Triphenylphosphine Oxide as a Crystallization Aid

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Since organic materials have been shown to have useful electrooptic[1] and electrical[2] properties, the problem of growing large high quality organic crystals has become acute.[3] In this paper we show that cocrystallization with triphenylphosphine oxide (TPPO) induces many organic compounds to crystallize readily as large blocky crystals that have sharp edges and well-defined crystal faces. TPPO itself forms high quality crystals easily, and we show here that this characteristic is carried over to its complexes. For organic compounds that form poor quality crystals or that are available in only small amounts, TPPO complexation is a new method for transforming these compounds into useful crystals.

TPPO is a good proton acceptor that is known to form complexes in solution with a wide variety of organic molecules.[4–6] These complexes are stabilized by strong hydrogen bonds between the phosphoryl oxygen and the proton donor of the substrate. Some solid-state complexes between TPPO and organic molecules have also been reported,[7–12] but there is no mention of crystal quality in these references.

Crystals of TPPO complexes were grown initially as a way to modify substrate properties by complexation.[13] Many of the starting materials, however, were observed to form small thin needles, while their TPPO complexes formed large chunky crystals. In Figure 1, substrate crystals grown by slow evaporation from toluene are compared to their TPPO complexes grown under the same conditions. These crystals were readily obtained from standard laboratory techniques like those an organic chemist would use to purify compounds by recrystallization.[14]

TPPO complexes of the compounds listed in Chart I, were prepared by dissolving equimolar amounts of the substrate and TPPO in toluene and then allowing the solution to evaporate slowly at room temperature. Crystals were removed from solution as they formed, quickly washed with acetone and petroleum ether, and then air dried.

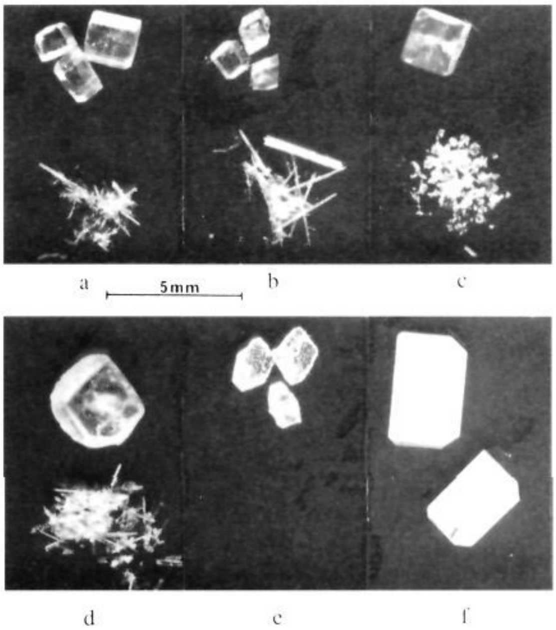
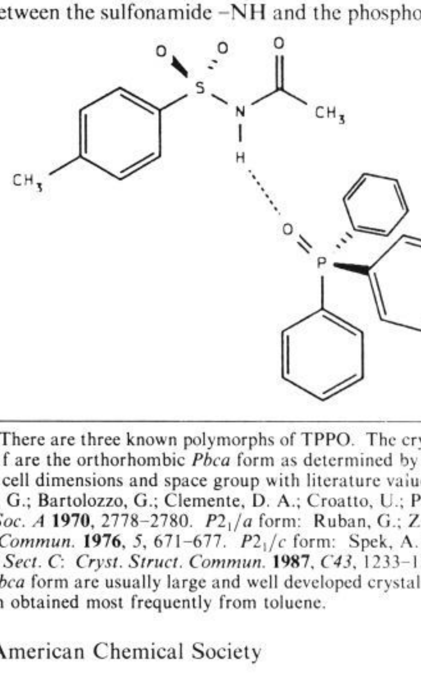


Figure 1. Comparison of toluene grown crystals of substrate (bottom-half of pictures a–e) and of complexes of substrates with TPPO (top half): (a) *N*-acetyl-*p*-toluenesulfonamide, I; (b) acetanilide, II; (c) triphenylcarbinol, III; (d) saccharin, IV; (e) phenol, V.; (f) neat TPPO crystals from toluene.[15] The scale is indicated by the bar marker.

