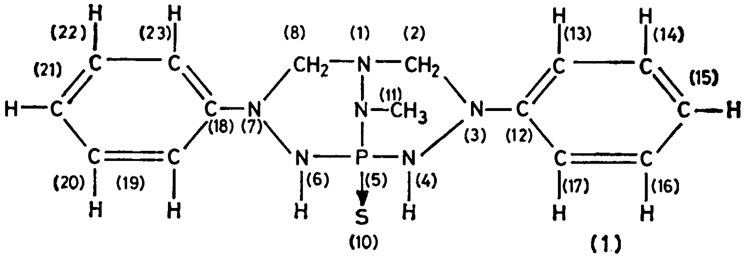
Heterocyclic Compounds Containing Phosphorus. Part 34.† Crystal and Molecular Structure of 9-Methyl-3,7-diphenyl-1,3,4,6,7,9-Hexa-aza-5λ^4-Phosphabicyclo[3.3.1]nonane-5-thione

By **André Grand** and **Jean-Bernard Robert**, D.R.F. Chimie Organique Physique, C.E.N.G. 85X, 38041 Grenoble Cédex, France
Jean-Pierre Majoral * and **Jacques Navech**,* Laboratoire des Heterocycles du Phosphore et de l'Azote, Université Paul Sabatier, 118, route de Narbonne, 31077 Toulouse Cédex, France

The structure of the title compound, determined by *X*-ray crystallography, shows that there is no symmetry plane in the molecule, and one of the two six-membered rings is in a chair form, with the other one in a boat conformation. The sum of the angles around nitrogen indicates that most of the nitrogen atoms α (or β) to phosphorus are pyramidal.

X-RAY diffraction studies of several amino- or hydrazinophosphine derivatives have been reported recently, each of which contained a P–N–C or P–N–N–P unit. As far as we know, however, the molecular structure of a phosphorus heterocyclic compound containing a P–N–N–C unit has not yet been reported. In connection with our research into the reactivity of phosphohydrazides, the structure of compound (1) would be of particular interest in explaining the nucleophilicity of nitrogen atoms α to phosphorus. We have observed such nucleophilic attack only for certain compounds containing a P–NH–NHPh sequence.[1,2] Moreover the preferred conformation of bicyclo[3.3.1]nonane type compounds has been the subject of many investigations, since they are very interesting from a stereochemical point of view. 3,7 Non-bonded interactions have been studied in particular, and have posed many problems, even for non-heteroatomic systems.[3] We now report the crystal and molecular structures of compound (1).



(1)

EXPERIMENTAL

We have previously described [1] the synthesis of 9-methyl-3,7-diphenyl-1,3,4,6,7,9-hexa-aza-5λ^4-phosphabicyclo-[3.3.1]nonane-5-thione (1). Crystals were obtained from hot benzene. From Weissenberg photographs, the space group was assumed to be $P2_12_12_1$ (systematic absences: $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd). The unit cell parameters were refined by a least-squares fitting of the angular position of 25 reflexions.

Crystal data. $C_{15}H_{19}N_6PS$, $M = 346.40$. Orthorhombic, $a = 8.454(3)$, $b = 11.400(2)$, $c = 17.225(2)$ Å, $U = 1\,660.07$ Å^3, $D_c = 1.39$ g cm^{-3}, $D_m = 1.40$ g cm^{-3}, $Z = 4$, $F(000) = 728$. Space group $P2_12_12_1$. The intensity of 2 755 independent reflexions ($2° < \theta < 30°$) was collected on an automatic ENRAF-NONIUS CAD-4 diffractometer with carbon monochromatized Mo-K_α radiation. The intensity of four standard reflexions ($0\bar{7}3$; 073; 380; $\bar{3}\bar{8}0$) was recorded periodically and no decrease was observed during the data collection. The data were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by the direct method using the MULTAN.[4] A set of 300 reflexions with $E > 1.51$ was used in the initial phasing. The E map with the best figure of merit allowed the location of all the non-hydrogen atoms. The structure was refined using the XFLSN program,[5] with the P, S, N, and C atoms anisotropic. Refinement with 1 989 reflexions ($F > 3\sigma$) reached an R_W value of 0.070 ($R_W = \Sigma|F_o - F_c|^2/\Sigma F_o{}^2$) and an R value of 0.084 ($R =$

