

Structure of Benzyl(diethylamino)diphenylphosphonium Chloride

BY J. C. J. BART, I. W. BASSI† AND M. CALCATERRA

Montedison 'G. Donegani' Research Institute, Via G. Fauser 4, Novara, Italy

(Received 14 July 1981; accepted 26 November 1981)

Abstract

Crystals of benzyl(diethylamino)diphenylphosphonium chloride, $C_{23}H_{27}NP^+Cl^-$, $M_r = 383.91$, are monoclinic, space group $P2_1/c$ with $a = 12.515$ (5), $b = 10.327$ (4), $c = 16.052$ (7) Å, $\beta = 94.83$ (4)°, $V = 2067$ (1) Å³; $Z = 4$, $D_o = 1.21$, $D_c = 1.23$ g cm⁻³. The molecular and crystal structures of the compound were determined by direct and Fourier methods and refined by least-squares techniques to $R = 0.082$ for 956 independent observed reflexions. The structure consists of chloride and benzyl(diethylamino)diphenylphosphonium ions, the latter with tetrahedral coordination around the P atoms. The most significant average bond distances are: P–C(sp^3) 1.76 (1), P–C(sp^2) 1.80 (1) and P–N 1.63 (1) Å. In addition to the basic system of σ bonding, $p\pi(N)-d\pi(P)$ bonding occurs. Delocalization of the lone electron pair on the N atom is enhanced by the positive charge on P. The P–C(sp^2) and P–N bonds are in a slightly distorted *staggered* conformation (*gauche* –, *gauche* +, and *trans*) with respect to the C(sp^2)–CH₂ bond of the benzyl residue. The diethylamino group shows disorder. The interionic distances conform to accepted van der Waals values.

Introduction

Phosphonium salts of the type $R_4P^+X^-$, where $R =$ alkyl, aryl, find various applications as insecticides and fungicides, as antistatic and softening agents for textiles and as corrosion inhibitors. The recent finding of the use of phosphonium cations with P–N bonds as vulcanization accelerators (Moggi & Mancini, 1977), in analogy to the common onium compounds, has stimulated our interest in these chemicals. In spite of the considerable attention that has been paid in recent years to the problem of π bonding between phosphorus and nitrogen, and to the measurement of P–N bond lengths, mainly in cyclic phosphazenes and phosphazanes, few experimental studies have been made of monophosphazane-type phosphonium cations. In fact, most of the known compounds containing both P–N

and P–C linkages are phosphonic diamide or phosphinic amide derivatives. We have therefore found it worthwhile to establish the crystal and molecular structure of benzyl(diethylamino)diphenylphosphonium chloride (I).

Experimental

Colourless crystals of the title compound, obtained by crystallization from DMF, were kindly provided by Dr G. Moggi. Preliminary cell parameters and space group were obtained from Weissenberg photographs. Accurate cell dimensions together with the best orientation matrix were determined by a least-squares fit of χ , φ , ω and 2θ values from 12 independent reflexions, measured on a four-circle computer-controlled diffractometer equipped with a scintillation counter and pulse-height analyser.

A tiny crystal, $0.1 \times 0.1 \times 0.3$ mm, was found suitable for intensity-data collection on a Picker FACS-1 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) in the angular range $3^\circ < 2\theta < 40^\circ$. The moving-crystal moving-counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2.0 – 2.5° to allow for the variable separation of $K\alpha_1$ and $K\alpha_2$ peaks at various 2θ values. Background counts of 10 s were measured at each end of every 2θ scan. During data collection three standards, measured before every 50 reflexions, showed a gradual decay up to 10%. Of 1931 independent reflexions measured only 956 were considered observed on the basis of the criterion $I > 2.7\sigma(I)$ where $\sigma(I) = [N_s + (t_s/t_b)^2 N_b]^{1/2}$ and N_s is the total peak count during the time of scanning t_s , and t_b is the time spent in measuring the N_b background counts. An arbitrary intensity equal to 0.5 times the observable limit was assigned to the non-significant reflexions. All intensities were corrected for Lorentz and polarization effects but not for absorption as $\mu(\text{Mo } K\alpha) = 2.63 \text{ cm}^{-1}$. The structure was solved by the multiresolution tangent refinement method *MULTAN* (Germain, Main & Woolfson, 1971). After conversion of the observed structure factors into normalized structure factor amplitudes $|E|$, 400 reflexions with $|E| > 1.27$ were

† Deceased.

used in the phase-angle-determination procedure; 50 more weak reflexions were also introduced in the calculations to define the figure of merit ψ_0 . The total number of phase relationships found was 11150 of which 4990 were saved.