The crystals were confirmed to be TPPO complexes by a variety of techniques. Each batch of crystals was examined under a polarizing microscope to determine whether the crystals had homogeneous morphologies or whether mixtures of crystals were present. Usually the entire batch of crystals had one morphology which was different than that of crystals of starting material. Single crystals were removed from each batch for further tests, including solution NMR, solid-state IR, and melting point analysis. NMR results gave the stoichiometry of substrate to TPPO; IR patterns showed –OH and –NH peaks shifted to much lower frequencies (often below 3000 cm^{-1}) than in the substrate; and melting point analyses showed melting points that were sharper than those of mixtures of TPPO and substrate (e.g., I melts at 137–139 °C; I·TPPO, 146–148 °C; and I mixed with TPPO, 126–146 °C). X-ray powder patterns were run on TPPO, acetanilide (II), and their complex to verify that the complex gave a unique pattern. A single-crystal X-ray structure determination was done for I, showing that complexation occurs via a hydrogen bond between the sulfonamide –NH and the phosphoryl oxygen.[16]



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(1) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690–703.

(2) Greene, R. L.; Street, G. B. *Science (Washington, D.C.)* **1984**, *226*, 651.

(3) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987, Vol. 1 and 2.

(4) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875–3891.

(5) Hädzi, D.; Smerkolj, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, 1188–1191.

(6) Arnett, E. M.; Joris, L.; Mitchell, E. J.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2365–2377.

(7) Golic, L.; Kaucic, V. *Cryst. Struct. Commun.* **1976**, *5*, 319–324.

(8) Antipin, M. Yu.; Akhmedov, A. I.; Struchkov, Yu. T.; Matrosov, E. I.; Kabachnik, M. I. *J. Struct. Chem.* **1983**, *24*, 888–893.

(9) Bailey, A. S.; Cameron, T. S.; Evans, J. M.; Prout, C. K. *Chem. Commun.* **1966**, *19*, 664–666.

(10) Declercq, J. P.; Germain, G.; Putzeys, J. P.; Rona, J.; Van Meerssche, M. *Cryst. Struct. Commun.* **1974**, *3*, 579–582.

(11) Thierbach, Von D.; Huber, F. *Z. Anorg. Allg. Chem.* **1981**, *477*, 101–107.

(12) Lariucci, C.; de Almeida Santos, R. H.; Lechat, J. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1825–1828.

(13) Etter, M. C.; Gillard, R. D.; Gleason, W. B.; Rasmussen, J. K.; Duerst, R. W. *J. Org. Chem.* **1986**, *51*, 5405–5408.

(14) Etter, M. C.; Jahn, D. A.; Donahue, B. S.; Johnson, R. B.; Ojala, C. *J. Cryst. Growth* **1986**, *76*, 645–655.

(15) There are three known polymorphs of TPPO. The crystals shown in Figure 1f are the orthorhombic *Pbca* form as determined by comparison of the unit cell dimensions and space group with literature values (*Pbca* form: Bandoli, G.; Bartolozzo, G.; Clemente, D. A.; Croatto, U.; Panattoni, C. *J. Chem. Soc. A* **1970**, 2778–2780. $P2_1/a$ form: Ruban, G.; Zabel, V. *Cryst. Struct. Commun.* **1976**, *5*, 671–677. $P2_1/c$ form: Spek, A. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 1233–1235). Crystals of the *Pbca* form are usually large and well developed crystals, and they are the form obtained most frequently from toluene.

