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Solid solution of triptycenequinone and triptycenehydroquinone as a non-stoichiometric quinhydrone. Bathochromic changes in color caused by local intermolecular interaction between *p*-benzoquinone and hydroquinone moieties

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Abstract

Binary crystal 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) was found to be a substitutional solid solution of TPQ doped by TPHQ with concentration of TPHQ < ca.0.2. The characteristic color (brown) of the solid solution may be ascribed to local intermolecular CT interaction between the *p*-benzoquinone and hydroquinone moieties of TPQ and TPHQ, respectively, enabled by a disorder in the binary crystal. It seemed appropriate to regard the solid solution as non-stoichiometric quinhydrone. Crystal structure of pure TPHQ is also reported. A common molecular arrangement in the crystals of pure TPQ and pure TPHQ, as well as the resemblance in the molecular structure, seems to be favorable for the formation of the solid solution.

Keywords

non-stoichiometric quinhydrone, triptycenequinone, triptycenehydroquinone, solid solution, intermolecular CT interaction

Introduction

Quinhydrones so far studied are mostly restricted to the CT complexes built by planar components,[1-3] because the planarity of the quinone molecules, that of hydroquinone as well, is favorable for the effective overlap of the π-electron systems. In the cases of quinones and hydroquinones having bulky, non-planar substituents, their molecular structures seem unfavorable for the overlap that is required to form CT complexes. This situation is expected to occur for 9,10-dihydro-9,10-[*o*]benzenoanthrarcene-1,4-dione (triptycenequinone, TPQ (Scheme 1 a)) and its counterpart, 9,10-dihydro-9,10-[*o*]benzenoanthracene-1,4-diol (triptycenehydroquinone, TPHQ (Scheme 1 b)). Moreover, it has been reported that external quinhydrone-type complex of TPQ with TPHQ was not formed owing to the intramolecular CT interaction. [4]

Our previous paper showed, however, that, in the crystals of pure TPQ and its alkyl derivatives, the *p*-benzoquinone moiety of TPQ participated in a weak intermolecular CT interaction with benzene or alkyl benzene moieties.[5,6] In addition, we recently obtained a series of binary crystals composed of TPQ and TPHQ. Interestingly, they were found to be non-stoichiometric binary crystals with mole fraction (x) of TPHQ < ca.0.2 in contrast to the fact that the hitherto reported quinehydrones are stoichiometric binary crystals between corresponding quinones and hydroquinones. The color of the present binary crystals (brown) was completely different from the color of their solutions (pale yellow) suggesting occurrence of a certain intermolecular interaction between *p*-

benzoquinone and hydroquinone moieties in the crystal. To our best knowledge such a non-stoichiometric quinhydrone-type CT complex has not been known so far.

In the present work, on the ground of solid state UV/visible spectral investigation and X-ray single crystal study on a binary crystal $(TPQ)_{1-x}(TPHQ)_x$ with x=ca.0.2, we will show that the binary crystal is a solid-solution of TPQ doped by TPHQ. Furthermore, a local, isolated intermolecular interaction between *p*-benzoquinone moiety of TPQ and hydroquinone moiety of TPHQ in the solid solution, which is enabled by a disorder structure, is responsible for bathochromic changes in color observed in the solid solution. The O-H stretching vibrational spectra of the binary crystals will be also examined in relation to the nature of the crystals. The crystal structure of TPHQ was also determined in the present work to find a close similarity of the molecular packing in TPQ and TPHQ. Their crystal structures will be briefly discussed in relation to the possibility of the formation of the solid solution.

