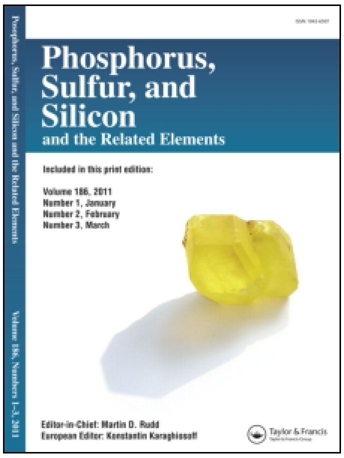


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOSPHORIC AMIDES. 9. CRYSTAL AND MOLECULAR STRUCTURES OF N- (DIPHENYLPHOSPHINOYL) ETHYLENIMINE AND ITS N-(β-CHLOROETHYL) PRECURSOR

B. Davidowitz[a]; T. A. Modro[a]; M. L. Niven[a]
[a] School of Chemical Sciences, University of Cape Town, Rondebosch, South Africa

To cite this Article Davidowitz, B. , Modro, T. A. and Niven, M. L.(1985) 'PHOSPHORIC AMIDES. 9. CRYSTAL AND MOLECULAR STRUCTURES OF N- (DIPHENYLPHOSPHINOYL) ETHYLENIMINE AND ITS N-(β-CHLOROETHYL) PRECURSOR', Phosphorus, Sulfur, and Silicon and the Related Elements, 22: 3, 255 — 263

To link to this Article: DOI: 10.1080/03086648508073364

URL: http://dx.doi.org/10.1080/03086648508073364

Phosphorus and Sulfur, 1985, Vol. 22, pp. 255–263
0308-664X/85/2203-0255/\$15.00/0

PHOSPHORIC AMIDES. 9. CRYSTAL AND MOLECULAR STRUCTURES OF *N*-(DIPHENYLPHOSPHINOYL) ETHYLENIMINE AND ITS *N*-(β-CHLOROETHYL) PRECURSOR

B. DAVIDOWITZ, T. A. MODRO and M. L. NIVEN

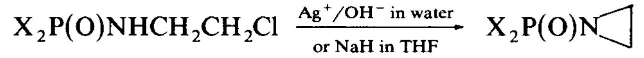
School of Chemical Sciences, University of Cape Town, Rondebosch, South Africa

(*Received January 15, 1985*)

Crystal and molecular structures of diphenyl *N*-(β-chloroethyl)phosphinamidate (**1**) and *N*-(diphenylphosphinoyl)ethylenimine (**2**) have been determined. The nitrogen and chlorine atoms in **1** are in a conformation close to gauche, so the molecule cannot be considered as an "early stage" of the intramolecular displacement of the β-Cl by the amidate nitrogen. The nitrogen atom in **2** is much more pyramidal than the nitrogen in the structurally-related diphenyl *N*,*N*-dimethylphosphinamidate. This difference in the geometry (and hence, hybridisation) of these two tertiary amidate nitrogens is correlated with the known difference in the solvolytic behaviour of the corresponding amidoesters.

INTRODUCTION

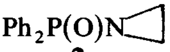
We have observed[1] that intramolecular nucleophilic displacement in *N*-(β-chloroethyl) phosphoramidates occurs exclusively *via* 1,3-attack by the amidate nitrogen atom at the β-carbon atom yielding *N*-phosphorylated ethylenimines (Eq. (1)).



(1)

We were therefore interested to see whether there was any "close contact" between the nitrogen and β-carbon atoms in the substrate molecule by examining selected molecular parameters of a crystalline *N*-(β-chloroethyl) derivative. Such a crystal structure could then be regarded as an "early stage" of the reaction pathway outlined in Eq. (1). Similar structural correlations have been discussed by Bürgi and Dunitz[2] and demonstrated for incipient nucleophilic attack on a diazonium group.[3] We have also found[4] that the ethylenimine substituent has a substantial effect on the reactivity of the adjacent phosphoryl centre relative to that of a simple tertiary phosphoramidate. In the *N*,*N*-dimethyl phosphoramidate the P—O bond is deactivated towards nucleophilic cleavage while the P—N bond is even more resistant to attack by nucleophiles. In the *N*-phosphorylated ethylenimines both the P—O and P—N bonds are strongly activated towards nucleophilic substitution. We were interested to see whether this difference in reactivity would be reflected in the molecular parameters of selected substrates. Thus we have synthesised and determined the crystal structures of the diphenyl *N*-(β-chloroethyl) phosphinamidate **1** which is the precursor of the *N*-phosphorylated ethylenimine derivative **2** and compare the results obtained for **2** with molecular parameters reported[5] for the diphenyl *N*,*N*-dimethyl phosphinamidate **3**.

