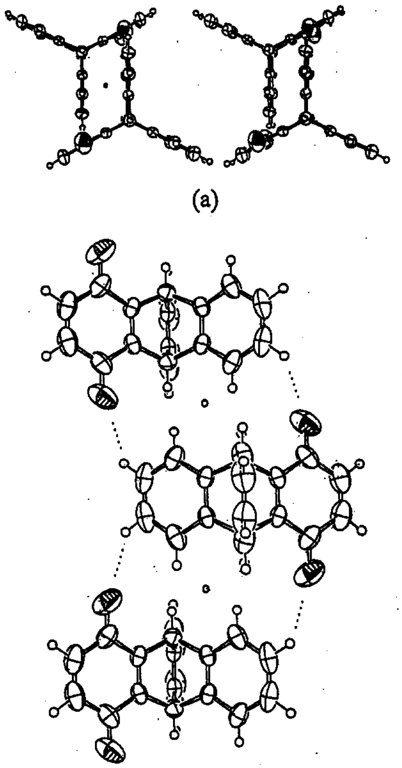
As can been in Fig. 2, the ribbon-like structures of TPQ are arranged in a layer parallel to the crystallographic *ac* plane. Two and three TPQ molecules in the adjacent layers are shown in Fig.3a and 3b, respectively. The intermolecular C···O and H···O distances are 3.382(4) and 2.56(3) Å, respectively, and C-H···O and H···O=C angles are 139(2)° and 165.9(7)°, respectively. These values satisfy the following geometrical criteria reported for the general C-H···O hydrogen bond;[14] i.e., the C···O and H···O distances are 3.0-4.0 and 2.4-3.0 Å, respectively; C-H···O angle is within 90°-180°. When the acceptor is a carbonyl group, the H···C=O angle is reported to be distributed around 120° and the C-H group lies in the plane defined by the O lone pairs.[14] In the present case these conditions for the C-H···O=C hydrogen bond are approximately satisfied. Thus, two TPQ molecules are regarded to be associated by a pair of C-H···O hydrogen bonds related by a center of symmetry. The C-H···O hydrogen bond may be facilitated through the change in the electronic states of A part caused by the D···A interaction. As shown in Fig. 2a, the C-H···O hydrogen bonds connect a ribbon-like structure in a layer and those in the adjacent one to result in a double layer (sheet-like supramolecular structure) parallel to the *ac* plane. In addition, as shown in Fig. 3b, the C-H···O hydrogen bonds contribute also to connect the double layer to form a three dimensinal structure (three dimensional supramolecule). The C-H···O hydrogen bonds quite similar to that in TPQ are found in the crystal of 6,7-dimethyl TPQ.



(a)

(b)

Fig. 2 (a): Schematic drawing of the layers of TPQ formed by the packing of the ribbon-like structure. The molecules shown by broken lines are shifted by 1/2 along the b axis compared to those shown by solid lines. The arc-like simbols and solid circles denote the positions of C-H···O hydrogen bonds and oxygen atoms, respectively.; (b): Crystal strucutre of TPQ projected onto the *ab* plane.



(a)

(b)

Fig. 3 The C-H···O hydrogen bonds of TPQ. (a): stereo view (projected along *b* axis); (b): three molecules projected along a direction perpendicular to the *b* axis. Dotted lines and small circles denote the C-H···O hydrogen bonds and center of symmetry, respectively.

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b) *Crystal data for TPQ:* $C_{20}H_{12}O_2$, M = 284.31, orthorhombic, *P*nma (no.62), a = 13.957(1), b = 12.601(1), c = 8.021(1) Å, V = 1410.7(2) Å^3, Z = 4, D_c = 1.339 g cm^{-3}, D_m = 1.31 g cm^{-3}, μ(Cu-Kα) = 6.856 cm^{-1}, F(000) = 592. 1243 independent reflections were measured on Rigaku AFC5R diffractometer (used throughout this work) with Cu-Kα radiation using θ-2θ scan ($2\theta \geq 120°$). The structure was solved by direct method and non-hydrogen atoms were refined with anisotropic thermal factors using full matrix least-squares based on F with absorption corrected data. The hydrogen atom attached to C(6) was included in the calculation with an isotropic thermal factor. The final wR(F) = 0.058 for 1096 independent observed reflections ($|F_o| > \sigma|F_o|$) and 108 parameters. Program teXsan was used throughout this work.

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