Experimental

Preparation of materials

TPQ and TPHQ were prepared according to the literatures.[4,7] Binary crystals $(TPQ)_{1-x}(TPHQ)_x$ were crystallized from acetonitrile solutions containing TPQ and TPHQ in various TPQ/TPHQ molar ratios between 0.1/0.9 and 0.95/0.05. The values of x were determined by means of proton NMR of the solutions of the binary crystals. The value of x was at most ca.0.2. The preparation of the TPHQ-rich binary crystals by the present method was unsuccessful. The color of the binary crystal varies from yellow of pure TPQ ($x = 0$) to dark brown of $(TPQ)_{1-x}(TPHQ)_x$ with x=ca.0.2 depending on x.[8]

A single crystal of the binary system suitable for X-ray work could be selected from crystals of $(TPQ)_{1-x}(TPHQ)_x$ with x = ca.0.2. Colorless single crystals of pure TPHQ used in the X-ray experiments were crystallized from acetonitrile solutions of the compound.

X-ray diffraction studies

Solid solution: Reflections of $(TPQ)_{0.8}(TPHQ)_{0.2}$ were measured on a Rigaku-AFC5R diffractometer with Mo K_α radiation (λ = 0.71073 Å, 2θ<55°). The structure was solved by a direct method and refined by full-matrix least-squares calculations based on F_o^2 with absorption correction (ψ-scan method) using a program package SHELXL-97.[9] Non-hydrogen atoms except for one mentioned below were included in the structure refinement applying anisotropic displacement parameters. The oxygen atom was found to be disordered over three sites with approximate populations of 0.52 (O1), 0.40 (O2) and 0.08 (O3). Isotropic displacement parameter (B_{iso}) was applied to O3. The hydrogen atoms except for the ones cited below were included in the refinement with B_{iso}'s. The hydrogen atom of the OH group and further two hydrogen atoms related to the disorder were not included in the refinement.

Crystal data and details of the data collection and processing for $(TPQ)_{0.8}(TPHQ)_{0.2}$: $(C_{20}H_{12}O_2)_{0.8}(C_{20}H_{14}O_2)_{0.2}$, i.e. $(C_{20}H_{12.4}O_2)$, M = 284.7, orthorhombic, space group *Pnma* (no.62), a = 13.984(1), b = 12.722(2), c = 8.024(2) Å, U = 1427.5(3) $Å^3$, Z = 4. T = 299 K. D_c = 1.325, D_m = 1.32 g cm^{-3} by floating. $F(000)$ = 594. Crystal dimensions: 0.6 x 0.35 x 0.3 mm, μ(Mo-Kα) = 0.085 mm^{-1}. Unique 1718 reflections measured (index range h: 0 to 18, k: 0 to 16, l: -10 to 0). The final $R_1(F)$ = 0.0882 for 897 reflections ($I > 2\sigma(I)$), and $wR(F^2)$ = 0.2835 and GOF = 1.075 for all reflections, w^{-1} =

$[\sigma^2(F_o^2) + (0.1591p)^2 + 0.1126p]$, where $p = [F_o^2 + 2F_c^2]/3$, 132 parameters. Max. shift/esd = 0.000, $\rho_{max} = 0.277$, $\rho_{min} = -0.408$ eÅ^{-3} on final difference map.

Pure TPHQ: A SMART 1000/CCD diffractometer was employed for the diffraction measurements of TPHQ at 293 K using graphite monochromated Mo-Kα radiations (λ = 0.71073 Å, $2\theta < 55°$). 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.[9] The asymmetric unit contains four molecules (Molecules 1, 2, 3, and 4). Non-hydrogen atoms except for the ones cited below were included in the structure refinements applying anisotropic displacement parameters. Isotropic ones were applied to seven atoms; C104 (Molecule 1), C301 and C316 (Molecule 3), C401, C409, O401 and O402 (Molecule 4). The positions of all hydrogen atoms were calculated and they were included in the refinement with isotropic displacement parameters.