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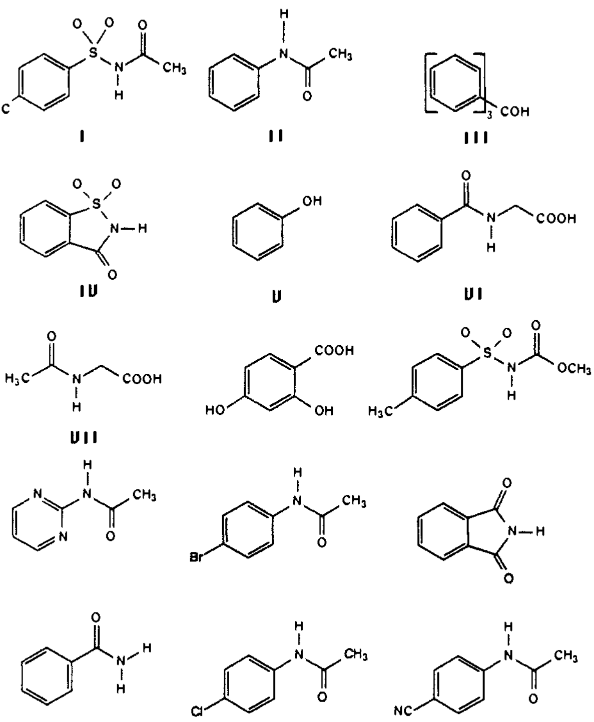
Chart I



For I–V, crystals of the TPPO complex readily grew bigger and were of much higher quality than crystals of the substrate alone. For most of the other compounds in Chart I, crystals of the complex from toluene are chunky, while crystals of the substrates are thin needles or plates. We have not tried to optimize the size of any of these crystals. Triphenylcarbinol·TPPO gave the largest crystal, 0.1 × 1 × 2 cm. When substrates are not soluble in toluene, TPPO complexes can usually be formed from other solvents. For example, VI and VII were complexed with TPPO from a mixture of THF and H_2O. We were unable to obtain crystalline TPPO complexes of several compounds related to those in Chart I. Work is in progress to prepare these complexes.

There are two factors contributing to the effect that TPPO has on crystal growth properties. One involves the presence of a very strong hydrogen bond, necessary for complex formation, that imparts partial ionic character to the crystal. The other is the bulky shape of TPPO molecules which inhibits the formation of lamellar structures that cause crystals to fracture easily and to grow as thin plates. We are presently testing the importance of these two factors by studying the crystal habits of other hydrogen-bonded complexes.

Acknowledgment. We gratefully acknowledge Prof. Doyle Britton, University of Minnesota, for solving the crystal structure of I and ONR for partial support of this work. Helpful discussions with Tom Panunto, University of Minnesota, are also appreciated.

Registry No. I, 1888-33-1; II, 103-84-4; III, 76-84-6; IV, 81-07-2; V, 108-95-2; VI, 495-69-2; VII, 543-24-8; TPPO, 791-28-6; 2,4-dihydroxybenzoic acid, 89-86-1; methyl [(4-methylphenyl)sulfonyl]carbamate, 14437-03-7; *N*-2-pyrimidinylacetamide, 13053-88-8; *N*-(4-bromophenyl)acetamide, 103-88-8; 1*H*-isoindole-1,3(2*H*)-dione, 85-41-6; benzamide, 55-21-0; *N*-(4-chlorophenyl)acetamide, 539-03-7; *N*-(4-cyanophenyl)acetamide, 35704-19-9.

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(16) Crystal data for I·TPPO: $C_{27}H_{26}NO_4PS$, f_w = 491.6, a = 19.573 (7) Å, b = 13.470 (14) Å, c = 10.030 (5) Å, V = 2605.7 Å^3, $P2_1/a$, Z = 4, D_x = 1.25 g/cc, Mo Kα, R_w = 0.058, R = 0.048 for 4362 reflections, $I > 1\sigma(I)$; Enraf-Nonius diffractometer, direct methods, full-matrix least-squares refinement, anisotropic temperature factors for non-hydrogen atoms, and isotropic temperature factors for hydrogen atoms, all of which were found on electron density difference maps. The –NH···O distance in the hydrogen bond is 2.705 (2) Å, and the N–H···O angle is 169.4 (2)°. Complete crystal structure details will be reported elsewhere.

