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Non-stoichiometric quinhydrone-type CT complexes: Mixed crystals of triptycenequinone and 1,4-dimethoxytriptycene with characteristic color caused by local CT interaction

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Abstract

1,4-Dimethoxytriptycene (diMeO-TP) and triptycenequinone (TPQ), non-planar donor and acceptor molecules respectively, were found to form two types of mixed crystals with limited solubility, i.e., $(\text{diMeO-TP})_x(\text{TPQ})_{1-x}$ with x=ca.0.25 and $(\text{diMeO-TP})_x(\text{TPQ})_{1-x}$ with x=ca.0.97. Crystal structures of the mixed crystals suggested that their characteristic colors, which are different from those of TPQ (yellow) and diMeO-TP (colorless), are caused by local CT interactions between 1,4-benzoquinone

and 1,4-dimethoxybenzene moieties in the crystals. The present mixed crystals can be regarded as non-stoichiometric quinhydrone-type CT complexes similar to that formed by TPQ and TPHQ (triptycenehydroquinone).

Keywords: Non-stoichiometric quinhydron; Dimethoxytriptycene; Triptycenequinone; Non-planar CT complex; Solid solution

Introduction

Quinhydrone is the typical CT complex composed of 1,4-benzoquinone and hydroquinone in 1:1 molar ratio [1-3]. 1,4-Benzoquinone has been known to form solid CT complexes not only with hydroquinone derivatives, but also with phenol and aniline derivatives [1, 4-10]. There are also quinhydrone-type complexes whose donor or acceptor or both contain such large ring system as phenanthrene derivative, 1,4-dihydro-9,10-anthracene, pyrene, perylene or naphthohydroquinone [11-14].

The molecules incorporated in the complexes mentioned above are planar or nearly planar ones and hence they are expected to be favorable for the formation of face-to-face contact between donor and acceptor molecules. Then, we tried to prepare CT complexes composed of non-planar quinones and hydroquinones to find dark brown crystals formed by 9,10-dihydro-9,10-[*o*]benzenoanthracene-1,4-dione

(triptycenequinone, TPQ, yellow) and 9,10-dihydro-9,10-[*o*]benzenoanthracene-1,4-diol (triptycenehydroquinone, TPHQ, colorless) [15]. Interestingly the crystal was proved to be not a 1:1 CT complex, but a mixed crystal (solid solution) with the composition $(TPHQ)_x(TPQ)_{1-x}$ where x < ca.0.2, which should be regarded as non-stoichiometric quinhydrone [15]. To our knowledge, this is the first example of the non-stoichiometric quinhydrone-type complex of 1,4-benzoquinones and hydroquinones [14,16]. The characteristic color of this crystal was ascribed to a local intermolecular CT-interaction enabled by an orientational disorder in the crystal [15].

In our effort to explore similar phenomena, TPQ and 1,4-dimethoxytriptycene (diMeO-TP, colorless), chemical structures of which are shown in Scheme 1, were found to form binary crystals, the color of which was brown, being completely different from that of TPQ. The present X-ray work revealed that the binary crystals were mixed crystal with the composition of $(diMeO\text{-}TP)_x(TPQ)_{1-x}$ with x=ca.0.25, in which TPQ and diMeO-TP are host and guest, respectively. The origin of the color of the mixed crystal appeared to be quite similar to that of $(TPHQ)_x(TPQ)_{1-x}$ as will be discussed in the present article.

To the best of our knowledge, crystalline state CT complex between 1,4-benzoquinone and 1,4-dimethoxybenzene has not been reported, although CT

interaction of them in solution has been known [17]. In relation to this, it is interesting that a solid state CT interaction between 1,4-dimethoxybenzene moiety of diMeO-TP and the 1,4-benzoquinone moiety of TPQ seems to be possible in the mixed crystal.

Crystal structures of pure diMeO-TP and a brown binary crystal $(\text{diMeO-TP})_x(\text{TPQ})_{1-x}$ with x=ca.0.97 will be also reported. Possible solid-state CT interaction in the latter one will be discussed briefly.

Experimental

Preparation of materials

TPQ and 1,4-dimethoxytriptycene were prepared according to the literatures [18-a] and [18-b], respectively.