TABLE 1

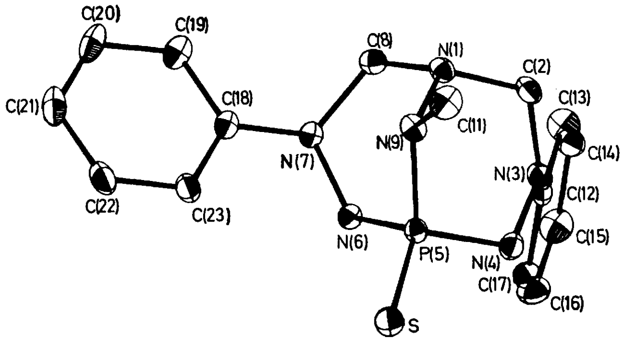
Fractional co-ordinates ($\times 10^4$) with standard deviations in parentheses

	x	y	z
N(1)	−409(4)	1 650(3)	6 986(2)
C(2)	−1 160(5)	793(3)	6 555(2)
N(3)	−465(4)	402(2)	5 806(2)
N(4)	−316(4)	1 385(3)	5 300(2)
P(5)	407(1)	2 584(1)	5 721(1)
N(6)	2 138(3)	2 130(2)	6 047(2)
N(7)	2 431(4)	2 063(2)	6 851(2)
C(8)	1 201(5)	1 432(3)	7 274(2)
N(9)	−457(4)	2 757(2)	6 583(2)
S(10)	347(1)	3 904(1)	5 029(1)
C(11)	−1 940(5)	3 379(4)	6 684(3)
C(12)	542(4)	−558(3)	5 675(2)
C(13)	541)6)	−1 523(4)	6 175(2)
C(14)	1 463(6)	−2 488(4)	6 018(3)
C(15)	2 419(6)	−2 533(5)	5 365(3)
C(16)	2 446(6)	−1 580(4)	4 891(2)
C(17)	1 511(5)	−593(3)	5 026(2)
C(18)	3 173(4)	3 049(3)	7 186(2)
C(19)	3 746(5)	2 968(4)	7 946(2)
C(20)	4 563(5)	3 886(5)	8 273(3)
C(21)	4 839(5)	4 907(5)	7 854(3)
C(22)	4 271(6)	4 982(4)	7 110(3)
C(23)	3 433(5)	4 078(4)	6 773(3)

---

† Part 33, J. P. Majoral, M. Revel, and J. Navech, *Phosphorus and Sulfur*, 1978, **4**, 317.

$\Sigma|F_o - F_c|/\Sigma F_o$). At this level of refinement, a Fourier difference map showed the hydrogen atoms. Including all the atoms, the R factors converged to $R_W = 0.04$ and $R = 0.04$.



X-Ray structure of compound (1)

The atomic co-ordinates are listed in Table 1. Tables 2 and 3 give the bond lengths and bond angles, and the structure is shown in the Figure. The structure factor table, and thermal parameters, are available as Supplementary Publication No. SUP 22647 (13 pp.).*

TABLE 2

Bond lengths (Å) with standard deviations in parentheses

N(1)–C(2)	1.456(5)	N(1)–C(8)	1.469(5)
C(2)–N(3)	1.459(5)	C(8)–N(7)	1.459(5)
N(3)–N(4)	1.425(4)	N(7)–N(6)	1.408(4)
P(5)–N(4)	1.664(3)	P(5)–N(6)	1.651(3)
N(1)–N(9)	1.442(4)	N(9)–P(5)	1.666(3)
P(5)–S	1.921(1)	N(9)–C(11)	1.451(5)
N(3)–C(12)	1.404(4)	N(7)–C(18)	1.411(4)
C(12)–C(13)	1.397(5)	C(12)–C(17)	1.387(5)
C(13)–C(14)	1.376(6)	C(17)–C(16)	1.395(6)
C(14)–C(15)	1.386(6)	C(15)–C(16)	1.360(6)
C(18)–C(19)	1.398(5)	C(18)–C(23)	1.389(5)
C(19)–C(20)	1.376(6)	C(23)–C(22)	1.379(5)
C(20)–C(21)	1.388(7)	C(21)–C(22)	1.371(7)