Crystal data and details of the data collection and processing for TPHQ: $C_{20}H_{14}O_2$, M = 286.31, hexagonal, space group $P6_3$ (no.173), $a = b$ = 27.864(3), c = 12.983(2) Å, U = 8730(2) Å^3, Z = 24. T = 293 K. D_c = 1.307 cm^{-3}, D_m = 1.32 g cm^{-3} by floating. $F(000)$ = 3600. Crystal dimensions: 0.35 x 0.17 x 0.13 mm, μ(Mo-Kα) = 0.084 mm^{-1}, 49798 reflections measured (index range h -36 to 31, k -26 to35, l -16 to16), 12100 unique (R_{int} = 0.0982). The final $R_1(F)$ = 0.1194 for 4971 ($>2\sigma(I)$) and wR_2 (F^2) = 0.3423 and GOF = 1.057 for all reflections, $w^{-1} = [\sigma^2(F_o^2) + (0.0797p)^2 + 25.40p]$ where $p = (F_o^2 + 2F_c^2)/3$, 761 parameters. Max. shift/esd = 0.001, $\rho_{max} = 0.53$, $\rho_{min} = -0.72$ eÅ^{-3} on final difference map. The structural solution mentioned above has a pseudo-center of symmetry and seemingly suggests space group $P6_3$/m (no.176). But mirror planes (horizontal to the 6_3-axis) located on Molecules 1-3 and those on Molecule 4 and its equivalents did not agree one another, so that we could not obtained any reasonable solution based on the space group $P6_3/m$.

Crystallographic data 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: CCDC207578 and CCDC207579 for TPHQ and $(TPQ)_{0.8}(TPHQ)_{0.2}$, respectively.

Infrared (IR) and UV/visible spectra

The IR spectra were measured by a Perkin Elmer FT IR spectrometer (PARAGON 1000PC). The UV/visible spectra of solutions were recorded on a Shimadzu UV2200 spectrometer. The solid state UV/visible spectra were observed by an Okuda Electronics MCPD-2000 spectrometer.

Results and Discussion

Characteristic color and UV/visible spectra of the binary crystal $(TPQ)_{1-x}(TPHQ)_x$

The color of the solution of the binary crystal $(TPQ)_{1-x}(TPHQ)_x$ was yellow and its UV/visible spectrum was a mere superposition of the spectra of the solutions of TPQ (yellow) and TPHQ (colorless). On the other hand, the color of the binary crystal was brown as can be seen from Fig. 1. Thus, the color of the binary crystal was completely different from those of pure crystalline TPQ (yellow) and TPHQ (colorless), although it varied to some extent to the naked eye depending on x. As an example, the solid state UV/visible spectra of $(TPQ)_{0.9}(TPHQ)_{0.1}$ is compared to that of pure TPQ in Fig. 2.

The absorption of the binary crystal extends to ca.700 nm region beyond the absorption edge of TPQ (ca.570 nm). This bathochromic shift observed for the binary crystal suggests the occurrence of some intermolecular CT interaction characteristic of the binary crystal. In order to obtain structural information on the interaction, the crystal structure of a binary crystal $(TPQ)_{0.8}(TPHQ)_{0.2}$ will be examined below.

Crystal structure of the binary crystal $(TPQ)_{1-x}(TPHQ)_x$

The crystal system of $(TPQ)_{0.8}(TPHQ)_{0.2}$ is orthorhombic and the space group is *P*nma. These crystal data are identical to those of pure TPQ.[5,10,11] The lattice constants of the binary crystal (a = 13.984(1), b = 12.722(2), c = 8.024 (2) Å) are quite similar to those of pure TPQ (a = 13.957(1), b = 12.601(1), c = 8.021(1) Å). The crystal structure of the binary crystal (Fig. 3) is essentially identical to that of pure TPQ except for the disorder of the oxygen atom mentioned later. Thus the binary crystal is considered to be a substitutional solid-solution in which TPQ molecules (host) are replaced in part by TPHQ molecules (guest). The b axis of the solid solution exhibited a significant expansion (ca.1%) as compared to that of pure TPQ. This observation can be ascribed to the facts that the size of the hydroxyl group of the guest molecule is relatively large and that the C=O bond in the host crystal is parallel to the b axis.

From the geometrical similarity in the molecular structure between the host and guest, the replacement of TPQ with TPHQ seems not to disturb the molecular packing in the host crystal seriously in accord with the basic rule of solubility.[12]

Furthermore, the hydroxyl groups of the substituted TPHQ and the oxygen atoms of TPQ are expected to form O-H···O hydrogen bonds, though in part, that stabilize the lattice energy of the binary crystal. This is also consistent with the basic rule.