Binary crystals $(\text{diMeO-TP})_x(\text{TPQ})_{1-x}$ were crystallized from acetonitrile solutions containing TPQ and diMeO-TP in various TPQ/diMeO-TP molar ratios. By means of TLC and proton NMR of the solutions of the binary crystals, the presence of the methoxy group in the crystals were confirmed and the values of x were determined by the latter method to be ca.0.25. The color of the binary crystal was brown.

The preparation of the diMeO-TP-rich binary crystals, $(\text{diMeO-TP})_x(\text{TPQ})_{1-x}$ was carried out by a similar method. The color of the binary crystal was brown when

the value of x was ca.0.97.

UV/visible spectra

The solid state UV/visible spectra were recorded by an Otsuka Electronics MCPD-2000 spectrometer from 220 to 800 nm with $BaSO_4$ as a reference.

X-ray diffraction studies

For the diffraction measurements of pure diMeO-TP, $(diMeO\text{-}TP)_x(TPQ)_{1-x}$ with x=ca.0.97 and $(diMeO\text{-}TP)_x(TPQ)_{1-x}$ with x=ca.0.25, a SMART 1000/CCD diffractometer was employed at room temperature using graphite monochromated Mo-$K\alpha$ radiations (λ = 0.71073 Å, 2θ < 55º). The structure was solved by a direct method and refined by full-matrix least-squares calculations against F_o^2 with absorption corrections (SADABS) using a program package SHELXL-97 [19]. Non-hydrogen atoms were included in the structure refinement applying anisotropic displacement parameters. Isotropic ones (U_{iso}'s) were applied for the refinement of hydrogen atoms. Crystal data and details of the data collection and processing for pure diMeO-TP: $C_{22}H_{18}O_2$, M = 314.36, triclinic, space group P-1 (no.2), a = 8.9940(16), b = 9.2558(18), c = 10.921(2) Å, α = 91.741 (4)º, β = 104.419(4)º, γ = 111.622(4)º, V = 811.0(3) Å^3, Z =

2. T = 299 K. D_c = 1.287 cm^{-3}. F(000) = 332.0. Crystal dimensions: 0.20 x 0.25 x 0.3 mm, μ(Mo-Kα) = 0.081 mm^{-1}. Unique 3109 reflections measured (index range *h:* -7 to 11, *k:* -10 to 11, *l:* -14 to 13). The final $R_1(F)$ = 0.0689 for 1905 reflections ($I > 2\,\sigma(I)$), and $wR(F^2)$ = 0.1899 and GOF = 0.936 for all reflections, $w^{-1} = [\sigma^2(F_o^2) + (0.1247p)^2 + 0.0000p]$, where $p = [F_o^2 + 2F_c^2]/3$, 290 parameters. Max. shift/esd = 0.000, ρ_{max} = 0.331, ρ_{min} = -0.284 eÅ^{-3} on final difference map.

Crystal data and details of the data collection and processing for $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$: $(C_{22}H_{18}O_2)_{0.97}(C_{20}H_{12}O_2)_{0.03}$, M = 313.46, triclinic, space group P-1 (no.2), a = 9.0039(14), b = 9.2551(14), c = 10.9277(17) Å, α= 91.743(3)º, β= 104.429(3)º, γ=111.594(3)º, V = 812.4(2) Å^3, Z = 2. T = 299 K. D_c = 1.224 cm^{-3}. F(000) = 330.9. Crystal dimensions: 0.46 x 0.26 x 0.15 mm, μ(Mo-$K\alpha$) = 0.081 mm^{-1}. Unique 3107 reflections measured (index range *h:* -11 to 11, *k:* -11 to 11, *l:* -13 to 7). The final $R_1(F)$ = 0.0946 for 2298 reflections ($I > 2\,\sigma(I)$), and $wR(F^2)$ = 0.2892 and GOF = 1.164 for all reflections, $w^{-1} = [\sigma^2(F_o^2) + (0.2000p)^2 + 0.0000p]$, where $p = [F_o^2 + 2F_c^2]/3$, 289 parameters. Max. shift/esd = 0.000, ρ_{max} = 0.399, ρ_{min} = -0.469 eÅ^{-3} on final difference map.