The E map phased with the phase-angle information derived for the solution with the highest value of ABSFOM and lowest value of RESID yielded the positional parameters of the heavy atoms. The organic skeleton was derived from a subsequent $F(hkl)$ and

$\rho(x,y,z)$ calculation. The positional and isotropic thermal parameters of the non-hydrogen atoms were refined to $R = (\sum |kF_o| - |F_c|) / \sum k|F_o| = 0.14$ by several cycles of block-diagonal least squares minimizing the function $\Delta = \sum w(|F_o| - |F_c|)^2$ according to the program of Immirzi (1967). Atomic scattering factors were calculated from the expression given by Vand, Eiland & Pepinsky (1957) using the values for the parameters given by Moore (1963). Cruickshank's (1965) weighting scheme $1/w = A + B|F_o| + C|F_c|^2$ was adopted, where $A = 2F_o(\text{min})$, $B = 1.0$ and $C = 2/F_o(\text{max})$. After anisotropic refinement the H atoms were introduced in the calculations in fixed positions, their coordinates being defined on stereochemical grounds. Refinement with the assumed B value of 5.0 \AA^2 for all H atoms then converged to $R = 0.082$ for the 956 non-zero reflexions. The final shifts of the atomic parameters were negligible and all well below the corresponding σ .

The final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit are listed in Table 1.*

All calculations were performed on the Univac 1110/20 computer of this Institute using a local program set.

Results and discussion

The molecular and crystal structures of the title compound are displayed in Figs. 1 and 2 (ORTEP; Johnson, 1965). Bond data are reported in Table 2. The structure of (I) is built up of well separated

* Lists of anisotropic thermal parameters of the non-hydrogen atoms and structure factors and an expanded version of Table 3 with references have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36593 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and B_{eq} ($= \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* g_{ij}$) values with estimated standard deviations in parentheses

	x	y	z	B_{eq} (\AA^2)
Cl	0.4972 (2)	0.6408 (3)	-0.1711 (2)	5.17 (9)
P	0.2813 (2)	0.6707 (3)	0.0437 (2)	4.20 (8)
N	0.2125 (7)	0.6242 (8)	0.1201 (5)	4.3 (3)
C(1)	0.3850 (8)	0.7797 (10)	0.0850 (6)	3.8 (3)
C(2)	0.3735 (10)	0.9100 (13)	0.0703 (8)	6.7 (4)
C(3)	0.4544 (11)	0.9946 (12)	0.1038 (8)	6.4 (4)
C(4)	0.5449 (10)	0.9493 (13)	0.1472 (7)	5.8 (4)
C(5)	0.5592 (10)	0.8183 (14)	0.1556 (8)	6.5 (4)
C(6)	0.4766 (10)	0.7355 (12)	0.1284 (8)	5.6 (4)
C(7)	0.2001 (8)	0.7598 (9)	-0.0349 (6)	3.3 (3)
C(8)	0.1007 (9)	0.8013 (13)	-0.0156 (7)	5.2 (4)
C(9)	0.0394 (9)	0.8735 (12)	-0.0765 (8)	5.6 (4)
C(10)	0.0795 (9)	0.9074 (11)	-0.1487 (8)	5.4 (4)
C(11)	0.1761 (10)	0.8632 (11)	-0.1674 (7)	5.2 (4)
C(12)	0.2388 (9)	0.7898 (11)	-0.1108 (7)	5.0 (4)
C(13)	0.3479 (9)	0.5426 (11)	-0.0025 (7)	5.1 (4)
C(14)	0.2788 (8)	0.4304 (11)	-0.0411 (6)	4.3 (3)
C(15)	0.2762 (10)	0.3099 (12)	-0.0040 (7)	5.9 (4)
C(16)	0.2154 (12)	0.2123 (12)	-0.0443 (10)	7.8 (5)
C(17)	0.1554 (10)	0.2344 (11)	-0.1146 (8)	6.1 (4)
C(18)	0.1541 (10)	0.3491 (12)	-0.1544 (7)	5.6 (3)
C(19)	0.2177 (10)	0.4492 (10)	-0.1190 (7)	4.8 (4)
C(20)	0.2055 (11)	0.6985 (13)	0.1980 (9)	6.9 (5)
C(21)	0.2743 (15)	0.6353 (22)	0.2674 (10)	11.5 (8)
C(22)	0.1119 (16)	0.5416 (21)	0.0964 (10)	11.4 (7)
C(23)	0.1014 (21)	0.4405 (18)	0.1413 (12)	13.8 (9)
H(2)	0.302	0.949	0.033	
H(3)	0.446	1.101	0.094	
H(4)	0.602	1.018	0.175	
H(5)	0.637	0.782	0.185	
H(6)	0.486	0.632	0.141	
H(8)	0.074	0.784	0.046	
H(9)	-0.041	0.907	-0.067	
H(10)	0.031	0.972	-0.192	
H(11)	0.200	0.881	-0.231	
H(12)	0.320	0.760	-0.126	
H(131)	0.394	0.582	-0.053	
H(132)	0.408	0.500	0.044	
H(15)	0.325	0.296	0.056	
H(16)	0.215	0.114	-0.015	
H(17)	0.104	0.155	-0.141	
H(18)	0.106	0.363	-0.215	
H(19)	0.220	0.543	-0.151	
H(201)	0.236	0.797	0.191	
H(202)	0.122	0.707	0.215	
H(211)	0.269	0.684	0.325	
H(212)	0.353	0.625	0.250	
H(213)	0.239	0.535	0.274	
H(221)	0.038	0.612	0.098	
H(222)	0.109	0.522	0.027	
H(231)	0.024	0.387	0.120	
H(232)	0.094	0.465	0.206	
H(233)	0.165	0.375	0.135	

