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A characteristic ribbon-like supramolecular structure and intermolecular D–A interactions in the crystals of triptycenequinones, triptycene-TCNQs and their clathrates as studied by X-ray investigations

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Abstract—A common ribbon-like structure was found in the crystals of triptycenequinones (TPQs), triptycene-TCNQs (TP-TCNQs) and their clathrates. The characteristic structure can be regarded as a supramolecular unit the formation of which is aided by weak intermolecular D–A interactions. This view is supported by the host–guest D–A interactions appeared in the crystals of the clathrates of 5,8-dimethyl-TPQ and 5,8-dimethoxy-TP-TCNQ. Intermolecular C–H···O hydrogen bonds seem to be present in TPQ derivatives. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Extended conjugated quinhydrones have been studied extensively,[1] but they have been mostly the CT complexes built by planar constituents. In our effort to explore CT compounds formed by bulky and three dimensional constituents we have been interested in the binary system of 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-dione (triptycenequinone, TPQ) and 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diol (triptycenehydroquinone, TPHQ).[2] In the course our investigation towards CT complex of TPQs and TPHQs, it seemed necessary to study the intermolecular interactions in the crystals of the TPQs themselves as a background for the understanding of the nature of the binary systems.

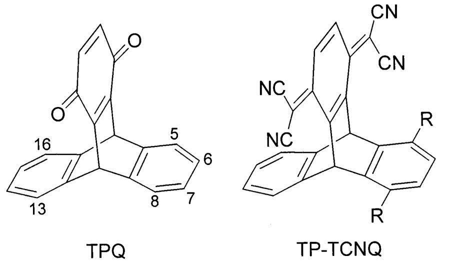
Despite the fact that TPQ and its derivatives contain both of the electron donor (D) and acceptor (A) parts (i.e. benzene and quinone moieties, respectively) in themselves, intermolecular D–A interactions have been considered to be difficult owing to an intramolecular D–A interaction.[3] But the possibility of weak D–A intermolecular interactions emerged from our X-ray work on TPQ and 6,7-dimethyl-TPQ, and we have proposed in the previous letter that weak D–A interactions between quinone and benzene moieties contribute to the formation of a characteristic, ribbon-like supramolecular structure found in their crystals.[4] Then we have extended our X-ray investigation to a variety of TPQ derivatives and a few related compounds to check the general validity of our previous proposal.

In this paper we will discuss the possible intermolecular D–A interactions in the crystal of several derivatives of TPQ and 9,10-dihydro-9,10-*o*-benzeno-1,4-bis(dicyanomethylene)anthracene (TP-TCNQ) and their clathrates (see Scheme 1).[5] We will also discuss intermolecular C–H···O hydrogen bonds in relation to the layer structures found for TPQ and its derivatives.

2. Results and discussion

2.1. A common motif of ribbon-like structure found for TPQ and TP-TCNQ derivatives

Crystal structures were determined for the following



1: 5,8,13,16-tetra-Me
2: 5,8-di-Me

3: R = H
4: R = OMe

Scheme 1.

Keywords: triptycenequinone; triptycene–TCNQ; ribbon-like structure; supramolecular chemistry; hydrogen bonding; intermolecular D–A interaction; X-ray crystal structure.

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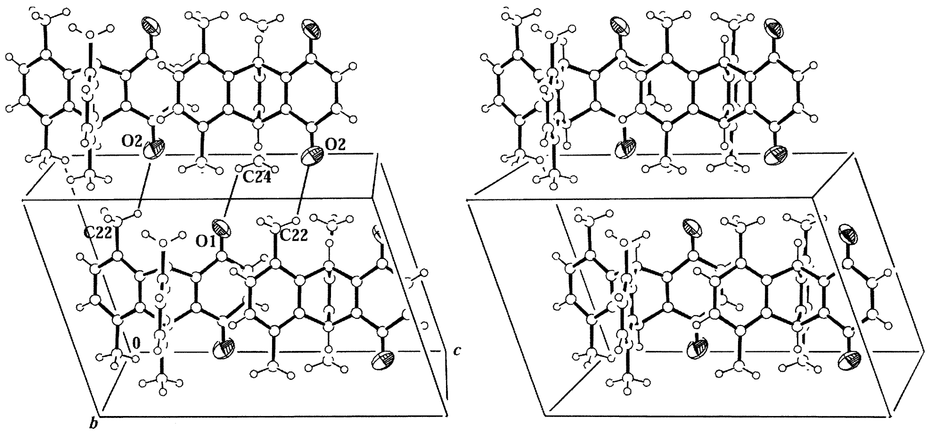