The IR spectra of the OH stretching vibration of pure TPQ, $(TPQ)_{1-x}(TPHQ)_x$ and pure TPHQ are shown in Fig. 4. The wavenumber of the OH stretching band of the solid solution (3410 cm^{-1}) is substantially constant regardless of x, and clearly different from that of pure TPHQ (3264 cm^{-1}). These observations suggest that the molecules of TPHQ are dispersed homogeneously in the host lattice to result in an almost uniform local environment around the OH groups.

As shown in Fig. 5, the disorder in the solid solution manifests itself in a distribution of the oxygen atom over three sites O1, O2, and O3, the population of them being approximately 0.52, 0.40 and 0.08, respectively. This disorder is caused by an orientational distribution of the molecules around its pseudo three-fold axis.

In the crystal of pure TPQ, a weak CT interaction between *p*-benzoquinone and benzene moieties contributes to the formation of a ribbon-like structure (Motif 2 defined in Fig. 3).[5,6] Since this molecular arrangement is maintained in the solid solution, the orientational disorder means that there may be a certain probability of the occurrence of face-to-face contact of the *p*-benzoquinone and hydroquinone moieties. This local or occasional *p*-benzoquinone/hydroquinone CT interaction, which is expected to be stronger than that between *p*-benzoquinone and mere benzene moieties, should be responsible for the bathochromic change in color of the solid solution. Therefore, the origin of the color of the solid solution is same as that found for ordinary stoichiometric quinhydrones, although the composition of it is in principle non-stochiometric. In this sense, the binary crystal $(TPQ)_{1-x}(TPHQ)_x$ should be referred as a non-stoichiometric quinhydrone-type CT complex.

Similarity and discrepancy in crystal structure between TPQ and TPHQ in relation to the formation of the solid solution

Molecular structure of pure TPHQ (Molecule 1) with the atom labeling is shown in Fig. 6. The crystal of pure TPHQ has a typical layer structure built by stacking the planar aggregation units depicted in Fig. 7.

It is interesting to note that the hexagonal unit cell of pure TPHQ has a close relationship with the orthorhombic unit cell of pure TPQ (see, caption of Fig. 7). Moreover, a molecular aggregation motif (Motif 1 defined in Fig.'s 3 and 7) is common to the layer structures of pure TPHQ and TPQ except for the position of the oxygen atom. The Motif-1's are arranged parallel to one another in pure TPHQ, while alternately anti-parallel in TPQ. The latter arrangement results in the ribbon-like supramolecular unit (Motif 2), to the formation of which a weak CT interaction between *p*-benzoquinone and benzene moieties contributes.[5,6] The absence of this motif in pure TPHQ crystal seems to be reasonable because it lacks the acceptor moiety in the molecule.

The crystals of pure TPQ and TPHQ are not isomorphous. This discrepancy between the end members prevents the formation of continuous solid solution. However, the guest molecules are considered to be able to dissolve in the host lattice within a limited solubility to form solid solution owing not only to the similarity in the molecular structure, but also to that in the pattern of the molecular aggregation.

Conclusion

We found that TPQ (yellow) and TPHQ (colorless) form non-stoichiometric quinhydrone-type CT complexes as a solid solution, in spite of the fact that they are *p*-benzoquinone and hydroquinone derivatives having bulky and non-planar substituents respectively. The solid solutions showed bathochromic changes (yellow to brown) in color, attributable to an intermolecular CT interaction between *p*-benzoquinone and hydroquinone moieties. According to the nature of solid solution, mole fraction x of TPHQ in the binary crystal can be freely varied within the range $0 < x <$ ca.0.2.

The present structural investigations showed that common structural features (layer structure with a common molecular aggregation motif (Motif 1)) observed both in the hexagonal pure TPHQ and the orthorhombic pure TPQ crystals enabled the non-stoichiometric mixing of TPQ and TPHQ in the binary crystal. It is also shown that the orientational disorder of TPQ and TPHQ molecules in the solid solution allowed a face-to-face contact of the moiety of *p*-benzoquinone of TPQ and that of hydroquinone of TPHQ, resulting in the intermolecular CT interaction between the moieties occurring in places.