TABLE 3

Bond angles (°) with standard deviations in parentheses

C(2)–N(1)–N(9)	113.0(3)	C(8)–N(1)–N(9)	109.7(3)
C(2)–N(1)–C(8)	116.8(3)	N(1)–N(9)–P	108.3(2)
N(3)–C(2)–N(1)	116.7(3)	N(7)–C(8)–N(1)	114.1(3)
C(2)–N(3)–N(4)	113.0(3)	N(6)–N(7)–C(8)	113.1(3)
N(3)–N(4)–P	114.4(2)	N(7)–N(6)–P	120.5(2)
N(4)–P–N(9)	108.9(2)	N(6)–P–N(9)	97.0(1)
N(4)–P–S	111.3(1)	N(6)–P–S	118.7(1)
N(4)–P–N(6)	102.5(2)	N(9)–P–S	116.7(1)
N(1)–N(9)–C(11)	113.2(3)	P–N(9)–C(11)	122.9(3)
C(12)–N(3)–C(2)	124.8(3)	C(12)–N(3)–N(4)	117.4(3)
C(18)–N(7)–C(8)	120.4(3)	C(18)–N(7)–N(6)	116.0(3)
N(3)–C(12)–C(13)	120.9(3)	N(3)–C(12)–C(17)	120.7(3)
N(7)–C(18)–C(19)	119.0(3)	N(7)–C(18)–C(23)	122.2(3)
C(13)–C(12)–C(17)	118.3(4)	C(19)–C(18)–C(23)	118.7(4)
C(12)–C(13)–C(14)	120.6(4)	C(12)–C(17)–C(16)	119.5(4)
C(13)–C(14)–C(15)	121.3(5)	C(17)–C(16)–C(15)	122.4(4)
C(18)–C(19)–C(20)	120.4(4)	C(18)–C(23)–C(22)	119.8(4)
C(19)–C(20)–C(21)	120.7(4)	C(23)–C(22)–C(21)	121.8(4)
C(14)–C(15)–C(16)	117.9(5)	C(20)–C(21)–C(22)	118.6(4)

RESULTS AND DISCUSSION

The hexa-azaphosphabicyclo[3.3.1]nonane (1) is not symmetrical with respect to the plane defined by the N(1), P(5), and N(9) atoms. Allowing for experimental error, the corresponding distances in the two hexa-atomic rings are equal (see Table 2), but the valence angle values are quite different in the two rings. Moreover, the N(9)P(5)N(4)N(3)C(2)N(1) ring exists in a chair conformation and the N(9)P(5)N(6)N(7)C(8)N(1) ring in a boat form [interatomic distances are respectively 3.00 and 2.61 Å for N(9)–N(3) and N(9)–N(7)].

These results can be related to those for the bicyclo-[3.3.1]nonane series. Bicyclo[3.3.1]nonane itself adopts a slightly flattened chair–chair conformation as shown by electron diffraction.[6-8]

(2) X = Y = O
(3) X = O, Y = S
(4) X = Y = S
(5) X = Y = NMe
(6) X = Y = NPh

The introduction of heteroatoms in positions 3 and 7, *e.g.* two oxygen atoms [compound (2)] or one oxygen atom and one sulphur [compound (3)], does not destabilize the chair–chair form but repulsion between the O · · · O or O · · · S heteroatoms is sufficient to distort the geometry and to bring about a flattening of the ' wings ' of the molecules.[9] In contrast, the repulsion between two sulphur atoms in positions 3 and 7 in compound (4) is strong enough to increase the relative proportions of the chair–boat conformations.[9] Dipole moment and n.m.r. studies indicate that the preferred conformation of 1,3-diazabicyclo[3.3.1]nonane (5) is a flattened chair–chair.[10] A twin-chair conformation also gives the best agreement with n.m.r. results for compound (6).[9]

In the hexa-azaphosphabicyclo[3.3.1]nonane (1) the N(3)–N(7) distance (*ca.* 3.2 Å) in the twin-chair conformation should be slightly greater than the sum of the van der Waals radii for nitrogen (1.5 Å). Moreover, the phenyl rings should be almost parallel and at a distance of >4.5 Å; thus, the effect of these groups should not be dramatic. Consequently we suggest that the destabilization of the chair–chair conformation in compound (1) could be due to the interaction of the quasi *p* doublets of the N(3) and N(7) nitrogen atoms: the so-called ' hockey-stick effect '.[9]

^{1}H N.m.r. data [1] show only a single AB system for the methylene protons. Thus, in solution, the molecule possesses a plane of symmetry, on the n.m.r. time-scale. which could arise from a rapid equilibrium between two or more conformations in solution. N.m.r. spectra recorded at temperatures as low as −120 °C do not show any variation in the AB system.