$Ph_2P(O)NHCH_2CH_2Cl$
1


2

$Ph_2P(O)NMe_2$
3

RESULTS AND DISCUSSION

Selected molecular parameters for **1**, **2** and **3** are listed in Table I. Perspective views of compounds **1** and **2**, together with atomic nomenclature, are shown in Figures 1 and 2.

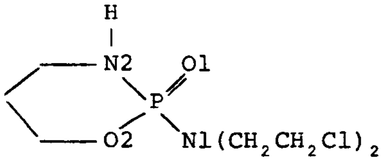
TABLE I

Intermolecular bond distances and angles for **1A**, **1B**, **2**, **3**[a] and **4**[a]

	1A	**1B**	**2**	**3**	**4**
Bond lengths, Å					
P(1)–O(1)	1.480(5)	1.481(5)	1.479(3)	1.48	1.53
P(1)–N(1)	1.629(5)	1.621(6)	1.672(3)	1.68	1.64
P(1)–C(11)	1.801(6)	1.799(6)	1.799(4)	1.79	
P(1)–C(21)	1.800(7)	1.799(6)	1.792(3)	1.78	
N(1)–C(1)	1.472(9)	1.456(9)	1.472(5)	1.50	1.58
			1.465(4)	1.48	1.48
C(1)–C(2)	1.502(12)	1.493(16)	1.464(5)		
Bond angles, deg.					
N(1)–P(1)–O(1)	113.0(3)	113.0(3)	117.6(2)	117.5	110
C(11)–P(1)–O(1)	109.2(3)	109.1(3)	111.8(2)	111.6	
C(11)–P(1)–N(1)	109.3(3)	109.9(3)	103.1(1)	103.8	
C(21)–P(1)–O(1)	114.9(3)	115.3(3)	112.8(2)	111.7	
C(21)–P(1)–N(1)	102.9(3)	102.8(3)	103.1(2)	103.9	
C(21)–P(1)–C(11)	107.3(3)	106.4(3)	107.4(2)	107.5	
X(1)–N(1)–P(1)[b]	120.8(5)	125.6(5)	118.2(2)	115.8	119
C(1)–N(1)–P(1)	119.5(5)	121.7(5)	117.9(2)	118.0	120
C(1)–N(1)–X(1)[b]	113.8(6)	108.0(5)	59.8(2)	115.1	116
Torsion angles, deg.					
N(1)–C(1)–C(2)–Cl(1)	73.1(7)	65.4			180
					176
Non-bonded distances, Å					
Intramolecular					
O(1) ··· C(2)	3.477(9)	3.381(13)	3.108(5)		
O(1) ··· N(1)	2.594(6)	2.588(6)			
Intermolecular		symmetry operation applied to second atom			
N(1B) ··· O(1A)	2.772(7)	$-x+1, -y+1, -z+1$			
N(1A) ··· O(1B)	2.757(7)	$-x, -y+1, -z+1$			
Deviation of N(1) from plane of atoms bonded to it, Å					
	0.183	0.165	0.690	0.303	0.20

[a] Data taken from Ref. 5 for **3** and Ref. 17 for **4**. The relevant atoms have been numbered in a manner consistent with this work and not as originally presented.

[b] X = H for **1**, X = C(2) for **2**, **3** and **4**.



4

Owing to its known cytostatic activity,[17] cyclophosphamide **4** represents the most important example of a phosphoramidate carrying the *N*-(2-chloroethyl) group, and hence molecular parameters reported[17] for **4** are also included in Table I. The P—O, P—N and N—C bond lengths for **1** are similar to those reported for (+)-cyclophosphamide **4**.

