The X-Ray Crystal Structure of a Ternary Cocrystallization Compound: *N,N*-Dimethyl-*o*-phenylenediamine–Fluoroboric Acid–Triphenylphosphine Oxide

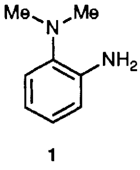
Antonio L. Llamas-Saiz,[a] **Concepción Foces-Foces,***[a] **José Elguero,**[a] **Pedro Molina,**[b] **Mateo Alajarín**[b] **and Angel Vidal**[b]

[a] *U.E.I. de Cristalografía, Instituto de Química-Física 'Rocasolano', CSIC, Serrano, 119, E-28006 Madrid, Spain*
[b] *Departamento de Química Orgánica, Facultad de Ciencias, Campus Universitario de Espinardo, E-30071 Murcia, Spain*

The *endo*-bidentate chelated structure of the title compound corresponds to protonation on the dimethylamino group; the oxygen atom of triphenylphosphine oxide acts as a double acceptor of hydrogen bonds.

There is currently considerable interest in cocrystallization processes, especially in the use of triphenylphosphine oxide (TPPO) as a crystallization aid.[1–3] In the reported examples, there are only two components, TPPO and a hydrogen bond (HB) donor. We now report that when equimolar quantities of *N,N*-dimethyl-*o*-phenylenediamine **1**, aqueous fluoroboric acid **2** and TPPO **3** were mixed at room temperature, in ethanolic solution, and then evaporated to dryness, (*o*-aminophenyl)dimethylammonium tetrafluoroborate–triphenylphosphine oxide complex was formed in quantitative yield. Crystallization from dichloromethane–diethyl ether, gave single crystals suitable for an X-ray crystal structure determination.

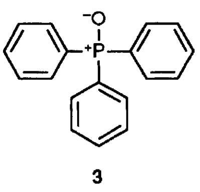
The structure of the resulting ternary complex shows that the acid proton of **2** is linked to N(7), which appears to be the most basic of the four possible sites [N(7), N(10), O(11) and BF_4^-]. An examination of the Cambridge Structural Data Base (CSD, January 1991 release)[4] shows that it is the first time that the $C_8H_{13}N_2^+$ cation has been characterized by X-ray crystallography (Fig. 1).† Both nitrogen atoms are close to sp^3 hybridization. The shortening of the C–N bond of the amino group with respect to those of *o*-phenylenediamine[5] [1.407(2) Å] may be due to the greater overlapping of the lone pair with the aromatic π-electrons; the angle between the computed lone pair direction and the phenyl ring is 76° *versus* 66 and 70°. The C–N and N–Me distances are not significantly different from those displayed for seven structures (CSD) containing *N,N*-dimethylamino groups in *ortho*-positions and acting as bidentate metal ligands. The N···N distance is within the normal range (2.757–2.936 Å) and the N atoms are placed



1

HBF_4

2



3

---

† *Crystal data* for $C_{18}H_{15}PO{\cdot}C_8H_{13}N_2^+BF_4^-$: Philips PW1100 diffractometer, Cu-Kα radiation, graphite monochromator, monoclinic, $P2_1/c$, a = 9.8408(3), b = 14.5446(5), c = 18.6512(11) Å, β = 96.490(3)°, V = 2652.5(2) Å^3, D_c = 1.258 g cm^{-3}, Z = 4, crystal dimensions 0.66 × 0.60 × 0.50 mm, ω/2θ scan, θ_{max} = 65°, 4517 independent reflections, $R(R_w)$ = 0.063 (0.069) for 3950 [$I > 3\sigma(I)$] observed reflections, empirical absorption correction (μ = 13.36 cm^{-1}). XRAY80 computer program. Patterson methods. Refinement on F_0 with two-block matrix. Anisotropic thermal model for the non-hydrogen atoms while H atoms, obtained unambiguously from difference Fourier synthesis, were refined isotropically. The BF_4^- anion appears to be disordered in two positions sharing the boron and one fluorine atoms. Min., max. final ΔF peaks −0.29, 0.42 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