The difference between the angles C(8)N(1)N(9) and C(2)N(1)N(9) on the one hand and between N(6)P(5)N(9) and N(4)P(5)N(9) on the other shows clearly that the N(1)N(9)P(5) unit favours the boat form (see Table 3). The position of the N(9)-methyl group favours the chair form side of the molecule, as is clear from the following algebraic distances to the N(1)N(9)P(5) plane: C(11), −0.86; N(4), −1.17; C(2), −1.13; N(6), 1.38; and C(8), 1.33 Å.

The molecular dimensions are very similar to those

---

* For details of obtaining this material, see Notice to Authors No. 7, *J.C.S. Perkin II*, 1979, Index issue.

TABLE 4

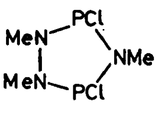
Molecular dimensions of heterocyclic compounds containing a P–N–N linkage (distances in Å and angle in degrees)

Compound	Ref.	P–N	N–N	∠N–P–N	∠P–N–N	Σ∠N[a]
(7)	11	1.674(3)	1.495	92.7(2)	111.1(3)	343.2
		1.666(4)				
(8)	12	1.678(6)	1.462(8)	99.4(7)	118.9(10)	350.2
		1.687(6)			118.0(10)	
(9)	13	1.645(3)	1.400(4)	101.4(2)	120.3(3)	359.3
		1.662(4)			116.5(3)	352.5
(10)	14	1.656(3)	1.422(4)	107.2(2)	120.8(2)	358.8
		1.661(3)			115.6(2)	345.6
(11)	15	1.72(3)	1.42(4)	98(1)	119(1)	
		1.69(3)	1.45(4)	98(1)	123(2)	
		1.69(3)	1.45(4)	96(1)	119(1)	345 (average)
		1.70(3)		101(1)	114(1)	
		1.65(3)		103(1)	111(2)	
		1.64(2)		105(1)	119(2)	
(12)	16	1.640(3)	1.448(5)	104.9(2)	113.1(3)	
		1.685(3)	1.444(5)	102.6(2)	114.2(3)	
		1.651(3)	1.442(5)	104.0(2)	113.3(3)	343 (average)
		1.664(3)		103.6(2)	114.3(3)	
		1.663(3)		102.3(2)	112.6(2)	
		1.670(4)		104.5(2)	114.0(2)	
(13)	17	1.66(8) (average)	1.44(5) (average)	103(3) (average)	114.2 (average)	346
						344

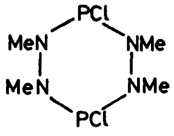
[a] For (P)–N–(P), Σ∠N = 360°.

reported[11-17] for the heterocycles (7)—(13) containing a P–N–N unit (Table 4). Some of the values (P–N and N–C bond lengths, N–P–N angles) are also close to those of cyclic compounds having an intracyclic P–N bond (P–N = 1.579—1.692; N–C = 1.455—1.509 Å; ∠N–P–N = 101.7—105.2°).[18-20]

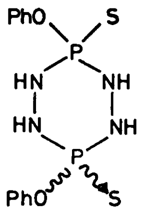
The sums of the valency angles at nitrogen are as follows: N(1), 339.5; N(3), 355.2; N(4), 354.7; N(6), 350.8; N(7), 349.5; N(9), 344.4. However, great care must be taken in considering the values for the angles at N(4) and N(6) because of the uncertainty in proton location.



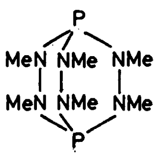
(7)



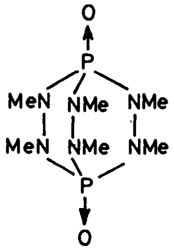
(8)



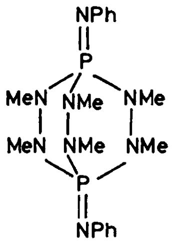
(9) (*cis*)
(10) (*trans*)



(11)



(12)



(13)

Assuming, in agreement with the proposition of Clardy *et al.*,[20] that trigonal planarity is achieved when the sum of the appropriate bond angles exceeds 355°, then only N(3) and N(4) are ' planar ' in compound (1); the geometry of the other nitrogen atoms is best described as a more or less ' closed ' pyramid [including N(7), directly linked to a phenyl group, which should be close to the planarity]. Nonplanarity of nitrogen atoms directly linked to phosphorus is also found in the heterocycles (7)—(13) (Table 4), except for the *cis*- and *trans*-tetra-azadiphosphorines (9) and (10) in which two of the four nitrogen atoms (nonadjacent and linked to a different phosphorus atom) are planar.