Acknowledgements

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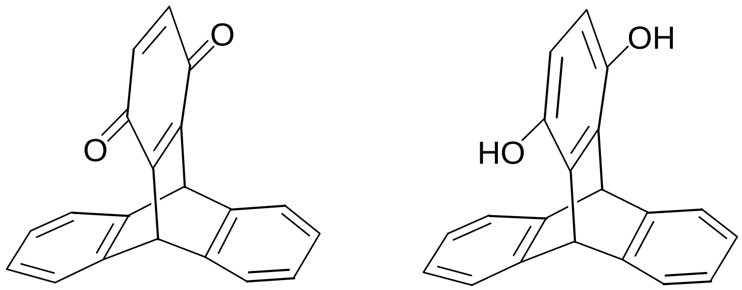
Scheme

Scheme 1. Molecular structures of TPQ and TPHQ.



a

TPQ

b

TPHQ

Scheme 1. Molecular structures of TPQ and TPHQ.

Figure captions

Figure 1. Photographs of crystals of pure TPQ, solid solution and pure TPHQ.

Figure 2. Solid state UV/visible spectra of pure TPQ and $(TPQ)_{0.9}(TPHQ)_{0.1}$.

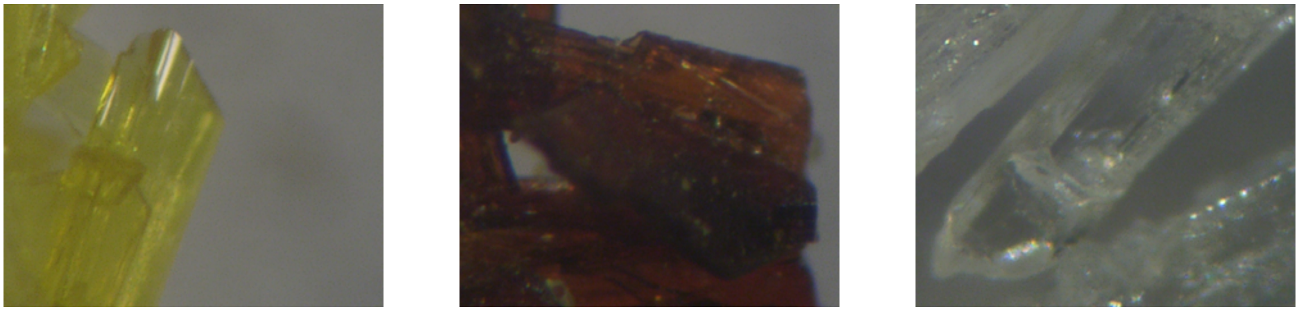
Figure 3. Layer structure in the crystal of $(TPQ)_{0.8}(TPHQ)_{0.2}$ projected onto the *ac* plane ($0<b<1/2$). The molecular arrangements enclosed by broken and one-point broken lines are referred to as Motifs 1 and 2, respectively. Symmetry code of O2' : x+1/2, y, -z+1/2.

Figure 4. Infrared spectra of the OH stretching vibration region; a: pure TPQ; b: $(TPQ)_{0.95}(TPHQ)_{0.05}$; c; $(TPQ)_{0.92}(TPHQ)_{0.08}$; d; $(TPQ)_{0.8}(TPHQ)_{0.2}$ and e: pure TPHQ.

Figure 5. Molecular structure found in $(TPQ)_{0.8(}TPHQ)_{0.2}$ showing a disorder of the oxygen atoms. The populations for O1, O2 and O3 are 0.52, 0.40 and 0.08, respectively. The position of O1 corresponds to that of the oxygen atom in TPQ.

Figure 6. X-ray structure of pure TPHQ (Molecule 1) with the atomic numbering scheme. For Molecules 2, 3 and 4, the first digit of the label of atom is ‘2’, ‘3’ and ‘4’, respectively.

