

Photochromic Inclusion Crystals of Phosphonium Halides with Aromatic Alcohols

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Some inclusion crystals of phosphonium salts with aromatic alcohols showed thermally reversible photochromism in the solid state. Corresponding to the color development, ESR signals appeared in the inclusion crystals. The crystal structures of the inclusion crystals were determined by X-ray analysis.

Organic photochromic compounds have received much attention in recent years because of their potential applications, such as information storage, electronic display systems, optical switching devices, ophthalmic glasses, and macro-scale mechanical motion of materials.^{1–6} Several types of organic photochromic compounds, such as naphthopyrans, spiropyrans, fulgides, and *N*-salicylideneanilines, have been discovered, and their properties have been studied mostly in solution. However, organic compounds showing photochromism in the crystalline state are very rare.⁷ It has recently been reported that diaryl-ethenes and *N*-salicylideneanilines show photochromism in the single-crystalline state.^{8–21} We report here various kinds of inclusion crystals of phosphonium salts with aromatic alcohols, such as phenol and naphthol, were shown to exhibit thermally reversible photochromism in the solid state.

We have previously reported some quaternary phosphonium salts **1a–1c** (Chart 1) form inclusion crystals with aromatic alcohols and alicyclic alcohols such as cyclohexane-1,3-diol, cyclohexane-1,4-diol, and cyclohexane-1,3,5-triol, in which the equatorial conformers are selectively included.²¹ Recently, we have found that phosphonium salts **2–5** form stable inclusion crystals with various kinds of aromatic alcohols **6–11**. For example, host **2** formed stable inclusion crystals with all the tested phenols **6** and **7** and naphthols **8–11** (Table 1). Hosts **3–5** also included several kinds of aromatic alcohols in the ratios indicated in Table 1.

Interestingly, these inclusion crystals show reversible color change upon photoirradiation in the solid state. For example, colorless prisms of the 1:1 inclusion complex of **3** with **7** turned into green crystals immediately upon photoirradiation (Figure 1). The green color faded on storage in the dark for a couple of days at room temperature and any detectable decomposition of the inclusion crystals was not observed. The faded crystals again developed green color upon photoirradiation. Similarly, colorless prisms of the 1:1 inclusion complex of **2** with **8** turned into orange crystals immediately upon photoirradiation (Figure 2).

Table 1. Inclusion Crystals of Phosphonium Salts **1–5** with Aromatic Alcohols **6–11**^{a)}

Guest	Host						
	1a	1b	1c	2	3	4	5
6	— ^{b)}	—	—	1:1:1(EtOH) ^{d)}	1:2:1(EtOH)	1:1	—
7	1:1 ^{c)}	1:1 ^{c)}	—	1:1 ^{c)}	1:1 ^{c)}	1:1 ^{c)}	1:1 ^{c)}
	green	green	—	green	green	green	green
8	1:1 ^{c)}	—	—	1:1 ^{c)}	—	—	—
	yellow	—	—	orange	—	—	—
9	1:1	1:2	—	1:1:1(EtOH): 1(H ₂ O) ^{e)}	—	—	—
	—	—	—	yellow	—	—	—
10	1:1	1:1	1:1	1:1 ^{c)}	1:1 ^{c)}	—	—
	—	—	—	orange	yellow	—	—
11	1:1	1:1	—	2:2:2(EtOH)	1:1 ^{c)}	1:2 ^{c)}	—
	—	—	—	—	brown	brown	—

a) The host:guest ratio was determined by ¹H NMR. b) No inclusion complexation. c) Photochromic. d) Co-included solvent molecule is shown in parenthesis.

The UV–vis spectral changes of the inclusion complex are shown in Figure 3. Corresponding to the color development, ESR signals ($g = 2.004$) appeared in the green crystals (Figure 4). The intensity gradually decreased and almost disappeared after standing for several weeks at room temperature in the dark (Figure 5). The radical species may be produced by photoinduced one-electron transfer from the guest aromatic alcohol to phosphonium cation as previously demonstrated in the case of viologen crystals.²² Similarly, most inclusion crystals of phosphonium salts **2–5** with various kinds of aromatic alcohols **6–11** showed similar photochromic properties in the solid state (Table 1).