Figure 1. Stereo drawing of the crystal structure of **1**. Oxygen atoms are drawn by ellipsoids. Upper and lower halves belong to adjacent layers. Solid lines between intermolecular hydrogen and oxygen atoms indicate the positions of possible C–H···O hydrogen bonds: C24–H24C···O1 and C22–H22C···O2.

compounds: 5,8,13,16-tetramethyl-TPQ (**1**), 5,8-dimethyl-TPQ (**2**), clathrate of **2** with *p*-xylene (2:1) (**2**–*p*-xylene (2:1)), clathrate of **2** with toluene (2:1) (**2**–toluene (2:1)), TP-TCNQ (**3**) and clathrate of 5,8-dimethoxy-TP-TCNQ (**4**) with benzene (1:1) (**4**–benzene (1:1)).

As can be seen in Fig. 1, the crystal of **1** shows a typical layer structure. The crystal structures of **2**, **2**–*p*-xylene (2:1) and **2**–toluene (2:1)[6] are also characterized by their layer structures similar to that found in **1**. Packing patterns of molecules within the layers are shown in Fig. 2(a)–(c), for **1**, **2** and **2**–*p*-xylene (2:1), respectively. A common ribbon-like structure formed by face-to-face contacts between quinone and benzene moieties can be seen in these crystals. Similar ribbon-like structure was found for TPQ itself and 6,7-dimethyl-TPQ, as reported previously.[4]

Analogous ribbon-like structures were further found for **3** and a clathrate of **4**. In the crystal of **3** the face-to-face contact occurs between the TCNQ and the benzene moieties (see Fig. 2(d)). The crystal of **4**–benzene (1:1) also consists of the ribbon-like structure where the TCNQ and 5,8-dimethoxybenzene moieties are stacked in the face-to-face manner (Fig. 2(e)).

All of these ribbon-like structures mentioned earlier are characterized by a motif of face-to-face contact between electron donor and acceptor moieties of the molecules.

Then, one may expect a significant contribution of some intermolecular D–A interactions to the formation of the ribbon-like structure in addition to the usual van der Waals forces:[7] in other words, one may consider the structure as a supramolecule aided by weak intermolecular D–A interactions. This view is supported further by the following observations. (1) It can be seen for the derivatives of TPQ that the benzene groups substituted by methyl groups (better donors) are, if available, tend to be incorporated in the face-to-face contact in spite of the expected steric hindrance between C=O and CH_3 groups. (2) The approximate inter facial distance in the face-to-face contacts (d_m) are summarized in Table 1. The d_m values shorter than the van der Waals contact were observed for 6,7-dimethyl-TPQ,[4] **1**, **2** and clathrates of **2** and **4**. Although some of the values in the table are comparable to the van der Waals contact, this fact is not necessarily in conflict with the possibility of weak intermolecular D–A interactions, because rather long inter facial distances are reported for such well-known D–A complexes as hexamethylbenzene–chloranil,[10] anthracene–TCNQ[11] and hexamethylbenzene-1,2,4,5-tetracyanobenzene[12] (3.50, 3.50 and 3.54 Å, respectively). (3) The ribbon-like structure is absent in the crystals of triptycene itself,[13] and TPHQ and its derivatives having no excellent electron acceptor part.[14] (4) As indicated by the formation of the clathrates of **2** and **4** discussed later, their acceptor parts are able to participate in the intermolecular