Figure 7. Aggregation of TPHQ molecules in a layer viewed along the crystal *c* axis ($0<c<1/2$). Labels 1, 2, 3 and 4 indicate Molecules 1, 2, 3 and 4 respectively. The molecular arrangement enclosed by broken lines corresponds to Motif 1 defined in Fig.3. The unit cell vectors of TPHQ (hexagonal, a_h, b_h, c_h) and those of TPQ (orthorthombic, a_o = 13.957(1), b_o = 12.601(1), c_o = 8.021(1) Å)[4] are approximately related by the equations: $a_h = a_o - 3c_o$, $b_h = a_o + 3c_o$, and $c_h = b_o$.



TPQ **$(TPQ)_{0.8}(TPHQ)_{0.2}$** **TPHQ**

Fig. 1. Photographs of pure TPQ, solid solution, and pure TPHQ.

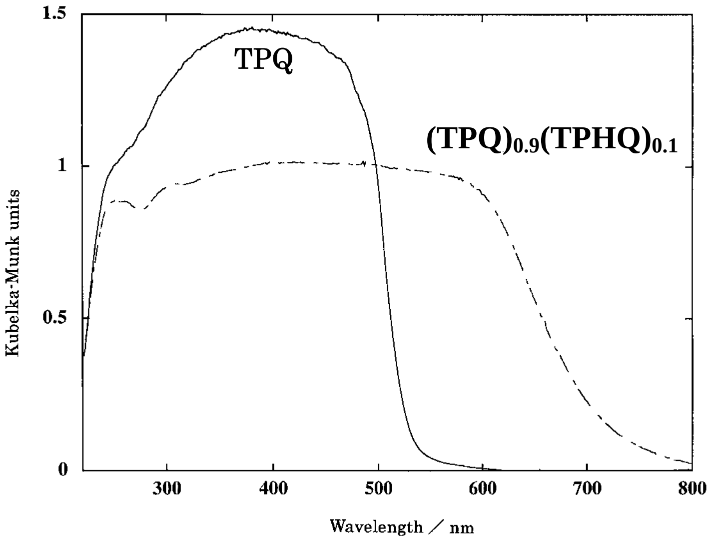
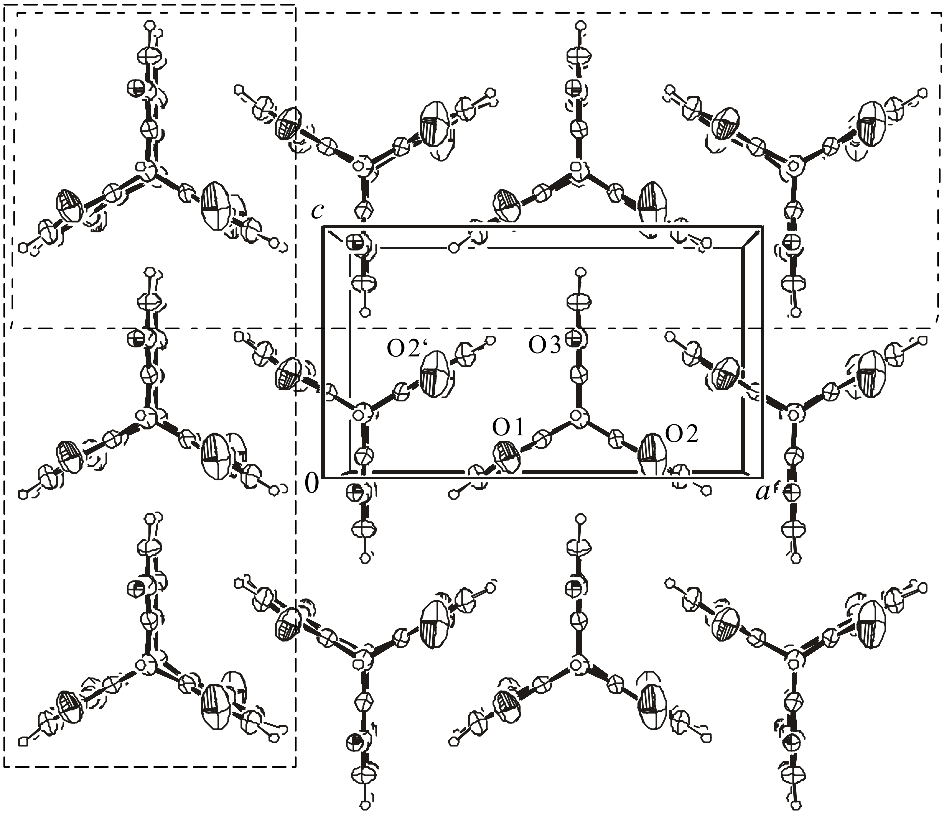


