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**[4-(*N,N*-Dimethylamino)phenyl]diphenylphosphine Oxide and its Partial Oxides: An
Isomorphous Crystal Series**

by

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Abstract

The title compound [4-(*N,N*-dimethylamino)phenyl]diphenylphosphine oxide (1) has been synthesized and its single-crystal X-ray structure determined. The structures of two ‘partial’ oxides [0.50% (2) and 0.25% (3)] isolated from the intermediate phosphine reaction product in the synthesis have also been determined, yielding an unusual isomorphous crystal series. An apparent P-O bond shortening paralleling the percent oxidized is also observed across the series [1.480(4)Å (100%); 1.351(4)Å (50%); 1.280(4)Å (25%)]. The packing in the crystals show primary one-dimensional chains with weak head-to-tail associations between the oxide oxygen (three-center) and two hydrogen atoms from separate methyl groups of the *N*-substituted amine [range: C-H...O, 3.115(4)-3.356(8) Å], extended into a sheet structure by peripheral inter-chain C-H (aromatic)...O (oxide) associations.

Introduction

It can be difficult to produce linear, one-dimensional (1-D) hydrogen-bonded arrays in organic molecules without the presence of secondary associations which usually cross-link these chains. There are several examples of adducts having 1-D arrays which utilize disubstituted molecules with interactive sites^[1] but the design of single molecules for this task usually requires one hydrogen-bond donor group substituted in an opposing direction to an hydrogen-bond acceptor element.^[2] However, neither donor nor acceptor group should preferentially bind to itself. For this reason carboxylic acids are not suitable as the donor element because of their tendency to form dimers^[3], usually across an inversion centre (although there are exceptions such as the relatively rare *catena* arrangement^[3,4] which is essentially a 1-D array). (2-Carboxyphenoxy)acetic acid^[5] also exhibits a single linear array, propagated through the acetic acid (O-H) and the carbonyl oxygen of the 2-carboxy group. Suitable donor groups include alcohols (O-H) and secondary amines (N-H) which ideally can

be the donor element in hydrogen-bonding associations, but in practice can prove to be the acceptor element as well, hence producing secondary interactions. Either carbonyl oxygens or heterocyclic nitrogens are most suitable for the acceptor element while nitro groups may also be considered although they also participate in secondary associations but more often are non-associated. It is unwise to have too many hydrogen-bond acceptor groups because these increase the probability of incorporation of a lattice water molecule in order to balance the hydrogen-bonding network.^[6] The oxygen of triphenylphosphine oxide (tppo) has also proved to be a useful hydrogen-bond acceptor but thus far only molecules containing strong hydrogen-bond donor elements (e.g. mineral acids,^[7] carboxylic acids,^[8] amines and amides (including sulfonamides and ureas)^[9] and phenols and carbinols^[10]) have provided examples of adducts with this compound. With these, the presence of a simple non-linear *single acceptor* (1:1) hydrogen-bonding association^[11] (graph set D^[12]) is found between the proton donor group and the tppo oxygen acceptor. Exceptions to this simple type of association among the tppo adducts are the *double acceptor* types, with *N,N*-dimethyl-*o*-phenylenediamine,^[11] with 3,4,5,6-tetrachloro-*o*-catechol,^[9] and the analogous compound with pentafluorophenol (where the second donor is a fluorine), and the lone *triple acceptor* example with *p*-toluenesulfonamide.^[10] The hydrate examples with terephthalic acid and adamantane carboxylic acid^[8] and with the diacetylene^[13] (where structure extension involves the water molecules) are exceptional but nevertheless involve standard single acceptor (water) O-H...O (tppo) associations.

The hydrogen-bond donor capabilities of dimethylamino substituents have been previously demonstrated^[10,14] on groups which would normally be considered weaker hydrogen-bond acceptors than the phosphine oxide. For this reason we decided to synthesize a simple triarylphosphine oxide analogue containing a single *para*-dimethylamino-substituted

phenyl group and to investigate the hydrogen-bonding array of the resultant solid using single crystal X-ray methods. Molecules containing opposing diphenylphosphine oxide and dimethylamino groups linked *via* biphenyl-4,4'-diyl-, *trans*-stilbenyl-4,4'-diyl- and azobenzene-4,4'-diyl-bridges have been previously synthesized^[15] but no structural data have been reported for these.

Reported in this paper are the synthesis and the single-crystal X-ray structure of [4-(*N,N*-dimethylamino)phenyl]diphenylphosphine oxide (dappo) (1) (the 100% oxidized or 'full oxide'), together with those of the unusual 'partial' oxides of this compound, the 'half-oxide' (2) (50% oxidized) and the 'quarter-oxide' (3) (25% oxidized), formed in the preparation of the parent phosphine (dapp) by partial facile oxidation.