Interesting properties of this new class of photochromic inclusion complexes prompted us to analyze details of intermolecular interactions in the four obtained photochromic crystals: 1:1 complex between **1a** and **10** (Figure 6); 1:1

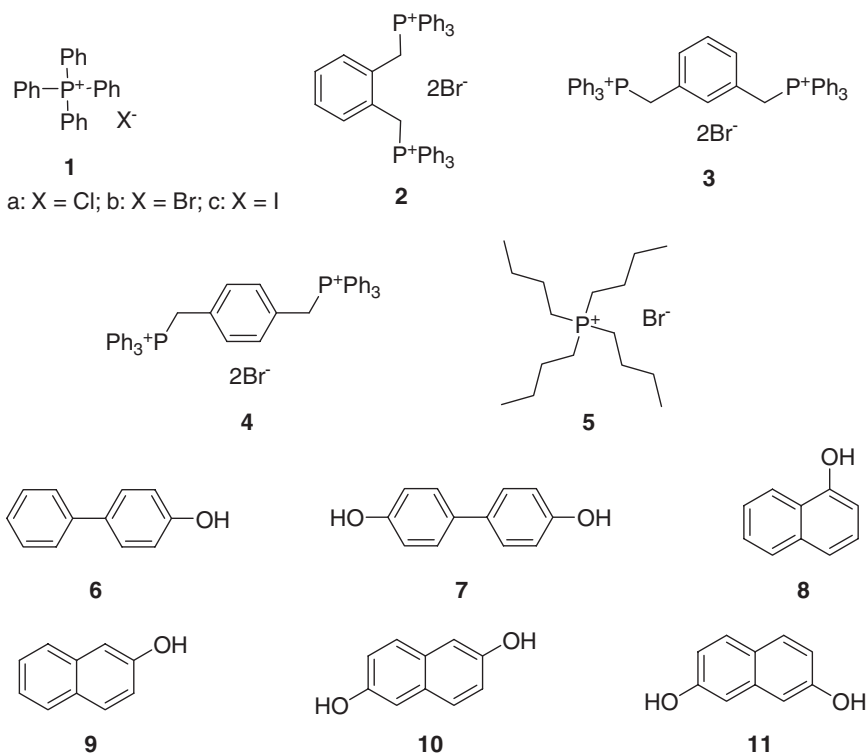
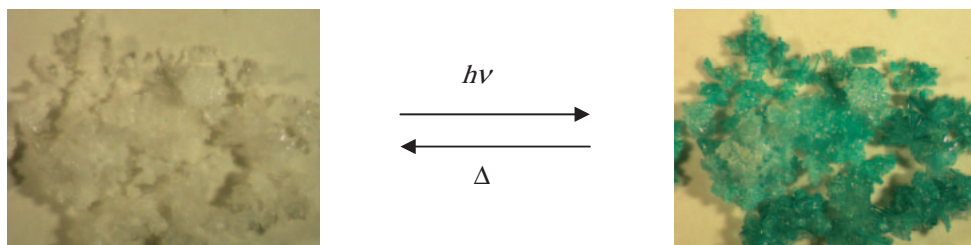
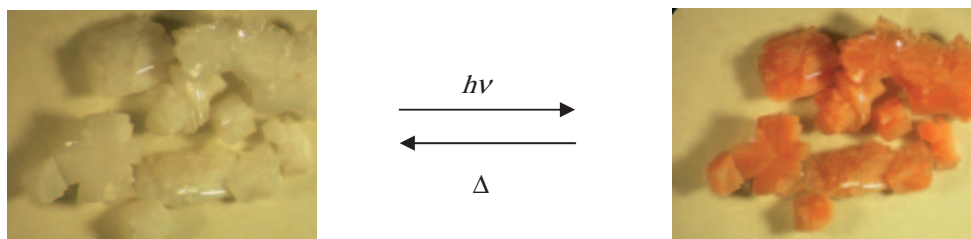


Chart 1.