These experimental results might seem to contradict observations on compounds with P–N–C bonds only, in which the nitrogen atoms are planar.[18,20] Nevertheless, nitrogen atoms of aminophosphines are sometimes pyramidal,[21-23] and a calculation of the structure of the $H_2P{-}NH_2$ molecule by the pseudo-potential method leads to a sum of 347° for the nitrogen valency angles.[24]

The P–N bond lengths indicate a significant degree of double bond character, as shown by comparison with the literature[25-32] values in Table 5. These bonds should have an order of 1.4 in most of the compounds (1) and (7)—(13) according to the results of Tyssee[33] and Mazhar-ul-Haque and Caughlan[34] [1.55 Å for P–N(6) and 1.50 Å for P–N(4) in 1]. Analogous interpretations can be proposed for the N(3)–N(4) and N(6)–N(7) bonds which have a fairly large Π character, as shown by comparison with the literature[35-37] values in Table 6.

The simultaneous presence of a pyramidal nitrogen atom (α to phosphorus or linked to a phenyl group) and of P–N, N–N, or N–C bonds possessing a certain degree

TABLE 5

P–N bond lengths

PN bond	Compound	Ref.	Lengths/Å
Single (P–N)	Theoretical	25	1.80
	$H_3N{-}PO_3^{2-}$	26	1.77
Double or with a large degree of double character (P ⩵ N)	$(H_2N)_3PBH_3$	27	1.65
	$[N{=}P(NMe_2)_2]_3$ (exocyclic bond)	28	1.68
	$(Cl_3PNMe)_2$ (equatorial bond)	29	1.629
	F_2PNMe_2	30	1.628
	$FP{=}NMe$	31	1.641
	H_2NPF_2	32	1.650

TABLE 6

N-N bond lengths

Bond	Compound	Ref.	Lengths/ Å
Large degree of double character	Diformylhydrazine	35	1.392
	Tetrakis(trifluoromethyl)-hydrazine	36	1.402
Single	Hydrazine	37	1.449

of multiplicity is in agreement with the reasoning of Dewar and Rona,[38] who have demonstrated that the structure R–NH_2 with a Π bond between R and N is most stable when the nitrogen atom is not planar, unless there is a very large degree of resonance stabilization. This can be proved by a comparison of nitrogen atoms having the same environment: *i.e.* N(4) and N(6) on the one hand, and N(3) and N(7) on the other. The shortest P–N and N–N bonds correspond to the most pyramidal nitrogen atoms N(6) and N(7).

Steric effects must be taken into account in order to explain the nonplanarity of nitrogen, as Clardy *et al.*[20] did for compounds (11) and (12). Hexa-atomic rings do not seem to be responsible, since hydrazine nitrogen atoms of the penta-atomic ring of (7) are also pyramidal. Strain might be responsible for this nonplanarity of nitrogen atoms and for the low value of some ∠N–P–N angles. It is also possible that the conformation of the bond to nitrogen is influenced by conjugation of the N(3), N(4), and N(6), N(7) lone pairs with the Π electrons of the phenyl groups. These groups are effectively in a favourable position, torsional angles around the N(3)–C(12) and N(7)–C(18) bonds being as follows: C(2)N(3)C(12)C(13), 22.2; C(2)N(3)C(12)C(17), −160.8; N(4)N(3)C(12)C(13), 175.9; N(4)N(3)C(12)C(17), −7.1; C(8)N(7)C(18)C(19), 48.7; C(8)N(7)C(18)C(23), −134.9; N(6)N(7)C(18)C(19), −169.1; N(6)N(7)C(18)C(23), 7.3°. N(3) is in a better position for conjugation than N(7), the torsional angle being *ca.* 22°. This result is in good agreement with the fact that N(3) is more planar than N(7).