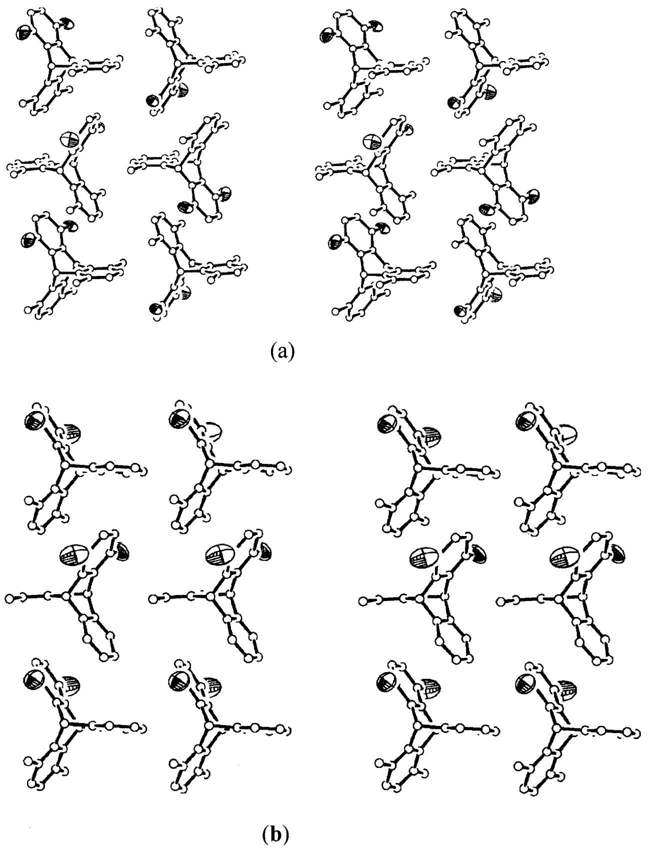

Figure 2. Stereo drawings of the ribbon-like motifs found for several compounds studied (oxygen and nitrogen atoms are drawn by ellipsoids and hydrogen atoms are omitted for clarity). (a): **1**; (b): **2**; (c) **2**–*p*-xylene (2:1); (d): **3** and (e): **4**–benzene (1:1) (at 143 K).

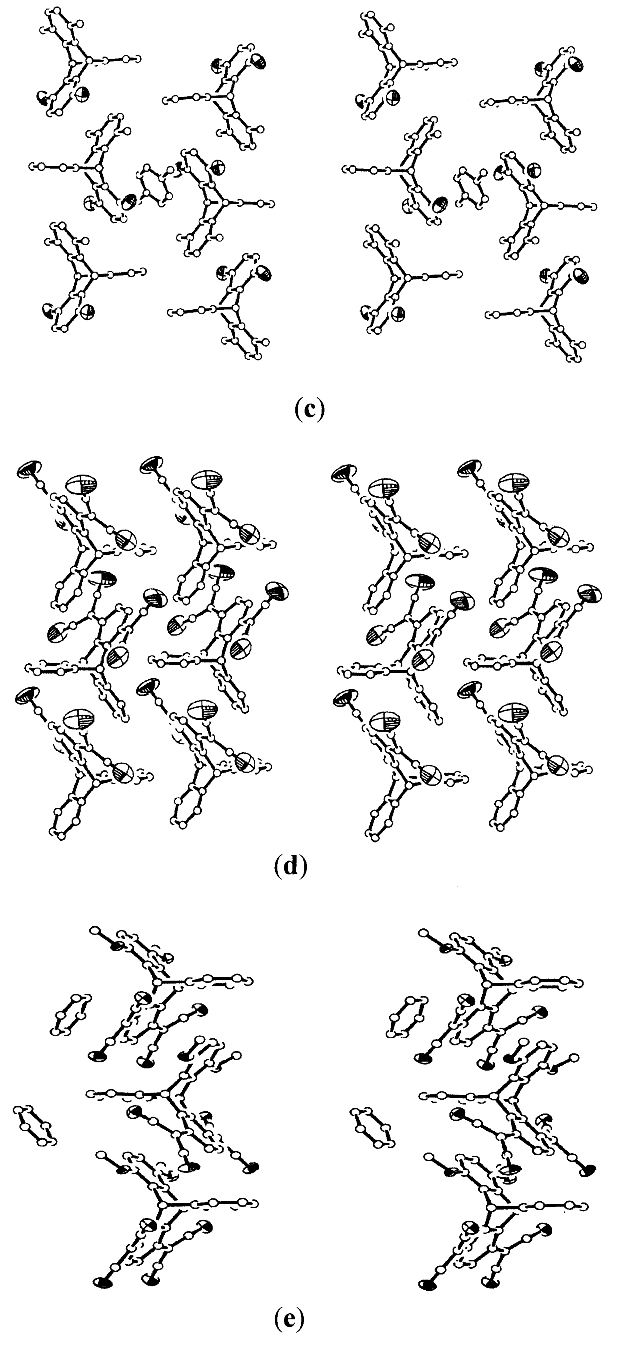

Figure 2. (*continued*)

D–A interactions, although intermolecular D–A interactions have been considered to be difficult for **2** owing to an intramolecular D–A interaction.[3]