Spectroscopic Evidence for the Formation of Singlet Molecular Oxygen ($^1\Delta_gO_2$) upon Irradiation of a Solvent-Oxygen ($^3\Sigma_g^-O_2$) Cooperative Absorption Band

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It is well-known that the presence of molecular oxygen ($^3\Sigma_g^-O_2$) in a variety of organic solvents causes an often substantial red shift in the solvent absorption spectrum.[1] This extra, broad absorption feature is reversibly removed by purging the solvent with nitrogen gas. Mulliken and Tsubomura assigned the oxygen-dependent absorption band to a transition from a ground state solvent–oxygen contact complex to a solvent–oxygen charge transfer (CT) state (sol$^{\bullet+}O_2^{\bullet-}$).[1] In addition to the broad Mulliken CT band, there are, often in the same spectral region, distinct singlet–triplet transitions ($T_1 \leftarrow S_0$) which are enhanced by molecular oxygen ($^3\Sigma_g^-O_2$).[2] Since both of these solvent–oxygen cooperative transitions may result in the formation of reactive oxygenating species, singlet molecular oxygen ($^1\Delta_gO_2$) and/or the superoxide ion ($O_2^{\bullet-}$), it follows that recent studies have focussed on unsaturated hydrocarbon oxygenation subsequent to the irradiation of the oxygen-induced absorption bands in both the solution phase and cryogenic (10 K) glasses.[3,4] In these particular experiments, oxygenated products characteristic of both $^1\Delta_gO_2$ and $O_2^{\bullet-}$ were obtained, although the systems studied appeared to involve the participation of one intermediate at the exclusion of the other.

In this communication, we provide, for the first time, direct spectroscopic evidence for the formation of $^1\Delta_gO_2$ following a solvent–oxygen ($^3\Sigma_g^-O_2$) cooperative absorption. We have observed, in a time-resolved experiment, a near-IR luminescence subsequent to laser excitation of the oxygen-induced absorption bands of mesitylene, *p*-xylene, *o*-xylene, toluene, and benzene at 355 nm and 1,4-dioxane at 266 nm. We suggest that this signal is due to $^1\Delta_gO_2$ phosphorescence.[5]

The following points are presented to support our claim that $^1\Delta_gO_2$ is indeed produced subsequent to irradiation of a solvent–oxygen absorption band.

1. The observed signal is $^1\Delta_gO_2$ phosphorescence. The λ_{max} of luminescence is 1270 nm, in agreement with previous $^1\Delta_gO_2$ assignments.[10-12] The lifetime of the time-resolved signal in each solvent, extrapolated to zero laser power, agrees with known $^1\Delta_gO_2$ lifetimes independently determined.[13,14] The addition of a $^1\Delta_gO_2$ quencher (sodium azide) to dioxane quenches the observed IR signal with a rate constant comparable to that known for $^1\Delta_gO_2$

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(1) Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966–5974.

(2) (a) Evans, D. F. *Nature (London)* **1956**, *178*, 534–353. (b) Evans, D. F. *J. Chem. Soc.* **1957**, 1351–1357.

(3) Onodera, K.; Furusawa, G.; Kojima, M.; Tsuchiya, M.; Aihara, S.; Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron* **1985**, *41*, 2215–2220.

(4) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 529–532.

(5) A complete description of the apparatus used to detect $^1\Delta_gO_2$ phosphorescence is reported elsewhere (ref 6–9). 355 nm and 266 nm correspond to the third and fourth harmonics, respectively, of a Nd:YAG pulsed laser. All $^1\Delta_gO_2$ phosphorescence experiments were performed in 1-cm cuvettes.

(6) Iu, K.-K.; Scurlock, R. D.; Ogilby, P. R. *J. Photochem.*, submitted for publication.

(7) Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 1611–1617.

(8) Iu, K.-K.; Scurlock, R. D.; Ogilby, P. R. *J. Photochem.* **1987**, *37*, 19–32.

(9) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599–4602.

(10) Khan, A. U. In *Singlet Oxygen, Volume I, Physical-Chemical Aspects*; Frimer, A. A., Ed.; CRC Press: Boca Raton, 1985; pp 39–79 and references cited therein.

(11) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.

(12) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756–5760.

(13) Monroe, B. M., in ref 10, pp 177–224 and references cited therein.

(14) τ(mesitylene) = 19 μs, τ(*p*-xylene) = 24 μs, τ(*o*-xylene) = 26 μs, τ(toluene) = 28 μs, τ(benzene) = 30 μs, τ(dioxane) = 26 μs.

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