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N,*N*′-Bis(ethyldiphenylphosphino)ethylenediamine *P*,*P*′-dioxide

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The molecule of the title compound, $C_{30}H_{34}N_2O_2P_2$ or $Ph_2P(O)N(Et)CH_2CH_2(Et)N(O)PPh_2$, has crystallographically imposed centrosymmetry. The P—N bond length of 1.656 (2) Å is less than the accepted value for a single P—N bond. The P—O bonds [1.4818 (18) Å] are also short because of double-bond character.

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.004 Å
R factor = 0.058
wR factor = 0.143
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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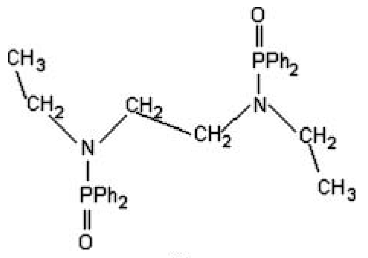
Comment

Owing to their application as catalysts, transition metal complexes with diphosphine ligands have been the subject of several investigations. In the past few decades, there has been considerable interest in the design of multiple mixed donors and their coordination behavior toward transition metal ions. It is believed that properly designed ligand systems would provide new properties and reactivity of the resulting metal complexes (Balakrishna *et al.*, 1999; Balakrishna & Walawalker, 2001; Balakrishna & Mague, 2001; Slawin *et al.*, 2001). The transition metal chemistry of bis(phosphino)amines and their derivatives is becoming increasingly important in view of their potential applications in organic synthesis. It has been found that many modified bis(phosphino)amine ligands have important applications in organometallic chemistry and catalysis (Hartwig *et al.*, 1991; Gleich & Herrmann, 1998; Ganguly & Roundhill, 1993; Cornils & Kuntz, 1995). Some bis(phosphino)amines derived from an ethylenediamine backbone have been reported (Balakrishna & Mague, 2001; Zubiri, Milton, Slawin & Woollins, 2004). Sulfide, selenide and oxide derivatives of piperazine and *N*,*N*′-substituted ethylenediamine-bound bisphosphines have also been obtained (Zubiri *et al.*, 2002; Balakrishna & Walawalker, 2001; Zubiri, Milton, Cole-Hamilton *et al.*, 2004). In addition, phosphine oxides containing P═O donor centers are known to be good ligands for hard metal ions including lanthanides and actinides. If these groups are organized on flexible organic backbones, extra complex stability is expected. The resulting complexes often have coordination numbers greater than six (Paine *et al.*, 2001).

A limited number of bis(phosphino)amine dioxide ligands are known (Zubiri *et al.*, 2002), and we now report a new bis(phosphino)amine *P*,*P*′-dioxide derived from *N*,*N*′-diethylethylenediamine, *viz.* the title compound, (I), having an O—P—N—C—C—N—P—O framework. Addition of diphenylchlorophosphine in dry diethyl ether to a solution of *N*,*N*′-diethylethylenediamine and Et_3N in dry diethyl ether at room temperature results in the immediate precipitation of a white solid. This reaction pathway is a general synthetic route for bis(phosphino)amine ligands, which contain P^{III} atoms (Balakrishna *et al.*, 1999). Although we have not used any oxidizing agent in this reaction, the final product, (I), has two O atoms that are bonded to phosphorus(V) centers. Thus, bis(phosphino)amine oxidizes readily in solution during the recrystallization step. A similar result has been reported for $Ph_2PN(C_2H_4)_2NPPh_2$ (Zubiri *et al.*, 2002).



(I)

A perspective view of the molecule of (I) is shown in Fig. 1, with selected bond lengths and angles in Table 1. Compound (I) possesses crystallographically imposed centrosymmetry; thus, the bond lengths and angles are equal for the two phosphorus centers in their tetrahedral environments, with the two P=O bonds oriented *trans* to each other. This configuration is in agreement with the result reported for bis(phosphino)amine, bis(phosphino)amine oxide and bis(phosphino)amine sulfide ligands (Balakrishna *et al.*, 1999; Zubiri *et al.*, 2002; Balakrishna & Mague, 2001). The P—N bond length of 1.656 (2) Å is comparable with that in $Ph_2P(O)N(C_2H_4N)P(O)Ph_2$ (1.646 Å; Zubiri *et al.*, 2002) and shorter than the normally accepted value for a single P^{III}—N bond (1.77 Å; Cruickshank, 1964). The value in (I) is closer to those typically found for the P—N bonds in cyclic phosphazanes (*ca* 1.6 Å) and is clearly indicative of multiple character (Balakrishna *et al.*, 1993). It is clear that the P^V center has accepted much of the lone-pair electron density from the backbone N atom because of the presence of the electron-withdrawing O atom. Similar trends are generally observed in P^V–N–P^{III} systems (Balakrishna, Teipel *et al.*, 2001).