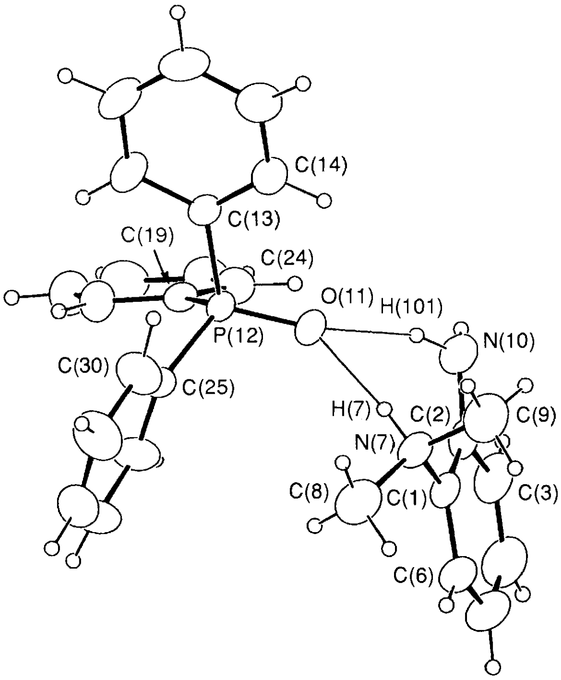


Fig. 1 Molecular structure of $C_{18}H_{15}PO{\cdot}C_8H_{13}N_2{}^+$ showing 30% probability ellipsoids for the non-hydrogen atoms. Selected distances (Å) and angles (°) and the hydrogen interaction geometry: O(11)–P(12) 1.493(2), C(1)–N(7) 1.469(4), C(2)–N(10) 1.382(4), N(7)···N(10) 2.836(4), N(10)–C(2)–C(1)/C(3) 122.8(3)/120.1(3), N(7)–C(1)–C(2)/C(6) 117.6(2)/120.5(3); N(7)–H(7)···O(11): 2.705(3), 1.85(3), 175(3); N(10)–H(101)···O(1): 2.912(4), 2.02(4), 163(4); P(12)–O(11)···H(7)/H(101) 142(1)/149(1), H(7)···O(11)···H(101) 62(2); P(12)–O(11)···N(7)/N(10) 141.1(1)/147.9(1) and N(7)···O(11)···N(10) 60.5(1).

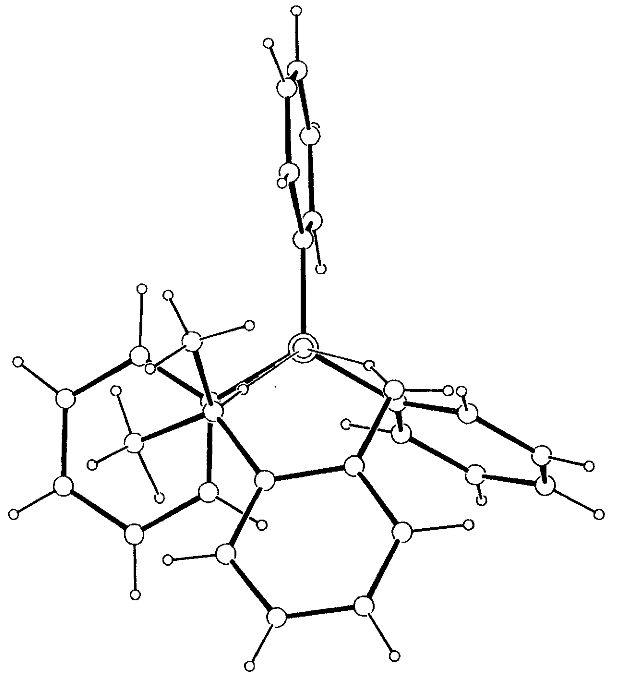
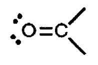
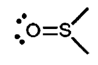


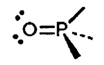
Fig. 2 Newman projection along the P(12)–O(11) bond including hydrogen bonds. Selected torsion angles (°): O(11)–P(12)–C(13)–C(14) −9.9(3), O(11)–P(12)–C(19)–C(24) −18.9(3), O(11)–P(12)–C(25)–C(30) 95.5(3), C(6)–C(1)–N(7)–C(8) −33.0 (4), C(6)–C(1)–N(7)–C(9) 94.3(3), H(7)···O(11)–P(12)–C(25)/C(19)/C(13) 4(2)/−115(2)/124(2) and H(101)···O(11)–P(12)–C(25)/C(19)/C(13) 135(2)/15(2)/−105(2).