Figure 1. Photographs of 1:1 inclusion crystals of **3** with **7** before (left) and after photoirradiation (right).Figure 2. Photographs of 1:1 inclusion crystals of **2** with **8** before (left) and after photoirradiation (right).

complex between **2** and **9** (and EtOH and H₂O) (Figure 7); 2:2 complex between **2** and **11** (and two EtOH) (Figure 8); and 1:1 complex of **5** and **7** (Figure 9). It has been discovered that all distances between hydroxy groups and P,C,H-atoms constituting cations are much above the appropriate sum of VdW radii. In fact, both tetrabutyl- and tetraphenylphosphonium cations stabilize prolonged existence of the radical anion to the same extent. Instead, two sets of the Br/Cl...HO distances have been found: one in the range of 2.13–2.29 Å and second in the range 2.36–2.46 Å. A Cambridge Crystallographic Data Base²³

survey showed that short Br⁻...HO distances <2.3 Å are rare (ca. 5% of the population of 1774 contacts found) and are formed with ternary ammonium cations, carboxyl groups, and small solvent molecules like MeOH, H₂O, and EtOH. As can be seen in Figures 6–9 captions in fact, most of the Br⁻/Cl⁻ anions in the above structures have at least one such short hydrogen bond.

Irradiation of the ground state of such a system containing strong Br/Cl...H hydrogen bonds splits electron pairs into an electronically excited state in which the Br/Cl anion is bound

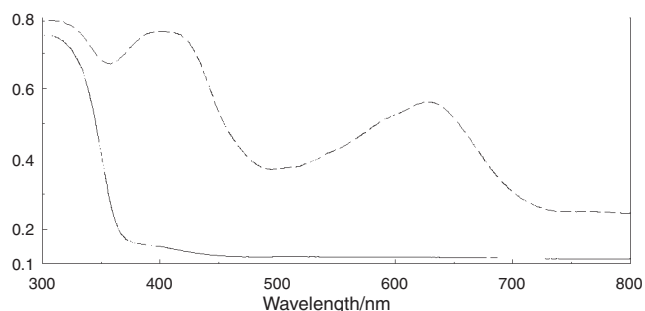


Figure 3. UV-vis spectra of 1:1 inclusion crystals of **3** with **7** before (solid line) and after photoirradiation (broken line).

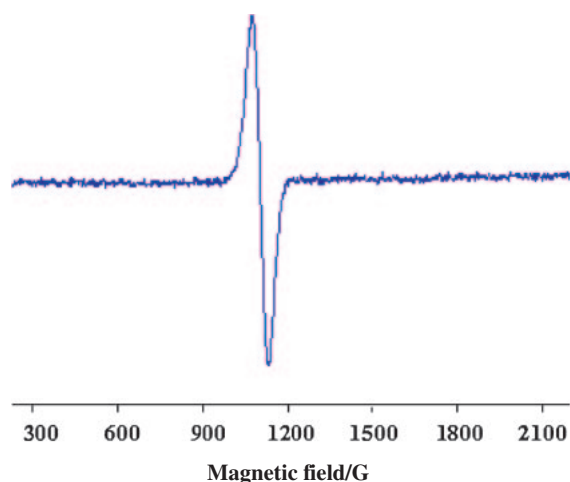


Figure 4. ESR spectrum of 1:1 inclusion crystals of **3** with **7** after photoirradiation in the solid state.