Crystal data and details of the data collection and processing for $(diMeO\text{-}TP)_{0.25}$

$(TPQ)_{0.75}$: $(C_{22}H_{18}O_2)_{0.25}(C_{20}H_{12}O_2)_{0.75}$, M = 291.81, orthorhombic, space group *Pnma* (no.62), a = 13.950(3), b = 12.677(2), c = 8.0111(16) Å, V = 1416.7(5) Å^3, Z = 4. T = 300 K. D_c = 1.368 cm^{-3}. $F(000)$ = 610. Crystal dimensions: 0.28 x 0.13 x 0.1 mm, μ(Mo-$K\alpha$) = 0.087 mm^{-1}. Unique 1561 reflections measured (index range *h:* -17 to 17, *k:* -15 to 15, *l:* -10 to 8). The final $R_1(F)$ = 0.0597 for 710 reflections ($I > 2\sigma(I)$), and $wR(F^2)$ = 0.1767 and GOF = 0.934 for all reflections, $w^{-1} = [\sigma^2(F_o^2) + (0.0836p)^2 + 0.0000p]$, where $p = [F_o^2 + 2F_c^2]/3$, 131 parameters. Max. shift/esd = 0.000, ρ_{max} = 0.175, ρ_{min} = -0.193 eÅ^{-3} on final difference map.

The oxygen atom in $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ was found to be distributed over two sites with populations of 0.77 (O1) and 0.23 (O2). The hydrogen atoms related to the disorder were not included in the refinement. Unfortunately, the methyl carbon atoms of the dimethoxy groups could not be found on the difference Fourier maps, despite the experimental facts indicating the presence of the methoxy group in the crystal (see, experimental section) [20].

Crystallographic data of pure diMeO-TP (CCDC620902) and $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$ (CCDC620903) have been deposited at the CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK and copies can be obtained on request, free from charge, by quoting the publication citation and deposition number.

Results and Discussion

UV/visible spectra of $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ and $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$

The color of the binary crystal $(diMeO\text{-}TP)_x(TPQ)_{1-x}$ was brown and completely different from those of pure crystalline TPQ (yellow) and diMeO-TP (colorless). The UV/visible spectrum of the solution of the binary crystal was a mere superposition of the spectra of the solutions of pure TPQ and diMeO-TP. As examples, the solid state UV/visible spectra of $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ and $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$ are compared to that of pure TPQ (Fig.1). It should be mentioned that the absorption of $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ extends to ca.700 nm region beyond the absorption edge of TPQ (ca.570 nm). Similar bathochromatic shift is observed for the binary crystal $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$. These phenomena suggest the occurrence of a certain intermolecular CT interaction in the binary crystals. Their crystal structures, as well as that of pure diMeO-TP, will be examined below to obtain structural information on the CT interaction.

Crystal structures of pure diMeO-TP, $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ and $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$

The crystal structure of pure diMeO-TP is shown in Fig. 2. There is a face-to-face contact of 1,4-dimethoxybenzene moieties in the crystal, but they overlap only slightly (see, the molecules M1 and M2 in Fig.2).

The close similarity of the lattice constant between pure diMeO-TP and $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$ indicates that the binary crystal is a mixed crystal of diMeO-TP (host) slightly doped by TPQ (guest). As can be seen from Fig.2, the replacement of diMeO-TP by TPQ in the crystal structure of diMeO-TP leads to a local face-to-face contact of 1,4-benzoquinone (electron-poor) moiety of TPQ and 1,4-dimethoxybenzene (electron-rich) moiety of DiMeO-TP. Although the overlap between the two moieties is slight (Fig. 2(b)), this situation can give rise to a local intermolecular CT interaction which seems responsible for the distinctive color (bathochromic change in color) of $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$. More stabilized local structure through the CT interaction is found in $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$, as mentioned below.