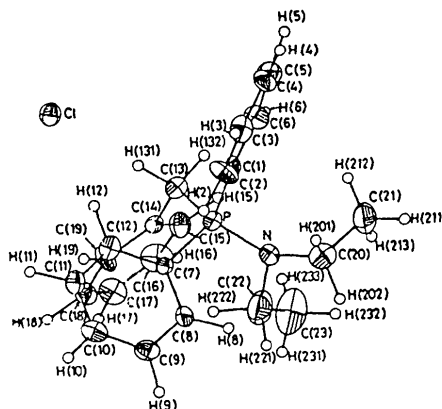


Fig. 1. View of the benzyl(diethylamino)diphenylphosphonium cation and chloride anion in (I), indicating the atom-labelling scheme and 30% probability thermal vibration ellipsoids.

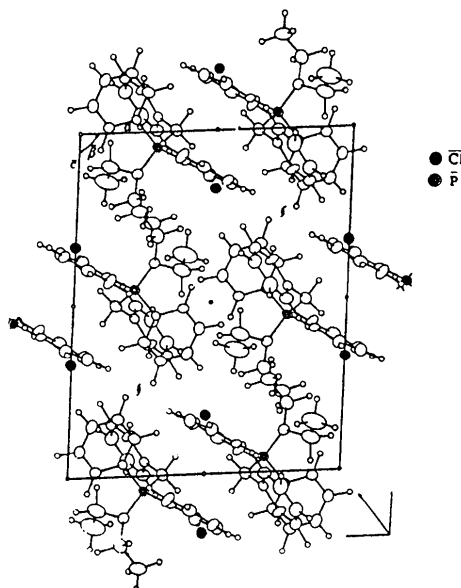


Fig. 2. Packing arrangement of (I) as viewed down the *b* axis of the unit cell.

Table 2. Molecular parameters

Standard deviations are appended as units in the last significant digit.

