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The Structure of Diphenylphosphinamide

By G. Oliva and E. E. Castellano

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369,
13560 *São Carlos SP, Brazil*

and L. R. Franco de Carvalho

Instituto de Química, Universidade de São Paulo, Cid. Universitária, 05508 *São Paulo SP, Brazil*

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Abstract. $C_{12}H_{12}NOP$, $M_r = 217·21$, orthorhombic, $P2_12_12_1$, $a = 5·520\,(1)$, $b = 11·863\,(2)$, $c = 16·378\,(3)$ Å, $V = 1072·61$ Å^3, $Z = 4$, $D_c = 1·34$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, μ(Mo $K\alpha$) = 0·231 mm^{-1}. The structure was solved by the heavy-atom technique and refined to an $R = 0·033$ for the 788 independent observed reflections with intensities above $3\sigma(I)$. The coordination around the P atom was confirmed to be nearly tetrahedral and not planar as would be required if the structures of some lanthanide adducts $La^{3+}(ClO_4^-)_3$.6diphenylphosphinamide were ordered.

Introduction. In the course of a recent investigation of an isomorphous series of structures of adducts between lanthanide salts and diphenylphosphinamide [DPPA, $(C_6H_5)_2P(O)NH_2$] (Castellano & Oliva, to be published), it was found that the complexes crystallize in the cubic space group ($F23$) with the tripositive ion sited on a special position of point symmetry 23. The cation was known to be coordinated to six DPPA ligands (Vicentini & Dunstan, 1971), probably through the O atoms of the phosphoryl groups and with approximate local symmetry O_h. For the structure to be ordered, the DPPA ligands must possess twofold symmetry in order to be accommodated in the g special position of symmetry number 24 to give the expected stoichiometry. This would imply a planar configuration around the P atom which is known not to be favoured on stereochemical grounds. Since progress in finding all atoms of the adduct compounds was slow, the determination of the structure of DPPA was undertaken to rule out eventually the possibility of a disordered arrangement of ligands in the lanthanide structures.

DPPA crystals were prepared as described elsewhere (Vicentini & Dunstan, 1971). A rectangular parallelepiped crystal of dimensions 0·4 × 0·6 × 0·8 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. 25 reflections, centered using least-squares refinement, produced the unit-cell dimensions and the orientation matrix for data collection. Intensities were measured by the θ–2θ scan technique at a rate of 2·8–6·7° min^{-1} determined by a prescan of 6·7° min^{-1}. 926 independent reflections were collected in the range $0 < \theta < 22°$ using graphite-monochromated Mo $K\alpha$ radiation. Of these, 788 had $I \geq 3\sigma(I)$. The intensity of a standard reflection was essentially constant over the length of the experiment. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. The atomic scattering factors used were those given by Cromer & Waber (1974) and the anomalous-dispersion correction coefficients those given by Cromer & Ibers (1974).

The P atom was readily located from a Patterson map and the rest of the non-hydrogen atoms were obtained from a difference synthesis. The structure was refined isotropically by full-matrix least squares to an R value of 0·11 and then anisotropically to $R = 0·06$ for the 788 reflections with intensities above $3\sigma(I)$. All H atoms were found from a difference synthesis at this

Table 1. *Atomic parameters with estimated standard deviations in parentheses and equivalent isotropic temperature factors calculated following Hamilton* (1959)

	x	y	z	$B_{\rm iso}$ (Å^2)
P	0·4577 (2)	0·0867 (1)	0·57011 (7)	2·12
O	0·2225 (5)	0·1492 (2)	0·5729 (2)	2·72
N	0·6883 (7)	0·1699 (3)	0·5549 (2)	2·96
C(1)	0·5311 (8)	0·0097 (4)	0·6622 (3)	2·18
C(2)	0·3681 (9)	−0·0727 (4)	0·6862 (3)	2·86
C(3)	0·4145 (10)	−0·1403 (4)	0·7533 (3)	3·34
C(4)	0·6276 (11)	−0·1235 (4)	0·7976 (3)	3·64
C(5)	0·7862 (10)	−0·0410 (4)	0·7754 (3)	3·59
C(6)	0·7414 (10)	0·0272 (4)	0·7069 (3)	2·87
C(7)	0·4405 (8)	−0·0229 (3)	0·4931 (3)	2·19
C(8)	0·6220 (9)	−0·1026 (4)	0·4871 (3)	3·23
C(9)	0·6077 (9)	−0·1888 (4)	0·4298 (3)	3·40
C(10)	0·4106 (11)	−0·1948 (4)	0·3777 (3)	3·51
C(11)	0·2303 (10)	−0·1143 (4)	0·3825 (3)	3·55
C(12)	0·2428 (9)	−0·0285 (4)	0·4407 (3)	2·90