The crystal system of $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ is orthorhombic and the space group is *Pnma*. These crystal data are identical to those of pure TPQ [21]. The lattice

parameters of the binary crystal (a = 13.950(3), b = 12.677(2), c = 8.0111(16) Å) are quite similar to those of pure TPQ (a = 13.957(1), b = 12.601(1), c = 8.021(1) Å) [21]. The crystal structure of $(\text{diMeO-TP})_{0.25}(\text{TPQ})_{0.75}$ and the molecular structure found in the crystal are shown in Figs. 3 and 4, respectively. The crystal structure of $(\text{diMeO-TP})_{0.25}(\text{TPQ})_{0.75}$ is basically identical to that of pure TPQ except for the disorder of the oxygen atom discussed later. Thus the binary crystal is considered to be a kind of substitutional mixed crystal (solid-solution) in which TPQ molecules (host) are replaced in part by diMeO-TP molecules (guest). The geometrical similarity in the molecular structure between the host and guest seems to tolerate formation of mixed crystals with limited solubility of the guest in spite of the discrepancy of the crystal structures of the end members.

As can be seen in Fig.4, the oxygen atom in the mixed crystal is distributed over two sites (O1 and O2), the populations of which are approximately 0.75 and 0.25, respectively. This population ratio agrees well with the compositional ratio of TPQ and diMeO-TP in the crystal. Furthermore, it is interesting that the bond lengths in the six-membered rings Q and M in Fig.4 are close to those of the quinone and 1,4-dimethoxybenzene moieties of pure TPQ and diMeO-TP, respectively. These findings suggest that most of the guest diMeO-TP molecules have a specific orientation

different from that of the host TPQ molecules with respect to the rotation around the molecular pseudo three-fold axis, although mere superposition of the host and guest might exist also at a lower probability.

In the crystal, as can be seen in Fig.3, Q and M parts are so situated as to be participated in a face-to-face contact between them, and overlap largely (Fig.3(b)). Therefore, the mutual location of the 1,4-benzoquinone moiety of TPQ and 1,4-dimethoxybenzene moiety of diMeO-TP is favorable for an intermolecular CT interaction between them. This local CT interaction is considered to be responsible for the bathochromic change in color observed for the mixed crystal. Thus, the origin of the color of the present mixed crystal is similar to that found for $(TPHQ)_x(TPQ)_{1-x}$ with $x <$ ca.0.2 [15]. As in the case of TPHQ/TPQ mixed crystal, the binary crystal $(diMeO\text{-}TP)_x(TPQ)_{1-x}$ should be referred to as a non-stoichiometric quinhydrone-type CT complex.