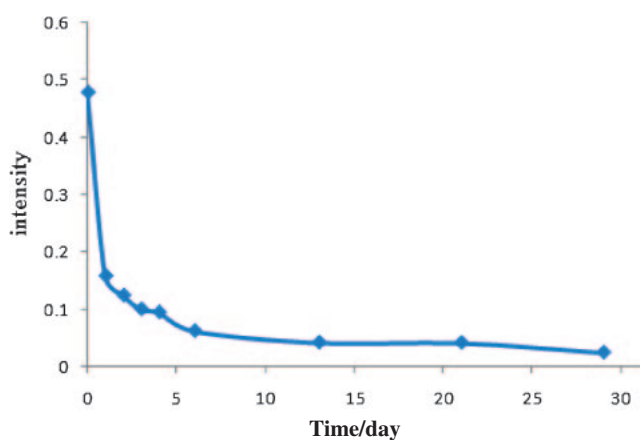


Figure 5. Intensity changes of ESR signals of the irradiated 1:1 inclusion crystals of **3** with **7** at room temperature upon standing.

to a proton and aromatic anionic radical. Such a system slowly comes back to the ground state via hydrogen rearrangement. A similar hydrogen bond driven process of radical formation upon irradiation was observed in phenol dimer, using high-resolution time-resolved spectroscopic methods.²⁴ In the structure of a 1:1 complex between **2** and **9** (and EtOH and

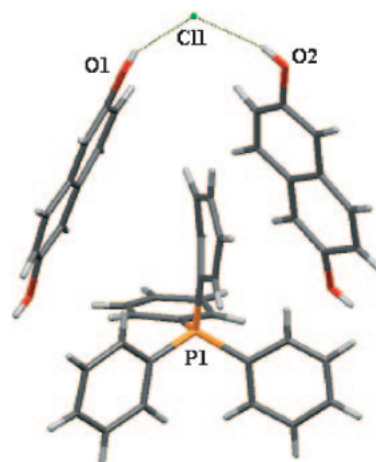


Figure 6. ORTEP diagram of the 1:1 complex between **1a** and **10** showing hydrogen-bonding pattern: O1-H1...Cl1 $[-x + 1, y - 1/2, -z]$ 0.82, 2.29, 3.042(18) Å, angle 152.4°; O2-H2...Cl1 0.82, 2.28, 3.069(16) Å, angle 160.3°.

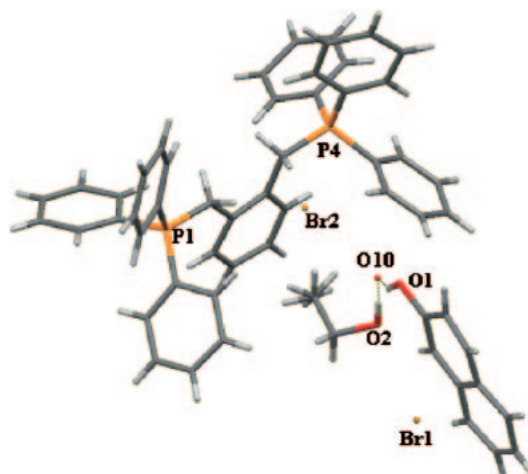


Figure 7. ORTEP diagram of the 1:1:EtOH:H₂O complex between **2** and **9** showing hydrogen-bonding pattern: O1-H1...O10 0.82, 1.87, 2.630(12) Å, angle 153.0°; O2-H2...O10 0.82, 2.01, 2.759(12) Å, angle 151.1°.

H₂O), a phenol hydrogen is donated to a water molecule with formation of a strong hydrogen bond.

In conclusion, the above complexes constitute a new class of photochromic compounds, where intermolecular interactions between host and solvent molecules change electronic structure of the guest aromatic alcohol which allows easy radical formation upon irradiation.

Experimental

General. ¹H NMR spectra were recorded in CDCl₃ on a JEOL JNM-EX270 FT-NMR spectrometer using CDCl₃ with tetramethylsilane (TMS) as an internal standard. UV-vis spectra were recorded on a JASCO V-550 spectrometer. ESR spectra were recorded on a JEOL JES-RE1X. The inclusion crystals were obtained by recrystallization of a mixture of the phosphonium salts **1-5** and aromatic alcohols **6-11** in EtOH solution.