The knowledge of the common ribbon-like structure described earlier seems to be an important background to understand the crystal structures and optical properties of CT complexes (mixed crystals) of TPQ's and TP-TCNQ's.[4]

2.2. Intermolecular D–A interaction in the clathrates studied

Table 1. Approximate inter facial distance (d_m) between the planes of D and A moieties (D···A) in the face-to-face contact

Compounds	D···A	d_m (Å)
TPQ[4]	B···Q	3.58
6,7-Dimethyl-TPQ[4]	dMB···Q	3.36
1	dMB···Q	3.37
2	B···Q	3.37
	dMB···Q	3.56
2–*p*-xylene (2:1)	dMB···Q	3.50
	p-xylene···Q	3.33
2–toluene (2:1)	dMB···Q	3.40
	Toluene···Q	3.33
3	B···TCNQ	3.61
4–benzene (1:1)	dMeOB···TCNQ	3.55
	Benzene[a]···TCNQ	3.30

(d_m): Definition of inter facial distance is difficult because two adjacent D and A planes are not exactly parallel. As an approximation we use the shortest distance between an atom on one plane and the mean plane of the other (d_m). (D···A): Q, B, dMB, dMeOB and TCNQ indicate quinone, benzene, dimethylbenzene, dimethoxybenzene and TCNQ moieties, respectively.

[a] The guest molecule.

The dark blue color of **4**–benzene (1:1) is clearly different from that of the solution (wine red). The UV/visible absorption spectrum of the crystal measured by the KBr disk method is shown in Fig. 3, together with that of a CH_2Cl_2 solution of **4**. The former spectrum exhibits a weak absorption band with the λ_{max}=ca. 770 nm which is not found in the latter spectrum. In the crystal of the clathrate, the planes of the guest molecules, as well as those of the dimethoxybenzene moieties of **4**, are arranged parallel to the planes of the TCNQ moieties of **4** (Fig. 4). Furthermore, it should be noted that a significantly short interfacial distance was found for the host–guest contact (Table 1). Thus, one or both of the D–A stacking structures shown in Fig. 4 seem responsible for the appearance of the new absorption band with the λ_{max}=ca. 770 nm.

The guest molecules in **2**–*p*-xylene (2:1) and **2**–toluene (2:1) are trapped by the acceptor part of **2** in a manner similar to the case of **4**–benzene (1:1) (see, Fig. 2(c) and (e)). The D–A interactions in these clathrates, however, appear not strong enough to cause apparent change in color between solution and crystal.

It should be mentioned briefly that **2**–toluene (2:1) decomposed gradually, while **2**–*p*-xylene (2:1) was stable, under ambient conditions. The difference in the thermal stability can be interpreted by the less bulky structure of the toluene molecule leading to a lower energy barrier hindering the movement of the molecule in the tunnel-like cavity (Fig. 2(c)).

2.3. C–H···O hydrogen bonds

In the previous paper we reported the presence of the C–H···O hydrogen bonds for the crystals of TPQ and 6,7-dimethyl-TPQ.[4] The crystals of **1**, **2** and **2**–*p*-xylele (2:1) also seem to contain the C–H···O hydrogen bonds indicated in Figs. 1, 5 and 6. The relevant intermolecular C···O and H···O distances ($R_{C\cdots O}$ and $R_{H\cdots O}$, respectively) are listed in Table 2. In general, the value of $R_{C\cdots O}$ in the C–H···O hydrogen bond has been known to be in the range of $3.0 < R_{C\cdots O}/\text{Å} < 4$.[15,16] All of the values of $R_{C\cdots O}$ listed in Table 2 are in accord with this criterion, indicating the possibility of the C–H···O hydrogen bonds. Moreover, the