We thank C.N.R.S. for financial support of this work.

[9/446 *Received, 19th March,* 1979]

REFERENCES

[1] J. P. Majoral, R. Kraemer, J. Navech, and F. Mathis, *J.C.S., Perkin I*, 1976, 2093.

[2] J. P. Majoral, M. Revel, R. Kraemer, H. Germa, and J. Navech, *J. Heterocyclic Chem.*, 1977, **14**, 749.

[3] J. A. Peters, J. M. A. Baas, B. van de Graaf, J. M. van der Toorn, and H. van Bekkum, *Tetrahedron*, 1978, **34**, 3313.

[4] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[5] W. R. Busing, K. O. Martin, and H. A. Levy, ORXFLS3 Report ORNL, 59-4-37, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1971.

[6] E. L. Osina, V. S. Mastryukov, L. V. Vilkov, and N. A. Belicova, *J.C.S. Chem. Comm.*, 1976, 12.

[7] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1636.

[8] E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

[9] N. S. Zefirov and S. V. Rogozina, *Tetrahedron*, 1974, **30**, 2345.

[10] E. Douglas and T. B. Ratcliff, *J. Org. Chem.*, 1968, **33**, 355.

[11] R. Ullmann and H. Nöth, *Chem. Ber.*, 1976, **109**, 2581.

[12] H. Nöth and R. Ullmann, *Chem. Ber.*, 1976, **109**, 1089.

[13] U. Engelhardt and H. Hartl, *Acta Cryst.*, 1975, **B31**, 2098.

[14] U. Engelhardt and H. Hartl, *Acta Cryst.*, 1976, **B32**, 1133.

[15] W. Van Doorme, G. W. Hunt, R. W. Perry, and A. W. Cordes, *Inorg. Chem.*, 1971, **10**, 2591.

[16] J. W. Gilje and K. Seff, *Inorg. Chem.*, 1972, **11**, 1643.

[17] A. W. Cordes, C. K. Fair, M. Bermann, and J. R. Van Wazer, *J. Cryst. Mol. Struct.*, 1975, **5**, 279.

[18] T. Prange, C. Pascard, J. Devillers, and J. Navech, *Bull. Soc. chim. France*, 1977, 185.

[19] R. A. Shaw, *Phosphorus and Sulfur*, 1978, **4**, 101.

[20] J. C. Clardy, T. L. Kolpa, and J. G. Verkade, *Phosphorus*, 1974, **4**, 133.

[21] E. Subramanian and J. Trotter, *J. Chem. Soc. (A)*, 1969, 2309.

[22] G. C. Holywell, D. W. H. Rankin, B. Beagely, and J. M. Freeman, *J. Chem. Soc. (A)*, 1971, 785.

[23] G. Bullen, F. S. Stephens, and R. J. Wade, *J. Chem. Soc. (A)*, 1969, 1804.

[24] M. Barthelat, R. Mathis, and F. Mathis, *J.C.S. Chem. Comm.*, 1977, 615.

[25] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

[26] E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Cryst.*, 1953, **6**, 621.

[27] C. E. Nordman, *Acta Cryst.*, 1960, **13**, 535.

[28] G. J. Bullen, *J. Chem. Soc.*, 1962, 3201.

[29] H. Hess and D. Forst, *Z. anorg. Chem.*, 1966, **342**, 240.

[30] E. D. Morris and C. E. Nordman, *Inorg. Chem.*, 1969, **8**, 1673.

[31] G. W. Adamson and J. C. J. Bart, *J. Chem. Soc. (A)*, 1970, 1452.

[32] A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwende, *J. Amer. Chem. Soc.*, 1971, **93**, 6772.

[33] D. Armon Tyssee, Ph.D. Thesis, University of California, Los Angeles, 1967.

[34] Mazhar-ul-Haque and C. N. Caughlan, *J.C.S. Perkin II*, 1976, 1101.

[35] Y. Tomiie, C. H. Koo, and I. Nitta, *Acta Cryst.*, 1958, **11**, 774.

[36] L. S. Bartell and H. K. Higginbotham, *Inorg. Chem.*, 1965, **4**, 1346.

[37] Y. Marino, I. Iljima, and Y. Murata, *Bull. Chem. Soc. Japan*, 1960, **33**, 46.

[38] M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, 1969, **91**, 2259.