Acta Cryst. (1993). C**49**, 393–394

Structure of 2,2,4,4,6-Pentaphenyl-2,4,1,3,5-diphosphatriazine;† a Six-Membered P_2N_3C Ring

Vadapalli Chandrasekhar, Tristram Chivers and Masood Parvez

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

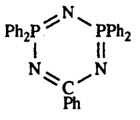
(*Received* 30 *June* 1992; *accepted* 15 *September* 1992)

Abstract

The structure of $Ph_4P_2N_3CPh$ consists of a nearly planar P_2N_3C ring in which the P atoms and two of the N atoms are related by a twofold axis. The endocyclic bond distances are P—N = 1.601 (2) and 1.626 (2), C—N = 1.334 (2) Å. The endocyclic bond angles are P—N—P = 116.4 (2), N—P—N = 116.4 (1), P—N—C = 120.1 (2) and N—C—N = 130.1 (3)°.

Comment

The title compound (I) was obtained as a minor product from the reaction of Ph_2PCl_3 with $Li[PhC(NSiMe_3)_2]$ (Chandrasekhar, Chivers, Kumaravel, Meetsma & van de Grampel, 1991), but it was not structurally characterized. The major product was the eight-membered ring 1,5-$Ph_4P_2N_4C_2Ph_2$, which was shown to exist in a distorted boat–boat conformation. The heterocycle (I) is also produced from the reaction of $PhC[N(SiMe_3)_2](NPPh_2)$ with PhSeCl in dichloromethane in a 1:2 molar ratio.



(I)

The largest deviation from planarity of the nearly planar six-membered P_2N_3C ring of (I) involves the symmetry-related N atoms, which are 0.067 Å out of, and on opposite sides of the P_2N_3C plane. No structural data for other P_2N_3C rings are available for comparison. The P—N bond lengths are 1.601 (2) and 1.626 (2) Å [*cf.* 1.584–1.610 Å in $Ph_6P_3N_3$ (Ahmed, Singh & Barnes, 1969)]. The C—N bond lengths are 1.334 (2) Å [*cf.* 1.302 (8)–1.328 (8) Å for 1,5-$Ph_4P_2N_4C_2Ph_2$ (Chandrasekhar, Chivers, Kumaravel, Meetsma & van de Grampel, 1991)].

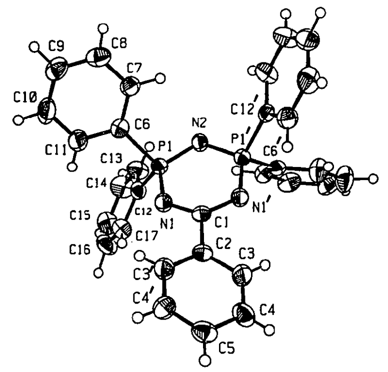


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of $Ph_4P_2N_3CPh$ (I). Ellipsoids are scaled to enclose 50% probability. H atoms are represented as spheres of arbitrary radii. Primes indicate symmetry-related atoms.

Experimental

Crystal data

$C_{31}H_{25}N_3P_2$
$M_r = 501.51$
Monoclinic
$C2/c$
$a = 15.760$ (2) Å
$b = 10.832$ (2) Å
$c = 16.611$ (2) Å
$\beta = 116.34$ (1)°
$V = 2541.3$ (7) Å^3
$Z = 4$

$D_x = 1.311$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71093$ Å
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.191$ mm^{-1}
$T = 296$ K
Block
0.40 × 0.23 × 0.22 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans (1.0–6.67° min^{-1})
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.948$, $T_{max} = 1.045$
4011 measured reflections
3892 independent reflections

2159 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.026$
$\theta_{max} = 30°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 15$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity variation: < 1.5%

Refinement

Refinement on F
Final $R = 0.049$
$wR = 0.040$
$S = 1.77$
2159 reflections
203 parameters
Only coordinates of H atoms refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.1$

$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974) and Stewart, Davidson & Simpson (1965)
Anomalous dispersion allowed for according to Ibers & Hamilton (1964)

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† IUPAC nomenclature: 2,2,4,4,6-pentaphenyl-1,3,5,2,4-triazadiphosphorinine.

0108-2701/93/020393-02$06.00

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\text{eq}} = \frac{8\pi^2}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
P(1)	0.41670 (5)	0.00680 (6)	0.25607 (5)	2.39 (2)
N(1)	0.4287 (1)	−0.1424 (2)	0.2603 (1)	2.58 (8)
N(2)	0.5000	0.0847 (3)	0.2500	2.5 (1)
C(1)	0.5000	−0.1944 (3)	0.2500	2.3 (1)
C(2)	0.5000	−0.3332 (3)	0.2500	2.4 (1)
C(3)	0.5576 (2)	−0.3985 (3)	0.2222 (2)	3.2 (1)
C(4)	0.5567 (2)	−0.5252 (3)	0.2213 (2)	3.8 (1)
C(5)	0.5000	−0.5903 (4)	0.2500	3.6 (2)
C(6)	0.4009 (2)	0.0591 (2)	0.3512 (2)	2.6 (1)
C(7)	0.4700 (2)	0.1276 (3)	0.4189 (2)	3.2 (1)
C(8)	0.4576 (2)	0.1638 (3)	0.4927 (2)	3.9 (1)
C(9)	0.3758 (3)	0.1353 (3)	0.4987 (2)	4.1 (1)
C(10)	0.3063 (2)	0.0686 (4)	0.4315 (2)	4.9 (2)
C(11)	0.3185 (2)	0.0304 (3)	0.3580 (2)	4.1 (1)
C(12)	0.3050 (2)	0.0401 (2)	0.1617 (2)	2.5 (1)
C(13)	0.2821 (2)	0.1608 (3)	0.1334 (2)	3.9 (1)
C(14)	0.1962 (2)	0.1889 (3)	0.0622 (2)	4.6 (1)
C(15)	0.1324 (2)	0.0981 (3)	0.0183 (2)	4.2 (1)
C(16)	0.1532 (2)	−0.0209 (3)	0.0459 (2)	4.1 (1)
C(17)	0.2390 (2)	−0.0514 (3)	0.1177 (2)	3.4 (1)