Discussion

Crystal structures of the phosphine oxides (1), (2) and (3)

The crystal structures of the 'full-oxide' (1) (shown in Fig. 1), the 'half oxide' (2) (in which the oxygen has 50% occupancy) and the 'quarter-oxide' (3) (in which the oxygen has 25% occupancy) reveal an unusual isomorphous series. The comparative cell dimensions for the three (Table 1), of which (1) and (3) were obtained at low temperature, show an expected volume contraction (54\AA^3) in the cell for that pair. The phenomenon whereby partial oxidation of the P in aryl phosphines has a small but significant precedence among crystallographically characterized examples in the CSD. Heinze^[16] reported that selective oxidation of the phosphorus centres in uncoordinated 'dangling arms' of a multidentate

phosphine ligand (triphos) in a series of Co(II) complexes occurs quite readily, but in the presence of dioxygen, reaction conditions quite unlike those employed in our syntheses. The first reported example of partial (incomplete) oxidation of the pendant-arm phosphine-P was in the Re(III) carbonyl bromide complex with bis(diphenylphosphino)methane^[17] where the occupancy factor for O was 30%. With the Pd(II) chloride complex with a similar diphosphine^[18] the pendant arm was 50% oxidised. The phenomenon has also been observed in structures of uncoordinated phosphines such as 1,1,1-tris(diphenylphosphinomethyl)propane where the three oxygens had occupancies of 11.3, 13.5 and 39.0%.^[19] In another example, the triphenylphosphine oxide-triphenylmethanol dimer^[20], the two molecules are related by pseudo-symmetry across a crystallographic inversion centre (50% occupancy) while with the 50% oxidized form of 1,4-bis(diphenylphosphino)butane, the two phosphine centers (one oxidized and the other unoxidised) are also 50% disordered across a crystallographic inversion center.^[21] This last example, 1-(diphenylphosphino)-4-(diphenylphosphinoxido)butane [dppbo (B)] is similar to the present series [compounds (1)-(3)] in being isomorphous with the parent 1,4-bis(diphenylphosphinoxido)butane [dppbo (A)].^[22]

An unusual structural feature is that within the set proceeding (1)-(3), the P-O bond distance shortens from the expected value from the structures of triphenylphosphine oxide^[23] [1.483(2) and 1.484(1) Å in the two monoclinic modifications and 1.479(2) Å in the orthorhombic modification] and with the triphenylphosphine oxide hemihydrates^[24] [1.484(1), 1.484(1) Å], and the adducts of tppo with compounds such as carboxylic acids^[8] where the molecules are linked by simple linear O-H...O hydrogen bonds [1.489 Å over 8 examples^[8]]. This 'normal' P-O distance is found in (1) [1.480(4) Å] and compares with 1.351(4) Å in (2) to 1.280(4) Å in (3), the decrease paralleling O occupancy. This contraction

in bond length is very unusual but is consistent with observations for the same set of previously considered structures^[18-20] having partially oxidised phosphine groups. The values in (1)-(3) compared to the distances for the other examples are as follows: [1.378(3) Å^[20] and 1.39(2) Å^[18] (both '50% oxides'); [1.399(4) Å (11.3%), 1.295(14) Å (13.5%), 1.368(5) Å (39.0%).^[16]]. This unusual phenomenon has not been addressed previously in the literature before our 50% 1,4-bis(diphenylphosphinoxido)butane example^[21] where it was observed that the bond shortening is an artefact of the crystallographic refinement process since the physical characteristics of the P-O bond [³¹P nmr shift and <(P=O) infrared stretching frequency] did not change for this pair, e.g. for dppbo (A) (100%)^[25] and dppbo (B) (50%)^[21], <(P=O) was 1185 and 1182 cm⁻¹ respectively, comparing with 1190 cm⁻¹ for (1) and 1195 cm⁻¹ for tppo.^[26] Moreover, a contraction of the C-P-C bond angles [mean: 105.9° (100%) *cf.* 103.5° (50%)] and an expansion C-P-O angles, [mean: 112.7° (100%) *cf.* 114.8° (50%)] indicated that the P moves towards the O rather than vice versa. An almost identical phenomenon is observed for this series (Table 2) where the comparative mean C-P-C and C-P-O angles for (1) (100%) and (2) (50%) are [106.1 *cf.* 103.9°] and [112.7 *cf.* 114.6°] respectively. A further parallel change occurs with the extension of the series to (3) (25%) [102.5° and 115.7°].