(a) Bond lengths (Å)		(c) Selected torsion angles (°)	
P—C(1)	1.80 (1)	C(14)—C(13)—P—C(1)	178 (8)
P—C(7)	1.81 (1)	C(14)—C(13)—P—C(7)	-67 (1)
P—C(13)	1.76 (1)	C(14)—C(13)—P—N	59 (1)
P—N	1.63 (1)	C(13)—P—C(1)—C(2)	133 (1)
av. C—C [C(1)...C(6)]	1.377 (11)	C(13)—P—C(1)—C(6)	-44 (1)
av. C—C [C(7)...C(12)]	1.373 (12)	C(13)—P—C(7)—C(8)	140 (1)
av. C—C [C(14)...C(19)]	1.376 (17)	C(13)—P—C(7)—C(12)	-43 (1)
C(13)—C(14)	1.54 (2)	C(13)—P—N—C(20)	141 (1)
N—C(20)	1.48 (2)	C(13)—P—N—C(22)	-69 (1)
N—C(22)	1.54 (2)	P—N—C(20)—C(21)	-104 (1)
C(20)—C(21)	1.50 (2)	P—N—C(22)—C(23)	134 (2)
C(22)—C(23)	1.28 (3)	C(21)—C(20)—N—C(22)	105 (1)
		C(20)—N—C(22)—C(23)	-73 (2)
		P—C(13)—C(14)—C(15)	-107 (1)
		P—C(13)—C(14)—C(19)	75 (1)
(b) Selected bond angles (°)		(d) Most significant non-bonded intramolecular distances (<3.6 Å)	
C(1)—P—C(7)	106.5 (5)	Cl...C(13)	3.56 (1)
C(1)—P—C(13)	105.9 (5)	Cl...H(12)	2.70
C(7)—P—C(13)	110.3 (5)	Cl...H(131)	2.46
N—P—C(1)	108.5 (5)	C(1)...C(12)	3.50 (2)
N—P—C(7)	112.0 (5)	C(1)...C(20)	3.12 (2)
N—P—C(13)	113.3 (5)	C(2)...C(12)	3.46 (2)
P—C(1)—C(2)	119.2 (8)	C(6)...C(13)	3.23 (2)
P—C(1)—C(6)	121.7 (9)	C(6)...N	3.49 (2)
P—C(7)—C(8)	117.9 (8)	C(7)...C(14)	3.54 (2)
P—C(7)—C(12)	120.8 (8)	C(7)...C(19)	3.49 (2)
P—C(13)—C(14)	117.6 (8)	C(7)...C(22)	3.34 (2)
C(13)—C(14)—C(15)	122.4 (9)	C(8)...N	3.09 (2)
C(13)—C(14)—C(19)	119.4 (10)	C(8)...C(22)	3.22 (3)
P—N—C(20)	123.9 (8)	C(12)...C(13)	3.32 (2)
P—N—C(22)	116.7 (8)	C(12)...C(19)	3.53 (2)
N—C(20)—C(21)	109.4 (12)	C(13)...C(22)	3.47 (2)
N—C(22)—C(23)	115.6 (16)	C(14)...N	3.43 (1)
C(20)—N—C(22)	113.0 (10)	C(14)...C(22)	3.37 (2)
		C(15)...C(23)	3.59 (2)
av. C—C—C [C(1),C(2)...C(6)]	119.9 (7)		
av. C—C—C [C(7),C(8)...C(12)]	119.9 (8)		
av. C—C—C [C(14),C(15)...C(19)]	119.8 (9)		

benzyl(diethylamino)diphenylphosphonium and chloride ions. As in the case of related phosphonium salts (Bart, Bassi & Calcaterra, 1980*a,b*, 1981*a,b*; Skapski & Stephens, 1974), the $[(C_6H_5)_2P(CH_2C_6H_5)-N(C_2H_5)_2]^+$ cation shows tetrahedral coordination around the P atom with an average P—C(sp^2) bond length of 1.80 (1) Å and a P—C(sp^3) distance of 1.76 (1) Å; the mean value of the C—P—C bond angles is 107.6° (range 105.9–110.3°). These values are in agreement with literature data concerning organophosphonium ions (Daly, 1970; Corbridge, 1974).

The main structural feature is the P⁺—N bond length of 1.63 (1) Å. Strictly comparable bonds (Table 3)* are only available for very few compounds: $[Me_2NNH-PPh_3]^+ Br^-$, 1.640 (3) Å, (Stödt & Kreher, 1978), $[P_4(NCH_3)_6CH_3]^+ I^-$, 1.65 (1) Å, (Hunt & Cordes, 1974) and the unrefined $[Ph_2P.NEt.P(Et)Ph_2]^+ I^-$, 1.75 (3) Å, (Payne, Mokuolu & Speakman, 1965). With the single-bond radii of P and N of 1.10 and 0.74 Å, respectively (Pauling, 1960), and the Schomaker & Stevenson (1941) electronegativity correction (0.07 Å), the corrected sum of the covalent radii stands at 1.77 Å, as found experimentally [1.769 (19) Å] in the P—N single σ bond of the phosphoramidate anion $NH_3PO_3^-$ (Hobbs, Corbridge & Raistrick, 1953; Cruickshank, 1964). P—N single-bond lengths are sensitive to the oxidation state of phosphorus and to coordination number and nature of the ligands of both atoms; values range from 1.911 (4) Å in a N→P coordinate bond (John, Schmutzler & Sheldrick, 1974) to less than 1.60 Å (Table 3). In P—N compounds with three- rather than four-coordinate N the P—N bond length is intermediate between the pure single-bond length (1.769 Å) and the value observed in phosphazenes (1.52–1.65 Å). Observed bond lengths in five- and six-coordinated P compounds are generally longer than in tetrahedral compounds and three-coordinated P.