The N atoms have an almost planar configuration (sum of angles 352.6°). This result is consistent with the reported ligands, $Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$, $[Ph_2P(S)N(Ph)CH_2]_2$ and $Ph_2P(O)N(C_2H_4)_2N(O)PPh_2$ (Balakrishna *et al.*, 1999; Balakrishna & Mague, 2001; Zubiri *et al.*, 2002). A similar geometry around the bridging N atoms has also been found in iminophosphorinophosphines (Balakrishna, Teipel *et al.*, 2001). The P=O bonds are shorter than those observed in $[Ph_2P(O)]_2NH$ [1.519 (2) Å] and $Ph_2P(S)NHP(O)Ph_2$ [1.54 (3) Å; Slawin *et al.*, 1996)], but agree well with those for $Ph_2P(O)CH_2N(H)Ph$ (Priya *et al.*, 2001) and $Ph_2P(O)N(C_2H_4)_2N(O)PPh_2$ (Zubiri *et al.*, 2002) (both 1.481 Å). The P—C bond lengths in compound (I) are in good agreement with the values reported for diphosphine and bis(phosphino)amine ligands (Lobana *et al.*, 1998; Balakrishna & Mague, 2001; Priya *et al.*, 2001).

N,*N*′-Bis(ethyldiphenylphosphino)ethylenediamine with its P—N—N—P backbone can be readily oxidized at the P atoms to form the new ligand system with oxygen donors. Owing to the presence of the long chain, the ligand is unlikely to exhibit chelate ring formation with metals, but the structure of the dioxide has remarkable flexibility. Thus, it can be used to make long-chain polynuclear metal complexes. Further studies into the generality of this process are in progress.

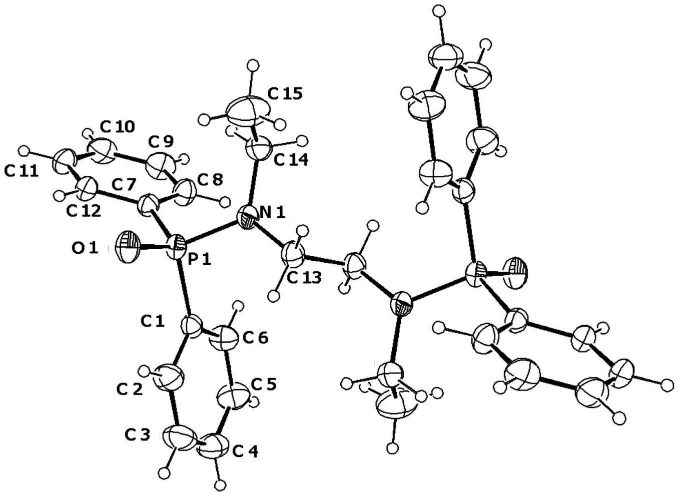


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms are related to labeled atoms by the symmetry operation $(2 - x, 2 - y, -z)$.

Experimental

A solution of PPh_2Cl (3.076 g, 13.98 mmol) in dry diethyl ether (15 ml) was added to a stirred solution of *N*,*N*′-diethylethylenediamine (0.811 g, 6.99 mmol) in dry diethyl ether (10 ml) at room temperature. Stirring was continued for 3 h and then Et_3N (1.41 g, 13.98 mmol) was added. Stirring was continued for 24 h at room temperature. The reaction mixture was then filtered and the white solid was dissolved in CH_2Cl_2. The solid was recrystallized from CH_2Cl_2/Et_2O; m.p. 569–571 K. Analysis found: C 65.25, H 6.66%; calculated for $C_{30}H_{34}N_2O_2P_2$: C, 69.80, H 6.59%. IR: 1117 (νP=O), 932 (νP—N) cm^{-1}; ^1H NMR (CH_2Cl_2): δ 2.7 (*q*, 4H, CH_2CH_2), 3.1 (*t*, 4H, N—CH_2), 0.75 (*t*, 6H, CH_2—CH_3), 7.8–7.4 (*m*, 20H, phenyl). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 31.6 (*s*, 2P).