The angles at the phosphorus atom, in the range 102.8(3)–115.3(3)° indicate that the configuration is largely tetrahedral. A similar variation in these angles was reported for (+)-cyclophosphamide **4**.[17] The angles at the nitrogen atom, in the range 108.0(5)°–125.6(5)°, indicate that it is more tetrahedral than the nitrogen atom N1 of **4**.[17] The deviation of the nitrogen atom from the H ··· C ··· P plane for the two independent molecules of **1** is in the range 0.165–0.183 Å, which is of the same order as the value of 0.2 Å calculated for **4** using data from ref. 17. The non-bonded distances O(1) ··· C(2), i.e., O ··· C_β, for **1** are greater than the sum of the van der Waals radii (3.20 Å),[18] and hence there is no obvious interaction between the phosphoryl oxygen and the β-carbon atom in the crystal.

The torsion angle[19] αN(1)–C(1)–C(2)–Cl in **1A** is 73.1(7)° and 65.4(9)° in **1B**. Thus the nitrogen and chlorine atoms are clearly not antiperiplanar, which would be the most favourable conformation for nucleophilic displacement of the chloride ion by the amidate nitrogen atom. Studies of acyclic systems (where rotation about the carbon–carbon bond yields any potentially available torsion angle) show that a torsion angle of 180° (antiperiplanar) leads to more facile elimination than any other

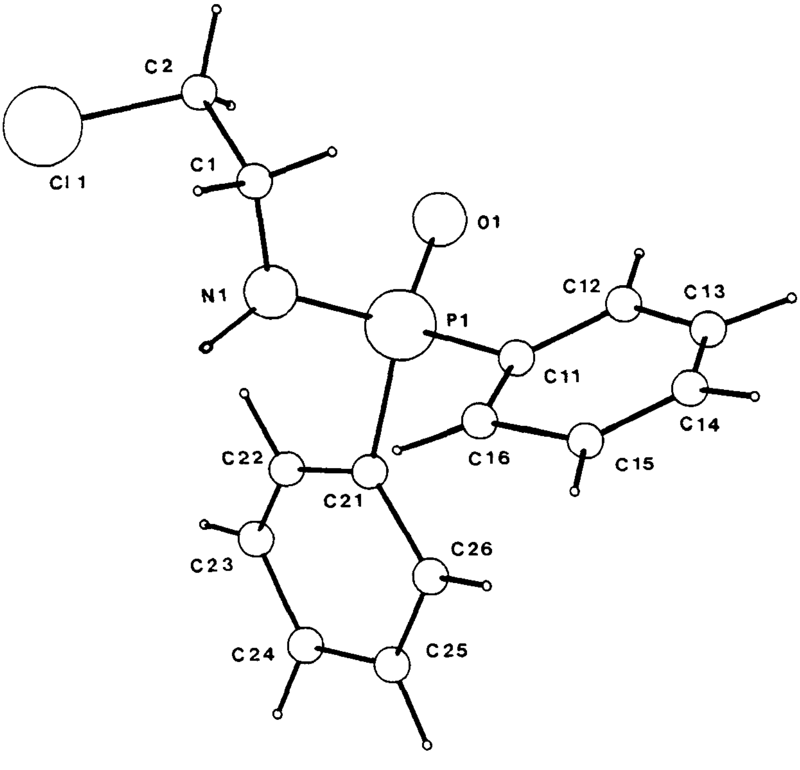


FIGURE 1 A perspective view of $Ph_2P(O)NHCH_2CH_2Cl$ **1**.