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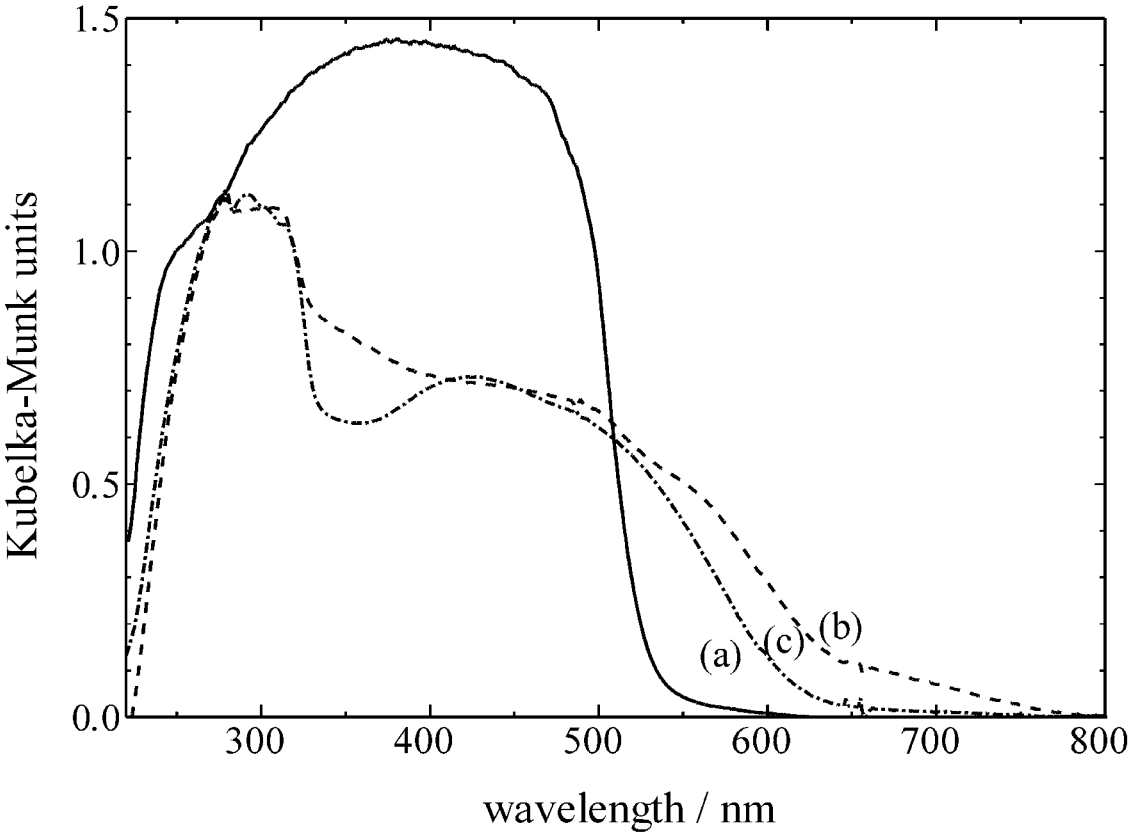
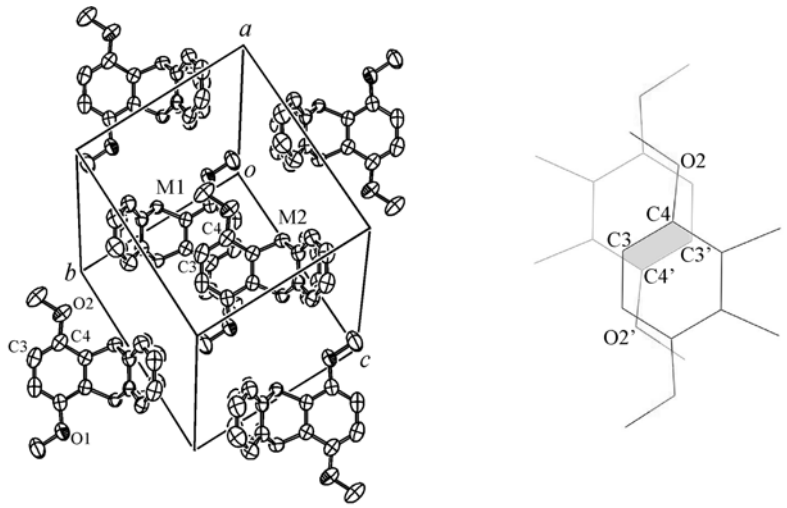


Fig. 1 Solid state UV/visible spectra of TPQ (a), $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$ (b) and $(diMeO\text{-}TP)_{0.97}(TPQ)_{0.03}$ (c). The absorption bands of the latter two specimens at around 400 nm are assignable to a characteristic band of diMeO-TP observed in its solution.

Fig. 1



(a) (b)

Fig. 2

Fig.2 Crystal structure of pure diMeO-TP.
(a) a perspective view of the crystal perpendicular to the phenyl rings of the 1,4-dimethoxybenzene moieties: Molecules M1 and M2 are related by an inversion center. Hydrogen atoms are omitted for simplicity. (b) the local view (perpendicular to the rings) concerning the overlap of the rings (lower: gray and upper: black): The overlapped area is painted in gray. The mean distance between the rings is 3.61 Å.