The molecules of all three polymorphs (1)-(3) form linear hydrogen-bonded chains which propagate through a three-centre (about O1) C-H...O association involving hydrogen atoms from two different methyl substituents on the amine group [C121-H12...O1^a, C122-H14...O1^a: a = -1/2 + x, 1/2 - y, -1/2 + z] (Fig 2a). The range for these C...O distances is 3.115(4)-3.356(8) Å (Table 2) and is analogous to the double acceptor O-H...O and N-H...O associations found with small incidence among the tppo adducts. The chains extend across the *ac* cell diagonal and are weakly linked peripherally through C-H (aromatic)...O three-

centre hydrogen bonds [C32, C33...O1^b ($b = \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), [range 3.150(5)-3.343(6) Å] (Fig. 2b), giving a two-dimensional sheet structure..

Conclusions

An isomorphous crystal series exists for the variable oxide compound [4-(*N,N*-dimethylamino)phenyl]diphenylphosphine oxide having the formula , (for O 0.25, 0.50, 1.0), suggestive of a continuous series. Paralleling the state of oxidation in this set is an apparent P-O bond shortening, a previously observed phenomenon among phosphine oxides, but not supported by spectroscopic evidence and considered as some artefact of the crystallographic refinement. The compound is found to form an extended two-dimensional C-H...O hydrogen-bonded array, indicating its added potential compared to tppo as a crystallizing aid in crystal chemistry.

Experimental

Preparations

[4-(*N,N*-Dimethylamino)phenyl]diphenylphosphine: The phosphine (dapp) was synthesized using the literature procedure.^[15] Butyl lithium (7.6 mL, 1.6 M in hexane) was added at *ca.* -60°C to a solution of 4-bromo-*N,N*-dimethylaniline (2.44 g, 1.22 x 10⁻² mol) in anhydrous THF (*ca.* 50mL) under argon. After 15 min, chlorodiphenylphosphine (2.18 mL, *d* 1.194 g cm⁻³) was slowly added, then the mixture was allowed to warm to room temperature and remain with stirring for 2 h. After hydrolysis with water (40 mL), the product was extracted with ether. Drying of the ether layer with magnesium sulfate and then evaporation under reduced pressure yielded a light yellow powder. Large colourless prisms of both the ‘half-oxide’ (2) and the ‘quarter-oxide’ (3) were both obtained from the same total room temperature evaporation product of a chloroform solution of this ‘phosphine’. The

assumption is that the phosphine underwent partial facile oxidation in the hydrolysis step of the preparation.

[4-(*N,N*-Dimethylamino)phenyl]diphenylphosphine oxide (1): The crude 'phosphine' was oxidized without further purification in acetone (20 mL) at 5 - 10°C, using hydrogen peroxide (2 mL, 30 wt.% solution in water) under stirring for 15 min. The mixture was then poured into cold water (100 mL) and extracted with chloroform. Subsequent separation, drying and removal of the organic solvent yielded a light yellow powder (2.15 g, 55%). Colourless prisms of (1) were obtained from the total evaporation of the chloroform at room temperature (m.p. 141-143°C). *m/z* 322(M+H, 100%) and 643 (2M+H, 96%); $\nu(\text{P=O})$ (KBr) 1190 cm^{-1} (s). The electrospray mass spectrum was run using 10 μL injections of *ca.* 1-10 $\mu\text{g mL}^{-1}$ acetonitrile solutions and recorded in positive ion mode on a Micromass Platform mass spectrometer. The infrared spectrum was recorded as a pressed disc in KBr on a Perkin Elmer Spectrum 1000 Fourier-transform spectrometer.

Crystallography

Crystal Data, Data Collection, Structure Solution and Refinement

Cell data and general details of data collection and structure refinement for compounds (1)-(3) are given in Table 1. X-ray diffraction data for compound (2) were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer while those for (1) and (3) were collected at low temperature [168(2) K] on a Siemens P4 diffractometer equipped with a SMART 1K (CCD) area detector. Crystal monochromatized Mo $\text{K}\alpha$ X-radiation (8 0.71073Å) was used for all compounds. Collection ranges were: for (1): *h*, -9 to 9; *k*, -7 to 7; *l*, -17 to 17; for (2): *h*, 0-12; *k*, 0 to 10; *l*, -22 to 22; for (3): *h*, -12 to 9; *k*, -11 to 11; *l*, -22 to 22. No significant crystal decomposition was in evidence for any compound. Data were corrected for Lorentz and polarization effects, in the case of the CCD data, applied to three-

dimensionally integrated diffraction spots, the data being processed using the program SAINT.^[27] No absorption corrections were applied. The structures were solved by direct methods and refined using full-matrix least-squares (SHELX-97^[28]), with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were either included in the refinement with coordinates and isotropic thermal parameters refined or were included at calculated positions and treated as riding models. Occupancy values for the oxygen atoms in (2) and (3) were obtained by least-squares refinement with the isotropic thermal parameter set at 0.04 \AA^2 for the low temperature structure (3) and 0.06 \AA^2 for the room temperature structure (2), after which these atoms were allowed to refine anisotropically.