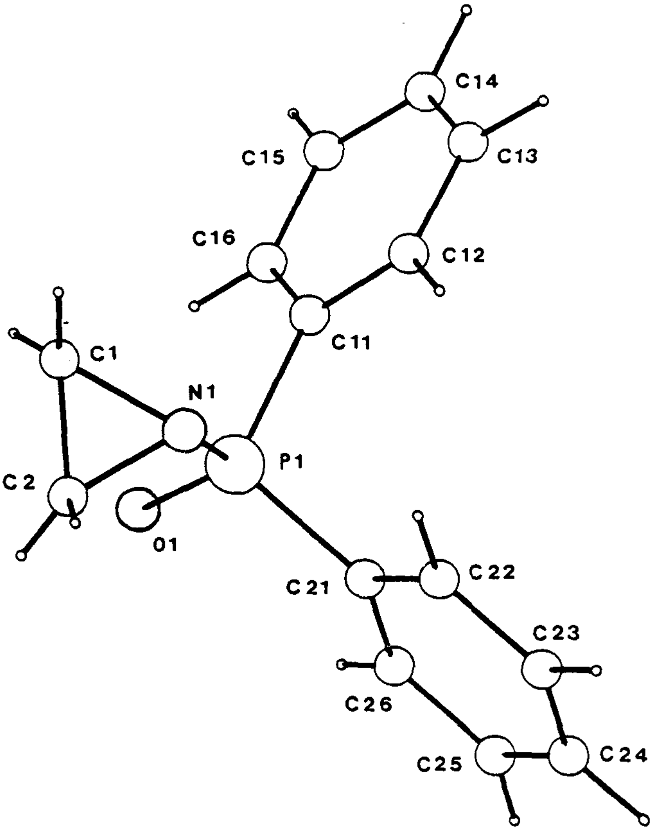
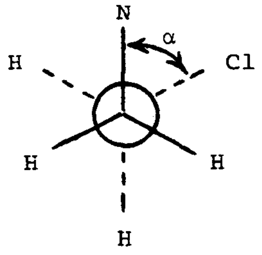


FIGURE 2 A perspective view of Ph$_2$P(O)N$\lhd$ **2**.

angle.[20] The Newman projection formula for **1** drawn along the C(1)–C(2) bond shows, however, that the nitrogen and chlorine atoms are in the unfavourable gauche conformation. Intermolecular hydrogen bonding occurs in **1** yielding *trans*-polymeric chains as shown in Figure 3. This contrasts with the hydrogen bonding in the phosphoramidates (MeO)$_2$P(O)NHAr in which the conformation of the $>$P(O)NH$<$ moiety was *cis* yielding dimers or *cis* polymeric chains.[21] It is proposed that the stability arising from the intermolecular hydrogen bonding in **1** is a predominant factor in determining the packing of the molecules in the crystal lattice. This has occurred at the expense of a favourable torsion angle close to 180° for the *N*-(β-chloroethyl) group.



$|\alpha| = 73.1(7)°$ **1A**, $65.4(9)°$ **1B**.

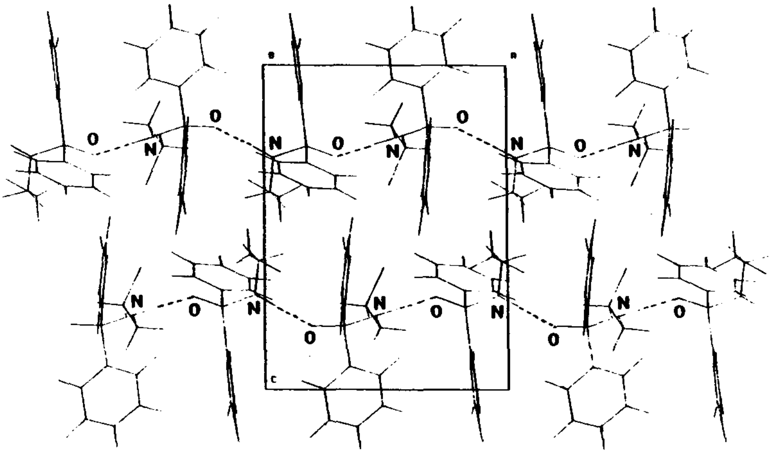


FIGURE 3 Packing diagram for $Ph_2P(O)NHCH_2CH_2Cl$ **1**; hydrogen bonding is indicated by dotted lines.

In (+)-cyclophosphamide **4** the torsion angle N(1)–C(1)–C(2)–Cl varies over the range 176–180°. In **4**, however, hydrogen bonds are formed between the phosphoryl group and the endocyclic HN group of three (+)-cyclophosphamide molecules which are related by a threefold axis in the unit cell, and trimers are formed.