The observed shortening of the P—N bond length in (I), as compared to the corrected covalent-radius sum, may be attributed to σ -bond-length variations due to the semi-polar character of the link or to contraction as a result of the difference in covalent radius between an sp^2 and sp^3 N. In addition, a certain degree of π character, *i.e.* donation of electrons from the lone pair of the nitrogen into the P—N bond, is to be considered. There is no direct way of distinguishing these effects. As a matter of fact, as π bonding is always possible when P is bound to an atom containing unpaired electrons, it is difficult to envisage a P—N bond without some multiple-bond character.

The bond-angle distribution around the N atom in (I) shows that hybridization of this atom is intermediate between sp^2 and sp^3 . This is not uncommon as first-row

* An expanded version of Table 3 giving structural data of phosphazenes has been deposited; see previous footnote.

Table 3. *Structural data of a selection of phosphazanes*

The full version of this table has been deposited; see deposition footnote.

Compound ^a	Coordination number ^b		$\langle \text{P-N} \rangle$ (Å)	Reference
	P	N		
(Bu'NPCl) ₂	3	3 pyr., trig.	1.689 (4)	Muir (1975)
[Ph ₂ P.NEt.P(Et)Ph ₂] ⁺ .I ⁻	3	3	1.88 (3)	Payne, Mokuolu & Speakman (1965)
	4	3	1.75 (3)	
[P ₄ (NMe) ₆ Me] ⁺ .I ⁻	3	3	1.71 (3)	Hunt & Cordes (1974)
	4	3	1.65 (1)	
[P ₂ N ₇ H ₁₀ Me ₂] ⁺ .I ⁻	4	3	1.61 (n.d.)	Ziegler (1967)
(Me ₂ NNHPPPh ₃) ⁺ .Br ⁻	4	3	1.640 (3)	Stödt & Kreher (1978)
[Ph ₂ BzPNEt ₂] ⁺ .Cl ⁻	4	3	1.63 (1)	This work
Me ₂ NPF ₂ B ₄ H ₈	4	3	1.593 (6)	Laprade & Nordman (1969)

(a) Abbreviations: Bz, benzyl; Et, ethyl; Me, methyl; Ph, phenyl. (b) The abbreviations 'pyr.' and 'trig.' signify atoms in pyramidal and trigonal environments.

elements tend to show large valence angles when bonded to second-row elements. Deviations from the plane formed by the atoms P, N, C(20) and C(22), represented by the equation $0.6087X - 0.7321Y + 0.3057Z + 2.7555 = 0$ (r.m.s. deviation 0.196 \AA) and referred to the a^* , b , c orthogonal-axis system, are -0.056 , 0.170 , -0.060 and -0.053 \AA , respectively. The stereochemistry of the N atom partly accounts for the spread in the P-N bond distances in phosphazanes, as listed in Table 3. In some species, as in [Bu'NPCl]₂, both pyramidal and planar nitrogen configurations are present (Muir, 1975). When the bonding arrangement of the five-valent tetrahedrally coordinated P is accompanied by sp^3 hybridization at N, chances for multiple bonding are less favourable, although eventually not nil. Namely, the d orbitals which were once thought (Cruickshank, 1961) to be unimportant in π -bond formation (the t_2 orbitals) have subsequently been shown to contribute considerably to such bonds (Bartell, Su & Yow, 1970). Although planarity (*i.e.* sp^2 hybridization) of the N is therefore not essential for π -bond formation (Dewar & Rona, 1969), the considerable flattening of the N pyramid in (I) suggests that the N lone pairs, accommodated in $2p_z$ orbitals, are involved in supplementary π bonding. The partial destruction of sp^3 hybridization of the N orbitals probably effectively increases the energy of the N p orbital to values closer to the relatively higher energy of the P d orbitals