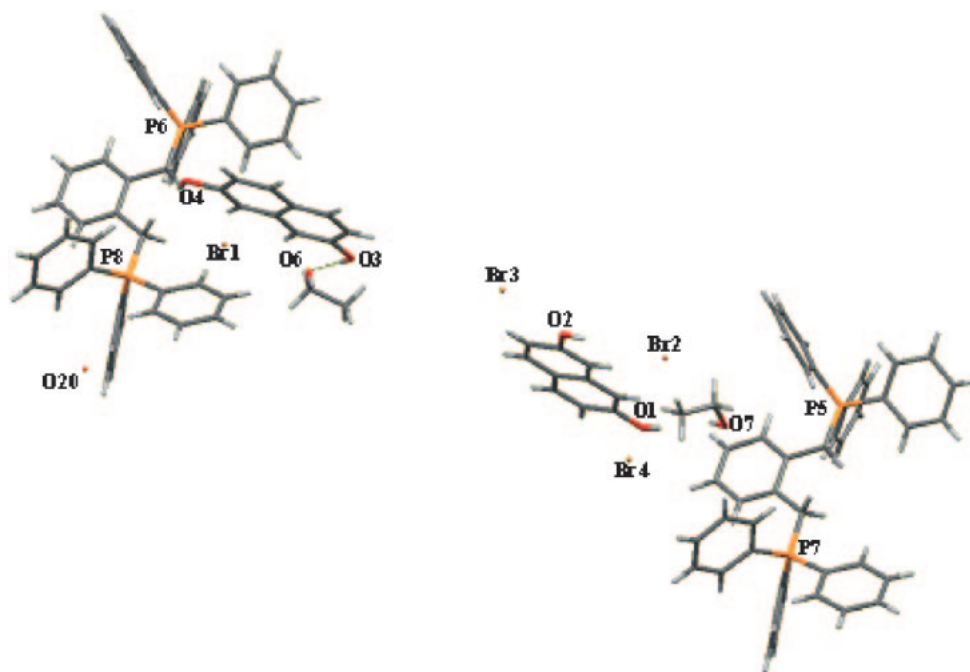


Figure 8. ORTEP diagram of the 2:2:2EtOH complex between **2** and **11** showing hydrogen-bonding scheme: O3–H3...O6 0.82, 1.98, 2.803(8) Å, 175.3°; O2–H2...Br2 1.08(10), 2.1(1), 3.170(5) Å, 157(8)°; O6–H6...Br1 1.01(7), 2.64(7), 3.308(6) Å, 124(5)°.

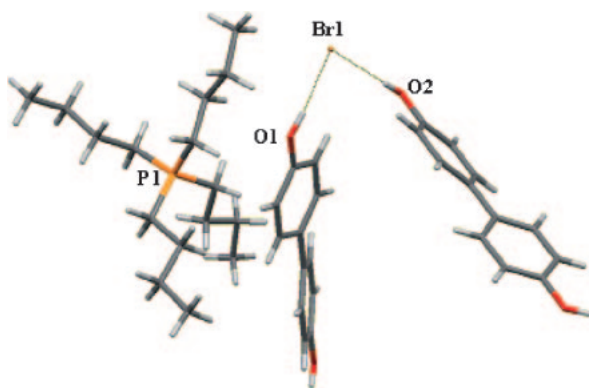


Figure 9. ORTEP diagram of the 1:1 complex of **5** and **7** showing hydrogen bonding between hydroxy group of biphenol and Br[−] anion: O1–H1...Br1 0.80(9), 2.43(9), 3.213(7) Å, angle 169(8)°; O2–H2...Br1 [*x*, *−y* + 3/2, *z* − 1/2] 0.85(8), 2.37(8), 3.211(6) Å, angle 173(7)°.