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Table 2. *Bond angles* (°)

O–P–N	112·5 (2)	C(3)–C(4)–C(5)	120·4 (5)
O–P–C(1)	114·8 (2)	C(4)–C(5)–C(6)	120·9 (5)
O–P–C(7)	109·3 (2)	C(1)–C(6)–C(5)	118·9 (5)
N–P–C(1)	104·9 (2)	P–C(7)–C(8)	120·2 (4)
N–P–C(7)	111·6 (2)	P–C(7)–C(12)	120·4 (4)
C(1)–P–C(7)	103·3 (2)	C(8)–C(7)–C(12)	119·4 (5)
P–C(1)–C(2)	116·5 (4)	C(7)–C(8)–C(9)	120·7 (5)
P–C(1)–C(6)	123·5 (4)	C(8)–C(9)–C(10)	119·9 (5)
C(2)–C(1)–C(6)	119·9 (5)	C(9)–C(10)–C(11)	119·7 (5)
C(1)–C(2)–C(3)	120·9 (5)	C(10)–C(11)–C(12)	120·5 (5)
C(2)–C(3)–C(4)	119·0 (6)	C(7)–C(12)–C(11)	119·7 (5)

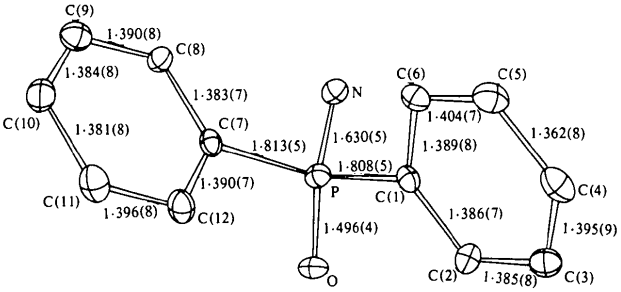

Fig. 1. View of the molecule showing the atom numbering and bond distances (Å).

stage. They were included with isotropic temperature factors and further refinement yielded a final $R = 0{\cdot}033$ and $R_w = 0{\cdot}035$. Unit weights were found appropriate. Atomic coordinates are listed in Table 1.* A final difference map was essentially flat.

Discussion. The molecule is depicted in Fig. 1 which also shows intramolecular bond distances. Angles between bonded atoms are given in Table 2. All bond lengths and angles are unexceptional. The phenyl groups are planar to within experimental accuracy with a dihedral angle of 76·2°. The phenyl C–C distances are essentially identical, with a mean value of 1·39 (1) Å. The phosphorous bond angles are close to tetrahedral, ranging between 114·8 (2) and 103·3 (2)°, as was found in the similar compound *N*,*N*-dimethylphosphinamide (Mazhar-ul-Haque & Caughlan, 1966). This rules out any possibility of the molecule possessing twofold symmetry, which indicates that the DPPA ligands in the lanthanide adducts, mentioned in the *Introduction*, must necessarily be disordered.

All calculations were performed on a PDP 11/45 computer with the *Enraf–Nonius SDP* crystallographic programs.

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* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35700 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Amino-1,3-thiazoline Hydrochloride

By B. M. Vedavathi and Kalyani Vijayan

Materials Science Division, National Aeronautical Laboratory, Bangalore 560017, *India*

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Abstract. $C_3H_7N_2S^+.Cl^-$, $M_r = 138{\cdot}62$, monoclinic, $P2_1/c$, $a = 7{\cdot}240\ (7)$, $b = 6{\cdot}176\ (2)$, $c = 13{\cdot}462\ (8)$ Å, $\beta = 100{\cdot}10\ (3)°$, $D_m = 1{\cdot}51$, $D_c = 1{\cdot}55$ Mg m^{-3}, $Z = 4$, $\mu = 7{\cdot}619$ mm^{-1}. Final $R = 0{\cdot}110$ for 657 observed reflections. The nonplanar thiazoline ring assumes an envelope conformation. The crystal structure is stabilized by NH···Cl hydrogen bonds and van der Waals interactions.

Introduction. 2-Amino-1,3-thiazoline (2-AT) is one of the two components into which the aminothiol radioprotectant (*S*)-2-aminoethylisothiouronium bromide hydrobromide (AETBr.HBr) is converted in the body. Despite being toxic, 2-AT is also known to have the radioprotective properties of its parent compound, AET (Distefano, Leary & Little, 1959). The X-ray analysis of its hydrochloride was therefore undertaken

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