The P—O bond lengths in **2** and **3** are similar to those quoted for **4**,[17] $(MeO)_2P(O)NHAr$[21] and **1** (Table I). The P—N bond lengths in **2** and **3** are identical (within experimental error) and are similar to those reported for **4**,[17] $(MeO)_2P(O)NHAr$[21] and **1**. An important difference between the molecular parameters of **2** and **3** is the pyramidality of the amidate nitrogen atom, i.e. the deviation of the nitrogen atom from the C(1) ··· P(1) ··· C(2) plane which can be taken as an indication of the difference in hybridisation and may be related to the chemical behaviour of these compounds. The angles at the nitrogen atoms of **2** and **3** are also different owing to the requirement of the three-membered ring in **2** (see Table I).

We have reported that the *N*-phosphorylated ethylenimines such as $(MeO)_2P(O)NC_2H_2$ **5** are much more reactive towards nucleophiles than the corresponding *N,N*-dimethylamino derivative $(MeO)_2P(O)NMe_2$ **6**.[4] This difference in reactivity was ascribed to the lack of conjugative interaction between the nitrogen atom and the adjacent phosphoryl centre in **5**, which allows facile attack by nucleophiles. The *N,N*-dimethylamino group in **6** deactivates this compound towards nucleophilic substitution by donating its electrons to the phosphoryl centre.[22] The observed chemical behaviour of **5** and **6** can be correlated with the crystal structures of their phosphinamidate analogues **2** and **3**. The nitrogen atom in **3** is much more planar than that of **2** (see Table I), which shows a greater possibility for d_π–p_π overlap between the phosphorus and nitrogen atoms in **3** relative to **2**, and by analogy, in **6** and **5**.

It is interesting to note, however, that the difference in nitrogen pyramidality of **3** relative to **2** is not reflected by a decrease in the length of the P—N bond with a concomitant increase of the length of the P—O bond (see Table I). This contrasts with the analogous molecular parameters measured for carboxamides; studies of *N*-acylated ethylenimines and other *N,N*-disubstituted analogues show that conjugative interactions in the latter compounds lead to a decrease in the C(O)—N bond length and an increase in the C—O bond length. Thus the C—N bond length in *N*-(4-bromobenzoyl)ethylenimine **7** is 1.41 Å while that in *N*-benzoylmorpholine **8** is 1.34 Å.[23] The nitrogen atom in **7** is pyramidal while in **8** it is planar.[23] The increase in the length of the C—O bond in *N,N*-disubstituted carboxamides relative to *N*-acylated ethylenimines is also reflected by the carbonyl stretching frequencies in *N*-acetylethylenimine and *N,N*-dimethylacetamide which are 1706 and 1652 cm^{-1}, respectively.[24]

A comparison of selected molecular parameters of **2** and **3** shows that the difference in the reactivity of their ester analogues in solution is reflected only in the degree of pyramidality of the nitrogen atom. The shortening of the C—N bond and the increase in the length of the C—O bond due to conjugative interactions in carboxylic amides is not paralleled by the corresponding P—O and P—N bonds in phosphinamidates. The results of kinetic measurements[4] show that electronically the NMe_2 and NC_2H_4 groups must be very different. The quasi-sp^2 hybridisation of the carbon atoms in the three-membered ethylenimine ring[25] (compared with classical sp^3 hybridised carbon atoms in the NMe_2 group) is probably the predominant factor in determining the overall difference in electron-donating ability of these two groups with respect to the phosphoryl centre and hence responsible for the observed difference in nucleophilic cleavage.

EXPERIMENTAL

General information and materials. ^1H n.m.r. spectra were recorded on a 100 MHz Varian XL 100 spectrometer using tetramethylsilane as an internal standard. Melting points (uncorrected) were recorded on a Fisher-Johns melting point apparatus. Analyses for C, H and N were carried out at the University of Cape Town. All solvents were purified by conventional means before use. Triethylamine was distilled from KOH pellets. 2-chloroethylammonium chloride was ground to a fine powder and dried under vacuum to constant weight over P_2O_5. Diphenylphosphinoyl chloride was prepared from diphenylphosphinic acid (Aldrich) and thionyl chloride.[6]