As has emerged from discussions concerning phosphazene compounds (Dewar, Lucken & Whitehead, 1960; Craig & Paddock, 1962; Paddock, 1964) actually two types of mutually perpendicular $p\pi(\text{N})-d\pi(\text{P})$ bonding are eventually active. However, in-plane (PNC) π' bonding, which is of importance in phosphonitrilic compounds and results from overlap of the P d_{xy} and $d_{x^2-y^2}$ orbitals with the third N trigonal orbital, is usually invoked for P-N bond distances below about 1.60 \AA ; this interaction is minimal for a bond angle of 120° , as in the case of (I). Comparison

to Ph₂FP=NMe [P-N $1.641(2) \text{ \AA}$] (Adamson & Bart, 1970) lends support to the view that overlap between the N p_z orbital and P d_{xz} orbital (x axis along P-N bond, z axis perpendicular to PNC plane) is quite effective in (I). This also appears from the fact that according to a calculation of the $p\pi-d\pi$ -overlap integral (Hoard & Jacobson, 1966) maximum overlap is found at a P-N distance of 1.635 \AA , close to the experimentally observed value in the present work. It also appears that overlap between the d orbitals on P with the p orbitals on a second atom increases with increasing charge on P, leading to contraction and stabilization of d orbitals which are normally too diffuse for bonding (Craig, Maccoll, Nyholm, Orgel & Sutton, 1954). Involvement of d orbitals is also enhanced under the action of highly electronegative substituent groups. Although it is not easy to estimate the contribution of π bonding, the following tentative scale of double-bond character: 50%, $1.56-1.60 \text{ \AA}$ (Paddock, 1964; Ansell & Bullen, 1968; Wagner & Vos, 1968); 40-50%, 1.604 \AA (Bullen & Dann, 1973); 30%, 1.646 \AA (Bullen, Stephens & Wade, 1969); 25%, 1.68 \AA (Olthof, Migchelsen & Vos, 1965; Ansell & Bullen, 1968); 15%, 1.695 \AA (Casabianca, Cotton, Riess, Rice & Stults, 1978) and 0%, 1.769 \AA (Cruickshank, 1964), attributes some 30-40% multiple bonding to the P-N link in benzyl(diethylamino)diphenylphosphonium chloride.

The phenyl C-C bond lengths are unremarkable [av. $1.376(8) \text{ \AA}$; range $1.32-1.42 \text{ \AA}$]; the mean value of the endocyclic bond angles is $119.9(4)^\circ$ (range $117.4-122.7^\circ$). Bond data for the diethylamino residue are inaccurate as a result of disorder in this part of the structure. The N-C(22) bond length (1.54 \AA) deviates from the standard paraffinic single C-N bond length for four- and three-covalent N [$1.479(5)$ and $1.472(5) \text{ \AA}$, respectively], probably as a result of the high thermal motion or disorder in this part of the structure. The nature of this structural effect has not been investigated further. The conformation of the

phosphonium cations may be described in terms of torsional angles around the P–C(sp^3) bonds. The P–C(sp^2) and P–N bonds are in nearly *staggered* conformation (*gauche* +, *gauche* –, and *trans*) with the C(sp^3)–C(sp^2) bond of the benzyl residue. Analogous geometries have been found for the benzyltriphenylphosphonium cation with average C(sp^2)–C(sp^3)–P–C(sp^2) torsional angles of 64 (5), –57 (4) and 184 (4)° (Bart, Bassi & Calcaterra, 1980*a,b*, 1981*a*). The orientations of the phenyl groups and diethylamino residue, expressed by the torsional angles around the P–C(sp^2) and P–N bonds in respect of the P–C(sp^3) bonds, are intermediate between *staggered* and *eclipsed*. No abnormally short non-bonded intramolecular distances were noted. The most significant of these distances are listed in Table 2.

The arrangement of the ions in the unit cell (Fig. 2) suggests that the observed disorder of the diethylamino residues [especially C(22) and C(23)] may arise from packing requirements. The shortest van der Waals distances for Cl...C, Cl...H, C...C, C...H and H...H amount to 3.77, 2.70, 3.48, 2.58 and 2.13 Å, respectively. The shortest C...H contact is quite short, although it is noticed that Hanson (1968) has reported distances between methyl groups of adjacent molecules to be as small as 3.13 Å.