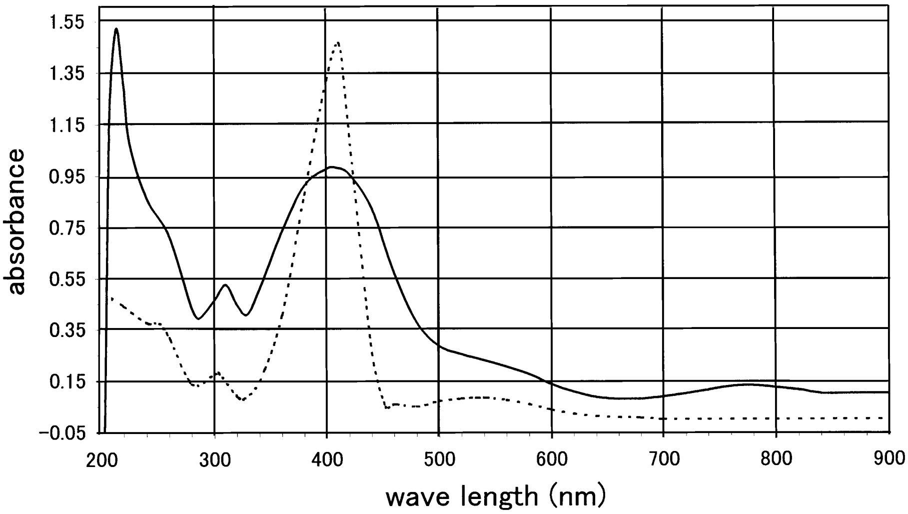

Figure 3. UV/visible spectra: solid line; **4**–benzene (1:1) (KBr disk) and broken line; a CH_2Cl_2 solution of **4**.

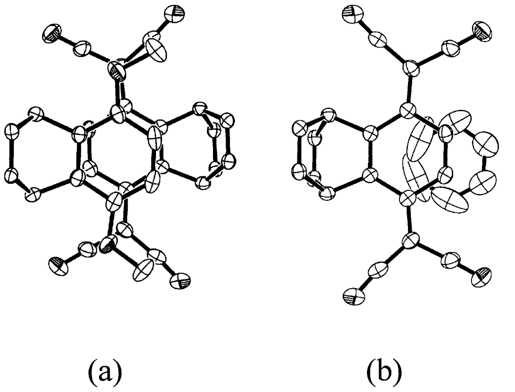

Figure 4. Stacking of adjacent molecular planes found in the crystal of **4**–benzene (1:1) at 143 K. (a) Stacking of the TCNQ and dimethoxybenzene moieties viewed perpendicular to the plane of the latter and (b) stacking of the TCNQ moiety and the benzene molecule viewed perpendicular to the plane of the latter.

values of the $R_{H\cdots O}$ for **1** and the two values for **2**–*p*-xylele (2:1) listed in Table 2 satisfy the reported criterion for $R_{H\ldots O}$, i.e. $2.4 < R_{H\cdots O}/\text{Å} < 3.0$,[15,16] even if one accounts for the deviations of 3 σ (estimated standard deviation) in the values of $R_{H\cdots O}$. The other values of $R_{H\cdots O}$ in Table 2 are also within the criterion, although they are based on the calculated positions of the relevant hydrogen atoms. Thus the values of $R_{H\cdots O}$ also support the possibility of the hydrogen bonds. It should be noted that these hydrogen bonds are so located as to connect adjacent layers to result in three-dimensional supramolecular structure.

Table 2. Intermolecular C···O and H···O distances ($R_{C\cdots O}$ and $R_{H\cdots O}$, respectively) for possible C–H···O hydrogen bonds in the crystals of **1**, **2** and **2**–*p*-xylene (2:1)

Compound	C–H···O	$R_{C\cdots O}$/Å	$R_{H\cdots O}$/Å
1	C24–H24C···O1	3.378(4)	2.71(3)
	C22–H22C···O2	3.538(4)	2.77(4)
2	C209–H209···O102	3.534(7)	2.58[a]
	C222–H22F···O102	3.409(10)	2.71[a]
	C122–H12D···O202	3.555(7)	2.60[a]
2–*p*-xylene (2:1)	C104–H106···O2	3.899(4)	2.96[a]
	C22–H222···O2	3.777(4)	2.87(3)
	C14–H14···O1	3.472(3)	2.73(2)

[a] The positions of the hydrogen atoms related to these $R_{H\cdots O}$ were calculated ones.