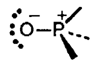
4



5



6



7

on the same side [ΔN(7), ΔN(10) = 0.026(2), 0.115(2) Å] of the distorted phenyl ring (χ^2 = 67.02 *versus* the expected value of 7.81 for a planar ring at 95% probability level).

The amine **1**, protonated on the dimethylamino group, acts as a bidentate chelating agent through two strong and linear hydrogen bonds (Fig. 1) with the oxygen of TPPO, like that in the only similar crystal structure previously described[6] $C_6Cl_4(OH)_2{\cdot}OPPh_3$ [O···O = 2.611(4)–2.689(4) Å]. Although the $C_6F_4(OH)F{\cdot}OPPh_3$ structure[7] presents an analogous geometrical situation [O···O/F = 2.645(2)/2.874(2) Å] only one hydrogen atom is involved in the short O···O contact to TPPO.

A search in the CSD for hydrogen-bonded phosphine oxide derivatives was performed. The HB interactions can be sorted as follows: (*i*) *Single acceptor*. In almost all examples (35 hits), a non-linear situation was found with an H···O=P angle of 135(11)° (angles of 135 and 134° were reported for H···O=C/S).[8,9] Only one case corresponds to a linear HB (171°). (*ii*) *Double acceptor*. There are only three compounds involved in bidentate interactions: the present compound, the one previously mentioned[6] (whose hydrogen atoms are not included in the CSD) and a Co complex.[10] Recently, Etter[2] described a chelated structure between a diarylurea and TPPO. From the directionality of the hydrogen bonds, the hybridization state of the oxygen atom can be assumed. The range of sum of angles around the O atoms is 315.8–360.0°, showing that both sp^2 and sp^3 hybridizations are present. Fig. 2 shows the Newman projection along the P–O bond.

The comparison of the hydrogen-bonded crystal structures of carbonyl **4**, sulfoxide **5** and phosphine oxide **6** derivatives shows that their HB patterns are very similar. Although all of them can act as double HB acceptors,[2,11] the most common situation corresponds to a bent single acceptor with an X=O···H angle of 135° (X=C, S or P).

Assuming that oxygen lone pairs are situated in the O···H direction, it is possible to conclude that a classical formula is adequate to represent **4**–**6**, irrespective of the possible hypervalent nature of X. This is consistent with recent calculations,[12] although the sum of angles around oxygen in phosphine oxides correspond to a hybrid between structures **6** (sp^2 oxygen) and **7** (sp^3 oxygen).

Received, 26th July 1991; Com. 1/03874E

References

1 M. C. Etter and P. W. Baures, *J. Am. Chem. Soc.*, 1988, **110**, 639.
2 M. C. Etter, Z. Urbañczyk-Lipkowska, M. Zia-Ebrahimi and T. W. Panunto, *J. Am. Chem. Soc.*, 1990, **112**, 8415.
3 M. E. Etter and S. M. Reutzel, *J. Am. Chem. Soc.*, 1991, **113**, 2586.
4 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146.
5 C. Stålhandske, *Cryst. Struct. Commun.*, 1981, **10**, 1081.
6 M. Yu. Antipin, A. I. Akhmedov, Yu. T. Struchkov, E.I. Matrosov and M. I. Kabachnik, *Zh. Strukt. Khim.*, 1983, **24**, 86–6.
7 T. Gramstad, S. Husebye and K. Maartmann-Moe, *Acta Chem. Scand., Ser. B*, 1986, **40**, 26.
8 P. Murray-Rust and J. Glusker, *J. Am. Chem. Soc.*, 1984, **106**, 1018.
9 A. Vedani and J. D. Dunitz, *J. Am. Chem. Soc.*, 1985, **107**, 7653.
10 R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1987, 907.
11 R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320.
12 A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1990, **112**, 1434.