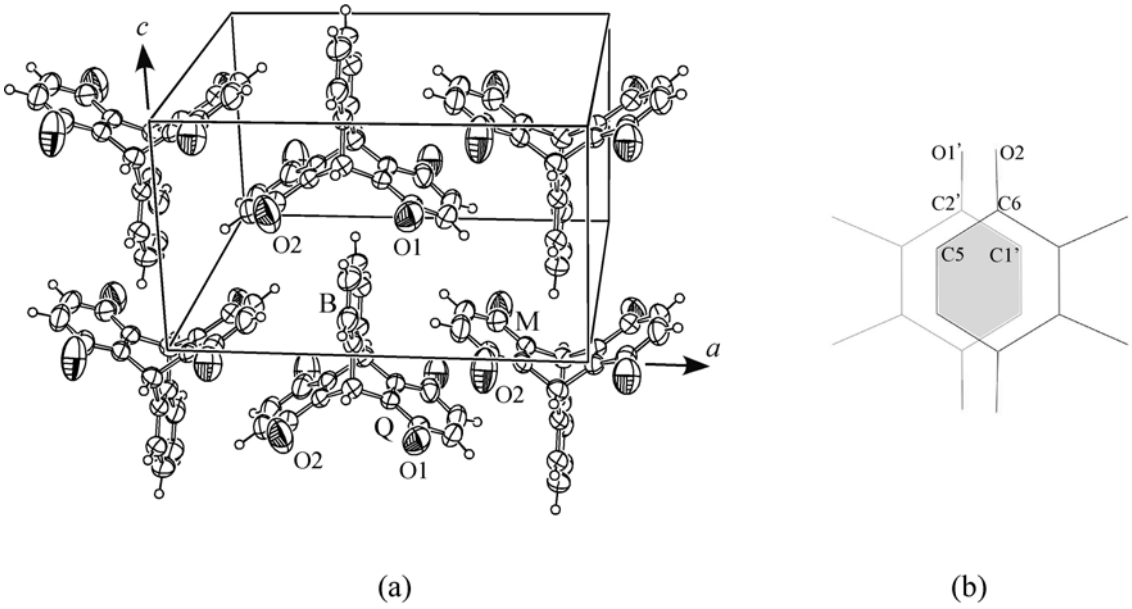


Fig. 3

Fig.3 Crystal structure of $(diMeO\text{-}TP)_{0.25}(TPQ)_{0.75}$.
(a) a perspective view of the crystal: Oxygen atoms of C=O and O-CH_3 groups (O1 and O2) are distributed on two sites to form a disordered structure. Hydrogen atoms are omitted for simplicity. (b) the local view (perpendicular to the rings) concerning the overlap of the rings Q (gray) and M (black): The overlapped area is painted in gray. The mean distance between the rings is 3.62 Å.

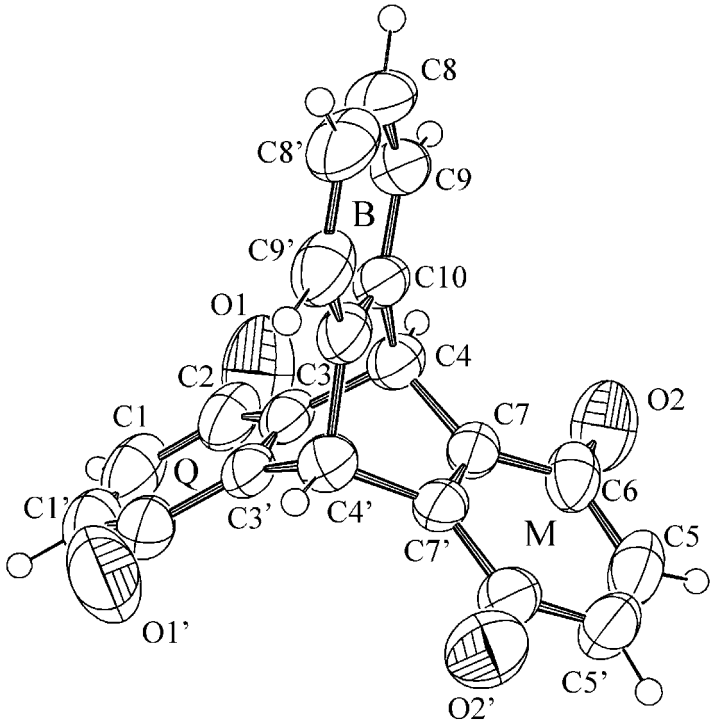


Fig. 4

Fig.4 The molecular structure found in (diMeO-TP)$_{0.25}$(TPQ)$_{0.75}$ with atom-labels. Six-membered rings having O1, O2 and C8 are distinguished by symbols Q, M and B, respectively. Bond lengths: for Q, C1-C1' 1.306(7), C1-C2 1.449(4), C2-C3 1.441(3), C3-C3' 1.349(4) and C2-O1 1.227(3) Å; for M: C5-C5' 1.353(7), C5-C6 1.402(4), C6-C7 1.408(4), C7-C7' 1.367(5) and C6-O2 1.186(11) Å; for B: C8-C8' 1.351(7), C8-C9 1.396(4), C9-C10 1.389(3) and C10-C10' 1.376(5) Å.