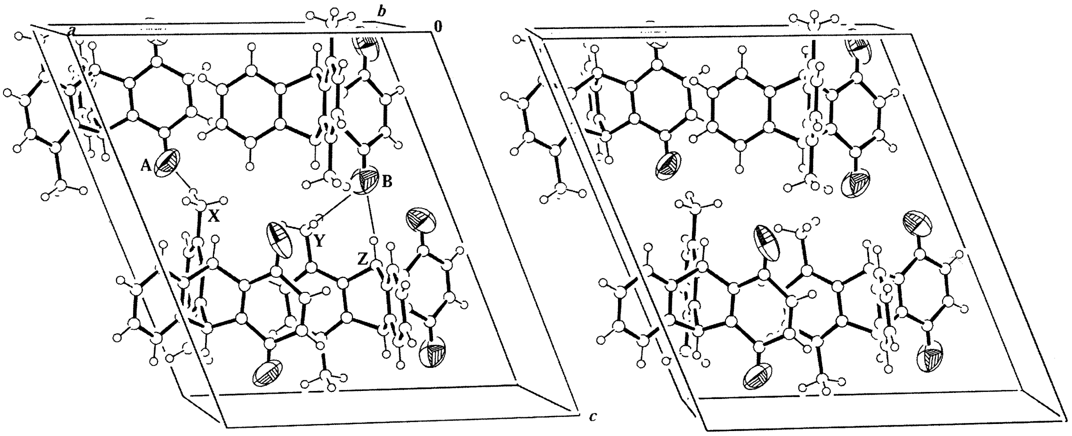

Figure 5. Stereo drawing of the crystal structure of **2**. Oxygen atoms are drawn by ellipsoids. A, B, X, Y and Z denote O202, O102, C122, C222 and C209, respectively. Solid lines between intermolecular hydrogen and oxygen atoms indicate the positions of possible C–H···O hydrogen bonds: C209(Z)–H209···O102(B), C222(Y)–H22F···O102(B) and C122(X)–H12D···O202(A).

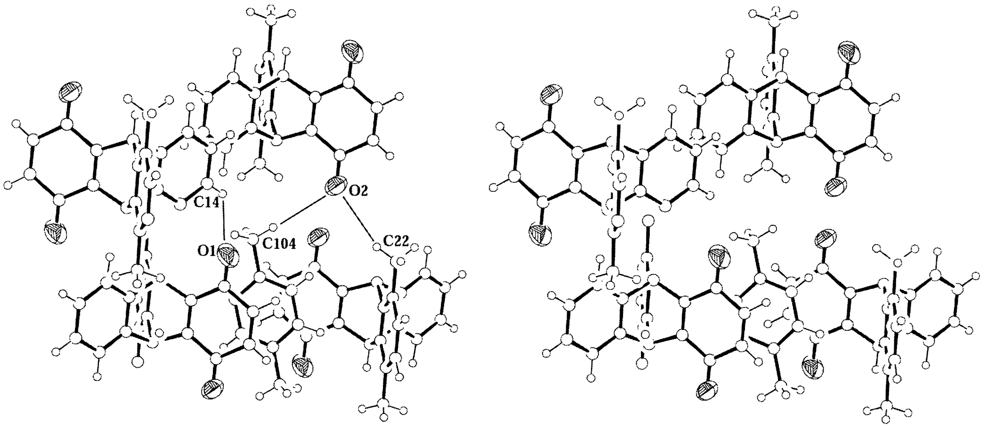

Figure 6. Stereo drawing of the crystal structure of **2**–*p*-xylene (2:1). Oxygen atoms are drawn by ellipsoids and several hydrogen atoms are omitted for clarity. Solid lines between intermolecular hydrogen and oxygen atoms indicate the positions of possible C–H···O hydrogen bonds: C22–H222···O2, C104–H106···O2 and C14–H14···O1.

3. Experimental

3.1. Preparation

TPQ and its derivatives were prepared by the method reported in the references with some modifications.[3,17] TP-TCNQ and its derivative were prepared from the corresponding 1,4-dimethyltriptycene and its derivatives.[18] The single crystals of **1**, **2** and **3** were crystallized from acetonitrile and those of **2**–*p*-xylene (2:1), **2**–toluene (2:1) and **4**–benzene (1:1)) were from *p*-xylene, toluene and benzene, respectively. Densities of the crystals were determined by a floating method at room temperatures.

3.2. UV/visible spectra

The UV/visible spectra were recorded on a Shimadzu UV2200 spectrometer.

3.3. Crystal structure determinations

A SMART 1000 diffractometer (Bruker) equipped with a cryostat was employed for the diffraction measurements using graphite monochromated Mo Kα radiations (2θ range 4–55°, for all of the crystals). Data collections for **1**, **2**, **3** and **2**–*p*-xylene (2:1) were carried out at room temperature, while for **2**–toluene (2:1) and **4**–benzene (1:1) at 123 and 143 K, respectively, by using a stream of cold nitrogen gas.