Preparation of diphenyl N-(β-chloroethyl) phosphinamidate **1**. Diphenylphosphinoyl chloride (5.92 g, 0.025 mol) and 2-chloroethylammonium chloride (3.48 g, 0.03 mol) were heated under reflux with stirring in 100 ml benzene. Triethylamine (6.07 g, 0.06 mol) in 15 ml benzene was added dropwise. The mixture was then heated under reflux for 7h and stirred at room temperature overnight. After filtering the reaction mixture and removing the solvent under reduced pressure the crude product was purified by recrystallisation from CCl_4 to give **1** (74%), m.p. 98–100°C, δ ($CDCl_3$) 8.02–7.80 and 7.58–7.40 (10 H, m, 2 × Ph), 3.67 (2 H, t, $J_{H,H}$ 6 Hz, CH_2Cl), 3.41–3.19 (2 H, m, NCH_2) and 3.19–2.90 (1 H, br.s. NH). (Found: C, 60.0; H, 5.35; N, 5.0. $C_{14}H_{15}ClNOP$ requires C, 60.12; H, 5.40; N, 5.01%.)

Preparation of N-(diphenylphosphinoyl) ethylenimine **2**. (**2**) was prepared from **1** by treatment with a slight excess of NaH (Merck) in tetrahydrofuran. The crude product was recrystallised from acetone/pet. ether, 87%, m.p. 120–121.5°C (lit.[7] 119–119.5°C from hexane), δ ($CDCl_3$) 8.18–7.70 and 7.65–7.36 (10 H, m, 2 × Ph) and 2.29 (4 H, d, $J_{H,P}$ 15 Hz, NCH_2CH_2). (Found: C, 68.9; H, 5.75; N, 5.7. Calc. for $C_{14}H_{14}NOP$: C, 69.13; H, 5.80; N, 5.76%.)

Solution and refinement of the structures. Suitable crystals were obtained by recrystallisation from carbon tetrachloride for **1** and from acetone/pet. ether for **2**. **2** was found to interact with commercial adhesive, and hence for X-irradiation purposes, a single crystal was inserted in a tube of Lindemann glass (.3 mm diameter) and wedged up at the sealed end using a glass fibre. For both compounds, accurate cell parameters were determined by a least squares analysis of the setting angles of 24 reflections in the θ range 16–17°, automatically located and centred on an Enraf-Nonius CAD4 diffractometer. Intensities were collected with ω-2θ scans; for both structures, the intensities of three reference reflections were checked every hour to monitor crystal decay. The data sets were corrected for Lorentz-Polarization but not for absorption. The solution and refinement of **1** is particularly interesting crystallographically;

further details of the X-ray investigation will appear elsewhere.[8] In brief, the structure was solved in the triclinic non-centrosymmetric space group P1 using the direct methods routines employed in a preliminary version of SHELX-S 84,[9] together with information from a Patterson synthesis obtained from SHELX-76.[10] The structure was then refined in P1; however with simple translations of atomic coordinates, the structure could also be refined in the centrosymmetric P$\bar{1}$ having 2 independent molecules. With this X-ray data set (5316 reflections, 2470 with $I_{rel} > 2\sigma I_{rel}$) the P1 structure appeared to be the better model. This is most likely because the weak reflections were generally not well-measured.[11] A second data set was subsequently obtained in which all reflections were very much more carefully measured.

In the light of the second data collection the P1 solution is undoubtedly the correct one, and is hence what is reported here.

In the final refinements of **1** the P and Cl atoms were treated anisotropically with all remaining atoms isotropic. The ring and methylene hydrogens were placed in calculated positions and allowed to refine with a single temperature factor. The hydrogens of the N—H groups, initially placed as located in a difference map, did not refine sensibly and were ultimately placed 1.00 Å from their respective nitrogens at positions calculated to yield linear N—H ··· O intermolecular hydrogen bonds (N ··· O in range 2.757(7)–2.772(7) Å). Such a situation is feasible from energy considerations.