References

- ADAMSON, G. W. & BART, J. C. J. (1970). *J. Chem. Soc. A*, pp. 1452–1456.
- ANSELL, G. B. & BULLEN, G. J. (1968). *J. Chem. Soc. A*, pp. 3026–3036.
- BART, J. C. J., BASSI, I. W. & CALCATERRA, M. (1980*a*). *J. Organomet. Chem.* **193**, 1–12.
- BART, J. C. J., BASSI, I. W. & CALCATERRA, M. (1980*b*). *Acta Cryst.* **B36**, 2616–2623.
- BART, J. C. J., BASSI, I. W. & CALCATERRA, M. (1981*a*). *Phosphorus Sulfur*, **9**, 347–355.
- BART, J. C. J., BASSI, I. W. & CALCATERRA, M. (1981*b*). *Inorg. Chim. Acta*, **57**, 261–268.
- BARTELL, L. S., SU, L. S. & YOW, H. (1970). *Inorg. Chem.* **9**, 1903–1912.
- BULLEN, G. J. & DANN, P. E. (1973). *Acta Cryst.* **B29**, 331–337.
- BULLEN, G. J., STEPHENS, F. S. & WADE, R. J. (1969). *J. Chem. Soc. A*, pp. 1804–1812.
- CASABIANCA, F., COTTON, F. A., RIESS, J. G., RICE, C. E. & STULTS, B. R. (1978). *Inorg. Chem.* **17**, 3232–3236.
- CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*. Amsterdam: Elsevier.
- CRAIG, D. P., MACCOLL, A., NYHOLM, R. S., ORGEL, L. E. & SUTTON, L. E. (1954). *J. Chem. Soc.* pp. 332–353.
- CRAIG, D. P. & PADDOCK, N. L. (1962). *J. Chem. Soc.* pp. 4118–4133.
- CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
- CRUICKSHANK, D. W. J. (1964). *Acta Cryst.* **17**, 671–672.
- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, ch. 14. Oxford: Pergamon Press.
- DALY, J. J. (1970). *Perspectives in Structural Chemistry*, edited by J. D. DUNITZ & J. A. IBERS, Vol. III, pp. 165–228. New York: John Wiley.
- DEWAR, M. J. S., LUCKEN, E. A. C. & WHITEHEAD, M. A. (1960). *J. Chem. Soc.* pp. 2423–2429.
- DEWAR, M. J. S. & RONA, P. (1969). *J. Am. Chem. Soc.* **91**, 2259–2264.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HANSON, A. W. (1968). *Acta Cryst.* **B24**, 1084–1096.
- HOARD, L. G. & JACOBSON, R. A. (1966). *J. Chem. Soc. A*, pp. 1203–1207.
- HOBBS, E., CORBRIDGE, D. E. C. & RAISTRICK, B. (1953). *Acta Cryst.* **6**, 621–626.
- HUNT, G. W. & CORDES, A. W. (1974). *Inorg. Chem.* **13**, 1688–1690.
- IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–749.
- JOHN, K. P., SCHMUTZLER, R. & SHELDRIK, W. S. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1841–1846.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LAPRADE, M. D. & NORDMAN, C. E. (1969). *Inorg. Chem.* **8**, 1669–1673.
- MOGGI, G. & MANCINI, L. (1977). *Ital. Pat. Appl.* LI 2526/77 (to Montedison).
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.
- MUIR, K. W. (1975). *J. Chem. Soc. Dalton Trans.* pp. 259–262.
- OLTHOF, R., MIGCHELSEN, T. & VOS, A. (1965). *Acta Cryst.* **19**, 596–603.
- PADDOCK, N. L. (1964). *Q. Rev. Chem. Soc.* **18**, 168–210.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 224–229. Ithaca: Cornell Univ. Press.
- PAYNE, D. S., MOKUOLU, J. A. A. & SPEAKMAN, J. C. (1965). *Chem. Commun.* p. 599.
- SCHOMAKER, V. & STEVENSON, D. P. (1941). *J. Am. Chem. Soc.* **63**, 37–40.
- SKAPSKI, A. C. & STEPHENS, F. A. (1974). *J. Cryst. Mol. Struct.* **4**, 77–85.
- STÖLDT, E. & KREHER, R. (1978). *Chem. Ber.* **111**, 2037–2046.
- VAND, V., EILAND, P. E. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303–306.
- WAGNER, A. J. & VOS, A. (1968). *Acta Cryst.* **B24**, 707–713.
- ZIEGLER, M. (1967). *Angew. Chem.* **79**, 322.