Crystal data

$C_{30}H_{34}N_2O_2P_2$
$M_r = 516.53$
Monoclinic, $P2_1/c$
$a = 10.0697$ (13) Å
$b = 12.7025$ (17) Å
$c = 10.7016$ (14) Å
$\beta = 94.706$ (2)°
$V = 1364.2$ (3) Å^3
$Z = 2$

$D_x = 1.257$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1657 reflections
$\theta = 2.5$–20.0°
$\mu = 0.19$ mm^{-1}
$T = 297$ (2) K
Block, colorless
0.17 × 0.14 × 0.14 mm

Data collection

Bruker SMART CCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.969$, $T_{max} = 0.970$
10798 measured reflections

2785 independent reflections
2254 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 26.4°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.143$
$S = 1.08$
2785 reflections
164 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.5414P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C7—P1	1.805 (2)	N1—P1	1.656 (2)
C13—N1	1.479 (3)	O1—P1	1.4818 (18)
C6—C1—P1	123.4 (2)	O1—P1—N1	118.38 (11)
C12—C7—P1	118.1 (2)	O1—P1—C7	111.77 (11)
N1—C13—C13^i	111.0 (3)	N1—P1—C7	104.75 (11)
N1—C14—C15	115.3 (3)	O1—P1—C1	110.24 (11)
C14—N1—C13	115.2 (2)	N1—P1—C1	103.69 (11)
C14—N1—P1	121.02 (17)	C7—P1—C1	107.18 (11)
C13—N1—P1	117.37 (16)		

Symmetry code: (i) $-x+2, -y+2, -z$.

The H atoms were positioned geometrically and refined with a riding model, with C—H = 0.93–0.97 Å and with U_{iso} constrained to 1.2 (non-methyl) or 1.5 (methyl) times U_{eq}(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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References

Balakrishna, M. S., Abhyankar, R. M. & Mague, J. T. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1407–1412.

Balakrishna, M. S., Klein, R., Uhlenbrock, S., Pinkerton, A. A. & Cavell, R. G. (1993). *Inorg. Chem.* **32**, 5676–5681.

Balakrishna, M. S. & Mague, J. T. (2001). *Polyhedron*, **20**, 2421–2424.

Balakrishna, M. S., Teipel, S., Pinkerton, A. A. & Cavell, R. G. (2001). *Inorg. Chem.* **40**, 1802–1808.

Balakrishna, M. S. & Walawalker, M. G. (2001). *J. Organomet. Chem.* **628**, 76–80.

Bruker (2001). *SAINT* (Version 6.26a), *SMART* (Version 5.625) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.

Cornils, B. & Kuntz, E. G. (1995). *J. Organomet. Chem.* **502**, 177–186.

Cruickshank, D. W. J. (1964). *Acta Cryst.* **17**, 671–672.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Ganguly, S. & Roundhill, R. M. (1993). *Organometallics*, **12**, 4825–4832.

Gleich, D. & Herrmann, R. S. (1998). *Organometallics*, **17**, 2141–2143.

Hartwig, J. F., Andersen, R. A. & Bergman, R. G. (1991). *Organometallics*, **10**, 1875–1887.

Lobana, T. S., Verma, R., Singh, R. & Castineras, A. (1998). *Transition Met. Chem.* **23**, 25–28.

Paine, R. T., Tan, Y. C. & Gan, X. M. (2001). *Inorg. Chem.* **40**, 7009–7013.

Priya, S., Balakrishna, M. S. & Mague, J. T (2001). *Inorg. Chem. Commun.* **4**, 437–440.

Slawin, A. M. Z., Smith, M. B. & Woollins, J. D. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3659–3667.

Slawin, A. M. Z., Woollins, J. D. & Zhang, Q. (2001). *J. Chem. Soc. Dalton Trans.* pp. 621–632.

Zubiri, M. R., Milton, H. L., Cole-Hamilton, D. J., Slawin, A. M. Z. & Woollins, J. D. (2004). *Polyhedron*, **23**, 693–699.

Zubiri, M. R., Milton, H. L., Slawin, A. M. Z. & Woollins, J. D. (2004). *Inorg. Chim. Acta*, **357**, 1243–1246.

Zubiri, M. R., Slawin, A. M. Z., Wainwright, M. & Woollins, J. D. (2002). *Polyhedron*, **21**, 1729–1736.