Compound **2** was solved by direct methods using SHELX-S 84,[9] and refined using SHELX 76.[10]

In the final refinements of **2** all non-hydrogen atoms were assigned anisotropic thermal motion, while the phenyl H's were placed at 1.00 Å from their parent carbons (their positions being dictated by the ring geometries) with a single isotropic temperature factor. Owing to the distortion from tetrahedrality of the carbons in the aziridine ring, their hydrogens were initially inserted at the positions revealed in the

TABLE II

Experimental data for the x-ray diffraction study of **1** and **2**

	1	**2**
Crystal Data		
Molecular formula	$C_{14}H_{15}ClNOP$	$C_{14}H_{14}NOP$
Space group	P1	Pbca
Crystal system	Triclinic	Orthorhombic
a Å	10.105(2)	11.902(4)
b Å	10.892(1)	16.556(2)
c Å	14.122(5)	12.879(1)
α	70.67(2)°	90.00(2)°
β	86.95(2)°	90.00(2)°
γ	82.27(2)°	90.00(2)°
Z	4	8
D_c/Mg m^{-3}	1.27	1.27
$\mu(M_0 - K_\alpha)$ mm^{-1}	0.31	0.16
F(000)	584	1024
Data Collection		
Crystal dimensions mm	0.28 × 0.35 × 0.50	0.22 × 0.25 × 0.34
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
Scan width in ω°	$(0.79 + 0.35 \tan\theta)$	$(0.74 + 0.35 \tan\theta)$
Aperture width mm	$(1.11 + 1.05 \tan\theta)$	$(1.13 + 1.05 \tan\theta)$
Stability of standard reflections %	1.35	1.43
θ Range°	1–25	1–25
Number of reflections collected	9846	2555
Number of reflections observed	4136	1285
Criterion for observed reflections	$I_{rel} > 2\sigma(I_{rel})$	$I_{rel} > 2\sigma(I_{rel})$
Refinement		
Number of variables	168	168
$R = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$	0.107	0.040
$Rw = \Sigma w^{\frac{1}{2}} \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma w^{\frac{1}{2}} \lvert F_o \rvert$	0.107	0.038
Weighting scheme	unit weight	$(\sigma^2 F)^{-1}$

TABLE III

Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms of **1A**, **1B** and **2**

	1A			**1B**			**2**		
	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
P(1)	1768(1)	1773(2)	2541(1)	3253(1)	7804(2)	8058(1)	668(1)	5318(1)	2098(1)
Cl(1)	−658(3)	4989(2)	3598(2)	4896(4)	5303(3)	6261(2)			
N(1)	405(5)	2491(5)	2895(4)	4550(5)	6982(5)	7730(4)	1766(2)	5688(1)	1442(2)
O(1)	2995(4)	2126(4)	2860(3)	1995(4)	7256(4)	8035(3)	−463(2)	5441(1)	1650(2)
C(11)	1770(6)	22(5)	3045(4)	3479(6)	7855(6)	9299(4)	1004(3)	4263(2)	2223(2)
C(12)	2935(6)	−765(6)	3451(5)	4683(7)	8127(7)	9561(5)	1991(3)	3989(2)	2658(3)
C(13)	2933(7)	−2121(7)	3838(5)	4821(9)	8248(8)	10509(6)	2164(3)	3166(2)	2790(3)
C(14)	1803(8)	−2671(8)	3795(6)	3783(9)	8078(8)	11151(7)	1367(3)	2617(2)	2463(3)
C(15)	651(8)	−1886(7)	3387(5)	2618(9)	7772(9)	10938(7)	398(3)	2890(2)	2009(3)
C(16)	614(7)	−545(6)	3029(5)	2417(8)	7667(7)	9982(6)	213(3)	3708(2)	1892(3)
C(21)	1568(6)	2243(6)	1204(5)	3327(6)	9444(6)	7213(4)	820(3)	5767(2)	3356(2)
C(22)	1567(8)	3565(8)	652(6)	3460(7)	9651(7)	6185(5)	1864(3)	5991(2)	3749(3)
C(23)	1426(9)	3941(9)	−405(7)	3478(7)	10918(7)	5521(6)	1931(4)	6325(2)	4745(3)
C(24)	1281(9)	3098(9)	−839(7)	3361(7)	11953(8)	5858(6)	982(4)	6425(2)	5323(3)
C(25)	1288(9)	1769(9)	−340(7)	3201(7)	11778(8)	6866(6)	−51(4)	6203(2)	4940(3)
C(26)	1455(7)	1349(8)	723(6)	3190(6)	10514(6)	7544(5)	−128(3)	5871(2)	3957(3)
C(1)	242(7)	2434(7)	3950(5)	4758(7)	5555(7)	8102(5)	1778(4)	5586(2)	307(3)
C(2)	599(7)	3651(7)	4101(6)	4158(11)	4973(11)	7431(8)	1580(4)	6384(2)	761(3)