Photochromic Measurement. Photo-coloration was carried out by irradiating crystalline powders of inclusion complexes using a 300-W Xenon-lamp (MAX 300, Asahi Spectra. Co., Ltd.) at room temperature. UV–vis spectra were monitored with a JASCO V-550 spectrometer at 25 °C.

X-ray Analyses. Suitable crystals were mounted on a glass fiber. Data collection was performed at 295 on a Nonius BV MACH diffractometer with graphite monochromated CuK α ($\lambda = 1.54178$ Å) or Kappa CCD system using MoK α radiation ($\lambda = 0.71073$). Structures were solved with direct methods using the SHELXS97²⁵ and refined with SHELXL97²⁶ software. Refinement was performed anisotropically for all non-hydrogen atoms using the full-matrix least-squares method. In general, hydrogen atoms were assigned to idealized positions and were allowed to

ride with thermal parameters fixed at 1.2Ueq of the parent atom. Due to crystal twinning hydrogen atom positions in solvent molecules were calculated, (if possible). Hydroxy group H-atoms were localized from $\Delta\rho$ maps and refined. The residual electron densities were of no chemical significance.

CCDC-705035–705038, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at “<http://www.ccdc.cam.ac.uk/conts/retrieving.html>” [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; FAX: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data: 1:1 Complex between 1a and 10. Monoclinic, space group $P2_1$: $a = 9.402(1)$, $b = 14.054(1)$, $c = 10.727(1)$ Å, $\beta = 91.65(9)^\circ$, $V = 1416.9(2)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.254$ Mg m^{−3}, $F(000) = 560$, $\mu(\text{Cu K}\alpha) = 1.948$ mm^{−1}, 2676 reflections collected in θ -range 4.12 to 74.25; 2535 used for structure refinement. Final R index $R1 = 0.0756$ [1221 reflections with $I > 2\sigma(I)$] and for all data $wR = 0.2121$, $S = 1.030$.

Crystal Data: 1:1:EtOH:H₂O Complex between 2 and 9. Orthorhombic, space group $Pna2_1$: $a = 25.029(5)$, $b = 11.199(2)$, $c = 16.955(3)$ Å, $V = 4752.5(16)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.390$ Mg m^{−3}, $F(000) = 2048$, $\mu(\text{Mo K}\alpha) = 1.817$ mm^{−1}, 10491 reflections collected in θ -range 1.63 to 27.48; 10491 used for structure refinement. Final R index $R1 = 0.0839$ [6607 reflections with $I > 2\sigma(I)$], and for all data $wR = 0.1665$, $S = 1.092$.

Crystal Data: 2:2:2EtOH Complex between 2 and 11. Monoclinic, space group $P2_1/c$: $a = 20.123(4)$, $b = 25.072(5)$, $c = 20.126(4)$ Å, $\beta = 113.35(3)^\circ$, $V = 9322(3)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.429$ Mg m^{−3}, $F(000) = 4128$, $\mu(\text{Mo K}\alpha) = 1.854$ mm^{−1}, 32676 reflections collected in θ -range 1.96 to 27.49; 19470 used for structure refinement. Final R index $R1 = 0.0751$ [15145 reflections with $I > 2\sigma(I)$] and for all data $wR = 0.1749$, $S = 1.092$.

Crystal Data: 1:1 Complex of 5 and 7. Monoclinic, space group $P2_1/c$: $a = 9.5750(3)$, $b = 22.5900(9)$, $c = 13.6160(4)$ Å, $\beta = 101.294(2)^\circ$, $V = 2888.1(2)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.209$

Mg m^{-3} , $F(000) = 1120$, $\mu(\text{Mo K}\alpha) = 1.499 \text{ mm}^{-1}$, 9065 reflections collected in θ -range 1.77 to 24.72; 4836 used for structure refinement. Final R index $R1 = 0.0744$ [3440 reflections with $I > 2\sigma(I)$] and for all data $wR = 0.1613$, $S = 1.08$.

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