All of the structures studied were solved by direct method and refined by full-matrix least-squares calculations based on F_0 and F_0^2 without absorption corrections using SHELXL-97.[19] In the structure refinement of each compound, non-hydrogen atoms were included in the least squares calculations with anisotropic thermal parameters. All of the hydrogen atoms of **1** and **3** were included in the refinement with isotropic thermal parameters without constraints. In the cases of **2**, **2**–*p*-xylene (2:1), **2**–toluene (2:1) and **4**–benzene (1:1), the hydrogen atoms except for those cited below were included in the refinements with isotropic thermal parameters without constraints. The hydrogen atoms included in the calculations with constraints were all of the hydrogen atoms of **2**, the hydrogen atoms belonging to the methyl group of *p*-xylene of **2**–*p*-xylene (2:1) and the toluene molecule in **2**–toluene (2:1), and three of the hydrogen atoms in the benzene molecule in **4**–benzene (1:1).

Crystal data and details of the data collection and processing for each crystal are given below. CIF files have been deposited in the CCDC under the number cited for each crystal.

3.4. Crystal data and details of the data collection and processing for 1

$C_{24}H_{20}O_2$, M=340.43, monoclinic, space group $P2_1/c$ (no. 14), a=9.186(1), b=15.280(2), c=13.837(2) Å, β=108.495(3)°, U=1841.9(5) Å^3, Z=4. T=300 K. D_c=1.228, D_m=1.22 g cm^{-3}, $F(000)$=720. Crystal dimensions: 0.2×0.25×0.3 mm^3, μ(Mo Kα)=0.077 mm^{-1}, 9698 reflections measured (index range h −11 to 11, k −18 to 19, l −13 to 17), 3636 unique (R_{int}=0.0469) which were used in all calculations. The final $R_1(F)$=0.0594 for 2395 (>$2\sigma(I)$) and $wR_2(F^2)$=0.1795 and GOF=1.017 for all reflections, $w^{-1}=[\sigma^2(F_0^2)+(0.1106p)^2+0.0063p$, $p=(F_0^2+2F_c^2)/3]$, 315 parameters. Max. shift/esd=0.000, ρ_{max}=0.233, ρ_{min}=−0.140 eÅ^{-3} on final difference map. CCDC 168158.

3.5. Crystal data and details of the data collection and processing for 2

$C_{22}H_{16}O_2$, M=312.37, monoclinic, space group Pn (no. 7), a=13.896(2), b=8.076(1), c=15.958(2) Å, β=112.293(2)°, U=1657.1 (4) Å^3, Z=4. T=293 K. D_c=1.252, D_m=1.13 g cm^{-3}, $F(000)$=1321. Crystal dimensions: 0.1×0.2×0.3 mm^3, μ(Mo Kα)=0.0738 mm^{-1}, 8827 reflections measured (index range h −17 to 17, k −8 to 9, l −19 to 20), 5782 unique (R_{int}=0.0461). The final $R_1(F)$=0.0608 for 2893 (>$2\sigma(I)$) and wR_2 (F^2)=0.1647 and GOF=0.951 for all reflections, $w^{-1}=[\sigma^2(F_0^2)+(0.0745p)^2+0.0000p$, $p=(F_0^2+2F_c^2)/3]$, 437 parameters. Max. shift/esd=0.000, ρ_{max}=0.132, ρ_{min}=−0.129 eÅ^{-3} on final difference map. CCDC 168159.

3.6. Crystal data and details of the data collection and processing for 2–*p*-xylene (2:1)

$C_{26}H_{21}O_2$, M=365.46, monoclinic, space group $P2_1/n$ (no. 14), a=9.422(1), b=13.888(2), c=15.208(2) Å, β= 99.556(2)°, U=1962.4(4) Å^3, Z=4. T=287 K. D_c=1.237, D_m=1.22 g cm^{-3}, $F(000)$=772. Crystal dimensions: 0.2×0.25×0.3 mm^3, μ(Mo Kα)=0.077 mm^{-1}, 10344 reflections measured (index range h −11 to 11, k −14 to 17, l −18 to 15), 3928 unique (R_{int}=0.0546). The final $R_1(F)$=0.0534 for 2330 (>2$\sigma(I)$) and wR_2 (F^2)=0.1520 and GOF=1.018 for all reflections, $w^{-1}=[\sigma^2(F_0^2)+(0.0806p)^2+0.0000p$, $p=(F_0^2+2F_c^2)/3]$, 325 parameters. Max. shift/esd=0.000, $\rho_{\max}$=0.163, $\rho_{\min}$=−0.209 eÅ^{-3} on final difference map. CCDC 168160.