difference map, and constrained to ride at 1.00(1) Å from the parent carbons, with a single isotropic temperature factor in each case.

For **2** a weighting scheme was employed $((\sigma^2 F)^{-1})$. Complex neutral atom scattering factors were taken from Cromer and Mann[12] for the C, O, N, P atoms and from Stewart, Davidson and Simpson[13] for H, with dispersion corrections from Cromer and Liberman.[14] All computations were performed at the Computer Centre of the University of Cape Town on a Sperry 1100/81 computer. The program PARST[15] was used for molecular geometry parameters and PLUTO[16] for drawings. Further details of the crystal parameters, data collection and structure refinement are given in Table II. Final atomic coordinates for both compounds are reported in Table III.*

ACKNOWLEDGMENTS

The authors with to thank the C.S.I.R. and University of Cape Town for financial support.

REFERENCES

1. B. Davidowitz and T. A. Modro, *S. Afr. J. Chem.*, **35**, 63 (1982).
2. H. B. Bürgi and J. Dunitz, *Acc. Chem. Res.*, **16**, 153 (1983).
3. J. D. Wallis and J. Dunitz, *J. Chem. Soc., Chem. Commun.*, 671 (1984).
4. B. Davidowitz and T. A. Modro, *J. Chem. Soc., Perkin Trans.*, **2**, 303 (1985).
5. M.-ul-Haque and C. N. Caughlan, *J. Chem. Soc., Perkin Trans.*, **2**, 1101 (1976).
6. N. Kreutzkamp and H. Schindler, *Arch. Pharm.* (*Weinheim, Ger.*), **293**, 296 (1960).
7. F. A. L. Anet, R. D. Trepka and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 357 (1967).
8. B. Davidowitz, T. A. Modro, M. L. Niven and K. J. Zemke, *S. Afr. J. Chem.*, submitted 1984.
9. G. M. Sheldrick, *SHELXS*-'84', private communication.
10. G. M. Sheldrick, *Computing in Crystallography*, H. Schenk, R. Olthof-Hazekamp, H. von Koningsveld and G. C. Bassi, eds. (Delft University Press, 1978) pp. 34–42.

---

*Structure factors, H-atom coordinates, anisotropic and isotropic temperature factors are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd, Cambridge CB 2 IEW, U.K.

11. R. E. Marsh, *Acta Cryst.*, **B37**, 1985 (1981).
12. D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968).
13. R. F. Stewart, E. R. Davidson and N. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
14. D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
15. M. Nardelli, '*PARST*', private communication.
16. W. D. S. Motherwell, '*PLUTO*', private communication.
17. I. L. Karle, J. M. Karle, W. Egan, G. Zon and J. A. Brandt., *J. Am. Chem. Soc.*, **99**, 4803 (1977).
18. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
19. Torsion angles follow the sign convention of W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).
20. J. M. Harris and C. C. Wamser, *Fundamentals of Organic Reaction Mechanisms* (John Wiley & Sons, Inc., New York, 1976) Chap. 4.3.
21. M. P. du Plessis, T. A. Modro and L. R. Nassimbeni, *J. Org. Chem.*, **47**, 2313 (1982).
22. I. Öney and M. Caplow, *J. Am. Chem. Soc.*, **89**, 6972 (1967).
23. C. W. Fong and H. G. Grant, *Aust. J. Chem.*, **34**, 2307 (1981).
24. T. Z. Papoyan, I. I. Chervin and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1530 (1968).
25. K. Yates, "*Hückel Molecular Orbital Theory*" (Academic Press, New York, 1978), Chap. VIII.2.2.