Note: A previous room temperature data set collected for compound (1) using the Nonius CAD-4 diffractometer gave a poor refinement residual and this prompted the low temperature CCD collection. This in turn gave a more satisfactory residual which was however considerably poorer than those for the partial oxides (2) and (3) and is consistent with an unexplained incidence of twinning and poor morphology with crystals of (1). The initial data set does provide a set of comparative room temperature unit cell parameters [a 10.518(4), b 8.735(1), c 19.044(7)Å, β 96.64(2)°, V 1737.9(9) Å³].

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FIGURES

Figure 1. Molecular conformation and atom numbering scheme for (1). Atoms are shown as 30% probability ellipsoids^[29]

Figure 2. (a) Head-to-tail chain extension showing the C-H...O hydrogen bonding as broken lines. The view is down the *b* cell direction

Figure 2. (b) Peripheral inter-chain C-H...O hydrogen bonding

Figure 1. Molecular conformation and atom numbering scheme for (1). Atoms are shown as 30% probability ellipsoids^[29]

Figure 2. (a) Head-to-tail chain extension showing the C-H...O hydrogen bonding as broken lines. The view is down the *b* cell direction

Figure 2 (b) Peripheral inter-chain C-H...O hydrogen bonding

Table 1. Comparative cell data for compounds (1), (2) and (3).

	Compound (1)	Compound (2)	Compound (3)
CCDC reference	206052	206053	206054
Formula	C ₂₀ H ₂₀ NOP	C ₂₀ H ₂₀ NO _{0.50} P	C ₂₀ H ₂₀ NO _{0.25} P
<i>M_r</i>	321.34	313.34	309.34
Crystal class	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.405(14)	10.491(7)	10.289(5)
<i>b</i> (Å)	8.672(12)	8.857(3)	8.841(5)
<i>c</i> (Å)	18.84(3)	18.71(1)	18.04(1)
∠ (deg.)	96.469(16)	96.11(3)	95.038(7)
<i>V</i> (Å ³)	1689(4)	1729(2)	1635(1)
<i>D_c</i> (g cm ⁻³)	1.263	1.204	1.257
<i>Z</i>	4	4	4
∫ (Mo Kα) (mm ⁻¹)	0.167	0.159	0.170
Temp. (K)	168(2)	293(2)	168(2)
2θ _{max} (deg.)	38	50	53
Crystal size (mm)	0.45 x 0.40 x 0.35	0.50 x 0.40 x 0.25	0.40 x 0.40 x 0.35
Total data	8681	3222	18724
Unique data	1360	3034	3275
<i>R</i> _{int}	0.086	0.031	0.035
<i>N</i> [<i>I</i> > 2.0σ(<i>I</i>)]	1154	1821	2507
<i>R</i> 1 *	0.060	0.0421	0.0358
<i>wR</i> 2 *	0.136	0.131	0.091
<i>S</i> *	1.05	0.75	1.08
<i>A</i> , <i>B</i> #	0.0647, 4.22	0.146, 0.00	0.0533, 0.0501

* $R1 = (\sum (F_o^* - F_c^*) / \sum F_o^*)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}$; $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$.

$w = [\Phi^2(F_o^2) + (AP)^2 + BP]^{-1}$ {where $P = [(\max F_o^2, 0) + 2(F_c^2)]/3$ }

Table 2. Comparative P-O bond distances (Å) and mean P cone angles (deg.)

compound	%O	P-O (Å)	C-P-C (deg.)	C-P-O (deg.)	Reference
(1)	100	1.480(4)	106.1	112.7	This work
(2)	50	1.351(4)	103.9	114.6	This work
(3)	25	1.280(4)	102.5	115.7	This work
dppbo (A)	100	1.481(2)	105.9	112.7	22
dppbo (B)	50	1.377(4)	103.5	114.8	21

Table 3. Hydrogen-bonding interactions (Å, deg.)

Compound	C141-H142...O1 ^a	C142-H144...O1 ^a	C32-H32...O1 ^b	C33-H33...O1 ^b
(1)	3.381(8)	3.356(8)	3.337(9)	3.273(9)
(2)	3.326(6)	3.335(6)	3.343(6)	3.276(6)
(3)	3.232(5)	3.115(4)	3.161(5)	3.150(5)

$$\mathbf{a} = -\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z; \quad \mathbf{b} = \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z.$$