3.7. Crystal data and details of the data collection and processing for 2–toluene (2:1)

$C_{25.5}H_{20}O_2$, M=358.43, monoclinic, space group $P2_1/n$ (no. 14), a=8.947(2), b=14.012(2), c=15.251(3) Å, β= 100.210(4)°, U=1881.7(6) Å^3, Z=4. T=123 K. D_c=1.265, D_m=1.25 g cm^{-3}, $F(000)$=756. Crystal dimensions: 0.15×0.15×0.4 mm^3, μ(Mo Kα)=0.0734 mm^{-1}, 10207 reflections measured (index range h −11 to 7, k −17 to 16, l −16 to 19), 3845 unique (R_{int}=0.0958,). The final $R_1(F)$=0.0842 for1760 (>2$\sigma(I)$) and wR_2 (F^2)=0.2628 and GOF=0.990 for all reflections, $w^{-1}=[\sigma^2(F_0^2)+(0.1361p)^2+0.0000p$, $p=(F_0^2+2F_c^2)/3]$, 318 parameters. Max. shift/esd=0.000, $\rho_{\max}$=0.284, $\rho_{\min}$=−0.406 eÅ^{-3} on final difference map. CCDC 168161.

3.8. Crystal data and details of the data collection and processing for 3

$C_{26}H_{12}N_4$, M=380.41, orthorhombic, space group $Cmc2_1$ (no. 36), a=17.526(4), b=8.038(2), c=13.758(3) Å, U= 1938.1(7) Å^3, Z=4. T=293 K. D_c=1.304, D_m= 1.32 g cm^{-3}, $F(000)$=784. Crystal dimensions: 0.04× 0.10×0.26 mm^3, μ(Mo Kα)=0.0740 mm^{-1}, 5141 reflections measured (index range h −21 to 18, k −9 to 8, l −17 to 17), 1994 unique (R_{int}=0.0843). The final $R_1(F)$=0.0514 for 827 (>2$\sigma(I)$) and wR_2 (F^2)=0.1099 and GOF=0.879 for all reflections, $w^{-1}=[\sigma^2(F_0^2)+(0.0366p)^2+0.0000p$, $p=(F_0^2+2F_c^2)/3]$, 160 parameters. Max. shift/esd=0.000, $\rho_{\max}$=0.104, $\rho_{\min}$=−0.126 eÅ^{-3} on final difference map. CCDC 168162.

3.9. Crystal data and details of the data collection and processing for 4–benzene (1:1)

$C_{34}H_{22}N_4O_2$, M=518.58, monoclinic, space group Cc (no. 9), a=17.981 (2), b=11.900 (1), c=13.593 (1) Å, β= 110.992(2)°, U=2715.4(5) Å^3, Z=4. T=143 K. D_c=1.269, D_m=1.21 g cm^{-3}, $F(000)$=968. Crystal dimensions: 0.2×0.42×0.5 mm^3, μ(Mo Kα)=0.079 mm^{-1}, 7150 reflections measured (index range h −22 to 19, k −15 to 14, l −12 to 17), 3596 unique (R_{int}=0.0463). The final $R_1(F)$=0.0439 for 3272 (>2$\sigma(I)$) and wR_2 (F^2)=0.1200 and GOF=1.054 for all reflections, $w^{-1}=[\sigma^2(F_0^2)+(0.0885p)^2+0.0000p$, $p=(F_0^2+2F_c^2)/3]$, 437 parameters. Max. shift/esd=0.000, $\rho_{\max}$=0.339, $\rho_{\min}$=−0.217 eÅ^{-3} on final difference map. CCDC 168163.

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5. The numbering schemes of the atoms applied here for the compounds studied (Scheme 1) are different from those of IUPAC.
6. The crystals of **2**–toluene (2:1) and **2**–*p*-xylene (2:1) are isostructural. As well as the *p*-xylene molecule in the latter, the toluene molecule in the former is located on the inversion center to result in an orientational disorder of the molecule.
7. It has been known that the intermolecular van der Waals interactions lead to closed packed crystal structure according to so-called 'projections to hallows principle'.[8] The ribbon-like motif is one of the structures that realize the closest packing of TPQ derivatives. In fact, similar ribbon-like structure has been reported for 2,3-dimethyl-TPQ.[9] In this case, however, the distances between the six membered rings (>ca. 3.73 Å) are longer than those found in the present cases.
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