Table 2. *Geometric parameters* (Å, °)

P(1)—N(1)	1.626 (2)	C(7)—C(8)	1.382 (4)
P(1)—N(2)	1.601 (2)	C(8)—C(9)	1.371 (4)
P(1)—C(6)	1.798 (3)	C(9)—C(10)	1.372 (4)
P(1)—C(12)	1.799 (3)	C(10)—C(11)	1.382 (4)
N(1)—C(1)	1.334 (2)	C(12)—C(13)	1.382 (4)
C(1)—C(2)	1.504 (5)	C(12)—C(17)	1.387 (4)
C(2)—C(3)	1.382 (3)	C(13)—C(14)	1.379 (4)
C(3)—C(4)	1.372 (4)	C(14)—C(15)	1.363 (4)
C(4)—C(5)	1.378 (4)	C(15)—C(16)	1.358 (4)
C(6)—C(7)	1.383 (4)	C(16)—C(17)	1.390 (4)
C(6)—C(11)	1.387 (4)		
N(1)—P(1)—N(2)	116.4 (1)	P(1)—C(6)—C(11)	120.0 (2)
N(1)—P(1)—C(6)	109.5 (1)	C(7)—C(6)—C(11)	118.9 (3)
N(1)—P(1)—C(12)	106.7 (1)	C(6)—C(7)—C(8)	120.2 (3)
N(2)—P(1)—C(6)	109.1 (1)	C(7)—C(8)—C(9)	120.6 (3)
N(2)—P(1)—C(12)	110.6 (1)	C(8)—C(9)—C(10)	119.7 (3)
C(6)—P(1)—C(12)	103.8 (1)	C(9)—C(10)—C(11)	120.2 (3)
P(1)—N(1)—C(1)	120.1 (2)	C(6)—C(11)—C(10)	120.4 (3)
P(1)—N(2)—P(1′)	116.4 (2)	P(1)—C(12)—C(13)	119.5 (2)
N(1)—C(1)—N(1′)	130.1 (3)	P(1)—C(12)—C(17)	122.1 (2)
N(1)—C(1)—C(2)	114.9 (2)	C(13)—C(12)—C(17)	118.4 (3)
C(1)—C(2)—C(3)	120.8 (2)	C(12)—C(13)—C(14)	120.6 (3)
C(3)—C(2)—C(3′)	118.4 (3)	C(13)—C(14)—C(15)	120.6 (3)
C(2)—C(3)—C(4)	120.7 (3)	C(14)—C(15)—C(16)	119.6 (3)
C(3)—C(4)—C(5)	120.9 (3)	C(15)—C(16)—C(17)	120.8 (3)
C(4)—C(5)—C(4′)	118.4 (4)	C(12)—C(17)—C(16)	120.0 (3)
P(1)—C(6)—C(7)	121.1 (2)		

Symmetry code: (′) $1 - x, y, 0.5 - z$.

Space groups *C*2/*c* and *Cc* were indicated from systematic absences (*hkl*, $h + k = 2n + 1$ and *h*0*l*, $h = 2n + 1$ and $l = 2n + 1$); the former was chosen and confirmed by successful analysis. Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods using *SAPI*91 (Fan, 1991). Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anistropic temperature factors for the non-H atoms. At an intermediate stage in the refinement a difference map revealed maxima consistent with the positions of the H atoms, which were incuded in the subsequent cycles of refinement with fixed isotropic temperature factors. All computer programs used in this study were part of the *TEXSAN* package (Molecular Structure Corporation, 1992) installed on a Silicon Graphics Personal Iris 4D/35 computer.

This work was supported by the NSERC (Canada). We thank Dr J. Fait for the X-ray data collection.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55551 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1015]

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Acta Cryst. (1993). C**49**, 394–398

Structures of (*E*,*E*)-*o*-Nitroacetophenone Azine (I), (*E*,*Z*)-*o*-Nitroacetophenone Azine (II) and (*E*,*E*)-*o*-Nitrobenzaldehyde Azine (III)

LEH-YEH HSU AND CHRISTER E. NORDMAN

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, *USA*

DAVID H. KENNY

Michigan Technological University, Houghton, MI 49931, *USA*

(*Received* 28 *April* 1992; *accepted* 14 *September* 1992)

Abstract

In compounds (I) and (II) the *o*-nitro group is *anti* to the methyl group where as in (III), which lacks the methyl, it is *syn* to the H atom. Distortions from planarity indicate that the nitro group experiences

0108-2701/93/020394-05$06.00