Fig. 2. Solid state UV/visible spectra of pure TPQ and $(TPQ)_{0.9}(TPHQ)_{0.1}$.



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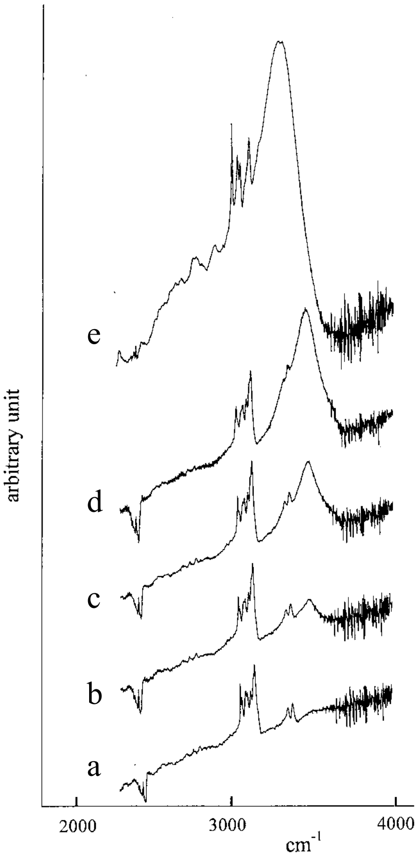

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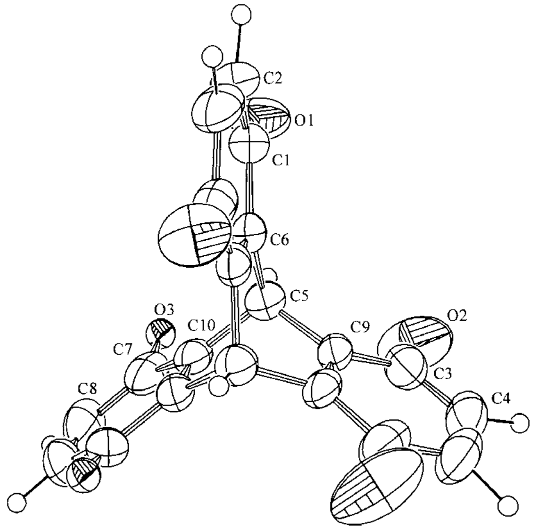
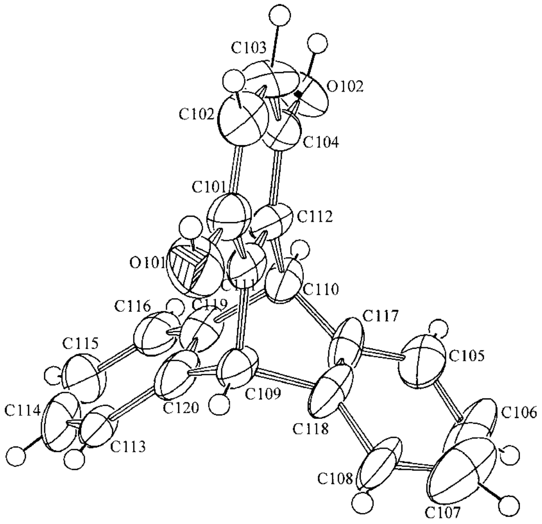


Fig. 5. Molecular structure found in $(TPQ)_{0.8}(TPHQ)_{0.2}$ showing a disorder of the oxygen atoms. The populations for O1, O2 and O3 are 0.30, 0.55 and 0.15, respectively. The position of O2 corresponds to that of the oxygen atom in TPQ.



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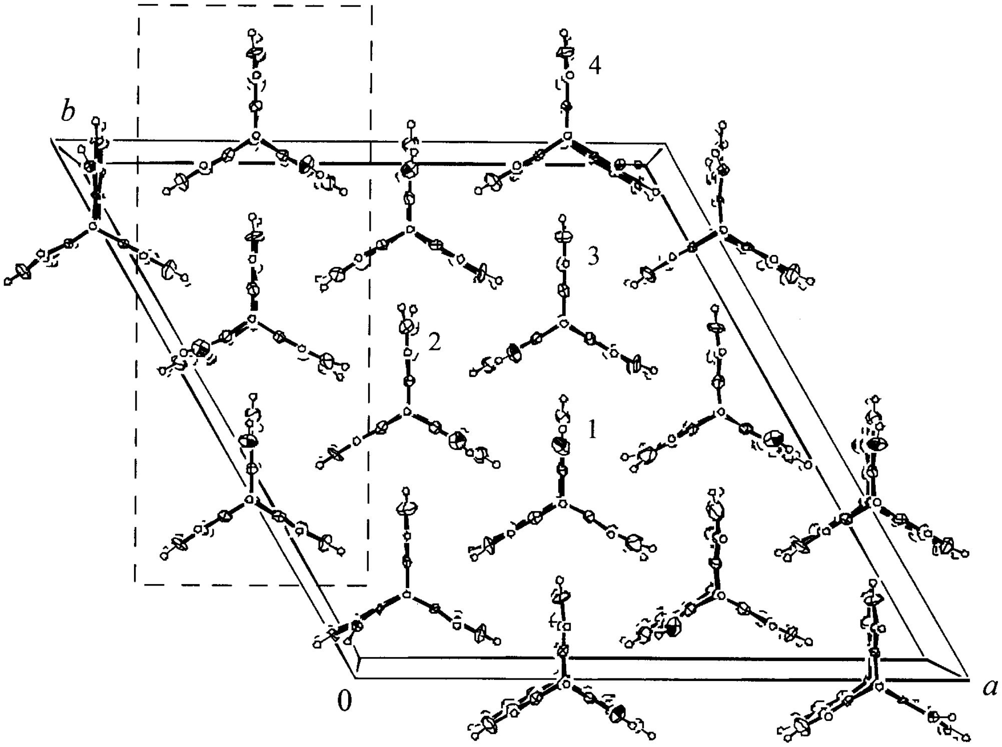

Fig. 7. Aggregation of TPHQ molecules in a layer viewed along the crystal *c* axis (0<*c*<1/2). Labels 1, 2, 3 and 4 indicate Molecules 1, 2, 3 and 4 respectively. The molecular arrangement enclosed by broken lines corresponds to Motif 1 defined in Fig.3. The unit cell vectors of TPHQ (hexagonal, $\boldsymbol{a}_\mathrm{h}$, $\boldsymbol{b}_\mathrm{h}$, $\boldsymbol{c}_\mathrm{h}$) and those of TPQ (orthorthombic, $\boldsymbol{a}_\mathrm{o}$ = 13.957(1), $\boldsymbol{b}_\mathrm{o}$ = 12.601(1), $\boldsymbol{c}_\mathrm{o}$ = 8.021(1) Å)^4 are approximately related by the equations: $\boldsymbol{a}_\mathrm{h} = \boldsymbol{a}_\mathrm{o} - 3\boldsymbol{c}_\mathrm{o}$, $\boldsymbol{b}_\mathrm{h} = \boldsymbol{a}_\mathrm{o} + 3\boldsymbol{c}_\mathrm{o}$, and $\boldsymbol{c}_\mathrm{h} = \boldsymbol{b}_\mathrm{o}$.