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The Structure of a Crowded Zwitterion, $[(C_6H_5)_3P^+][H_3COOC]CC[COOCH_3][N(C_6H_4Cl)(NCN^-)]$, Derived from Triphenylphosphine

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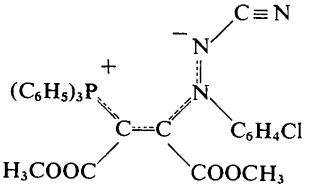
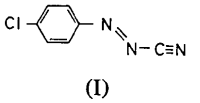
The molecular formula of the zwitterion produced by the reaction of $(C_6H_5)_3PO$ with *p*-$Cl(C_6H_4)NNCN$ and dimethyl acetylenedicarboxylate has been established to be



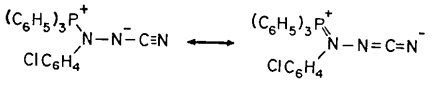
by means of an X-ray diffraction analysis of a single crystal. Although steric interactions cause a large out-of-plane torsion in the PCCNN chain, the bond lengths in the chain have values between single and double bonds. Even with a torsion of 37° in the central C–C bond, the $P^+\cdots N^-$ separation is only 2·88 Å. The methyl ester group near the P atom is approximately coplanar with the PCC moiety whereas the other methyl ester group is rotated by 69°. The material crystallizes in space group $P\bar{1}$ with $a=11{\cdot}868$ (±0·002), $b=12{\cdot}584$ (±0·003), $c=11{\cdot}682$ (±0·002) Å, $\alpha=110{\cdot}20$ (±0·02), $\beta=117{\cdot}74$ (±0·01) and $\gamma=68{\cdot}55$ (±0·02)°. The structure was solved by the symbolic addition procedure and refined to $R=6{\cdot}5\%$.

Introduction

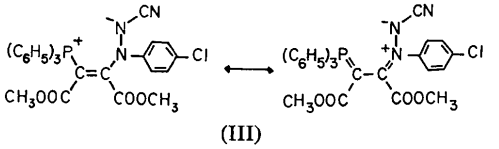
Triphenylphosphine oxide, $(C_6H_5)_3PO$, combines with 4-chlorobenzene *anti*-diazocyanide (I) to form a zwitterionic betaine (II), whose crystals are stable for only a few hours at 20°C. Dimethyl acetylenedicarboxylate reacts with (II) to give a stable derivative (III).



(I)

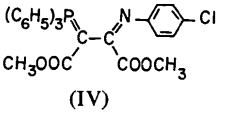


(II)



(III)

The structural formula of derivative (III) was determined by an X-ray diffraction analysis and reported by Huisgen, Brunn, Gilardi & Karle (1969). A full refinement of the structure of (III) is now complete and is reported in this paper. Molecule (III) corresponds in many details to a molecule (IV) whose crystal structure was determined by Mak & Trotter (1965).



(IV)

The addition of the electron-withdrawing chromophore (–N–C≡N) to (IV) results in the zwitterion (III), with electron delocalization occurring along the chain connecting the charge centers (the phosphorus atom and the diazo group). The addition of this group also adds to the crowding in the C(19)–C(20) region.

Experimental

The crystals used in this analysis were provided by Professor Rolf Huisgen of the Institute for Organic Chemistry, University of Munich. Crystal data are reported in Table 1. The cell parameters are derived from a least-squares fit of the angular (diffractometer) coordinates for 12 reflections. The intensity data were collected on a four-circle automatic diffractometer using the θ, 2θ scan technique with a $2{\cdot}0°+2\theta(\alpha_2)-2\theta(\alpha_1)$ scan over 2θ. The background was counted for 10 sec at each end of the scan. The intensities were corrected for Lorentz and polarization factors and normalized structure factors $|E|$ were derived.

Table 1. *Physical data*

Molecular formula	$C_{31}H_{25}ClN_3O_4P$
Molecular weight	569·99
Habit	Stout prisms
Color	Orange, transparent
Dimensions	0·25 × 0·20 × 0·15 mm
Space Group	$P\bar{1}$
Z	2
a	11·868 (2) Å
b	12·584 (3)
c	11·682 (2)
α	110·20 (2)°
β	117·74 (1)
γ	68·55 (2)
Volume	1402·4 Å^3
Density, calculated	1·350 g.cm^{-3}
Density, measured	1·34
Radiation	Cu $K\alpha$, Ni-filtered, 1·54178 Å
Linear absorption coeff., μ	20·77 cm^{-1}
No. independent reflections observed	4577

Phases were derived directly from the normalized structure factor magnitudes using the symbolic addition procedure (Karle & Karle, 1966). The procedure was initiated assuming the space group to be $P\bar{1}$, and three reflections were given symbolic phases. The criterion $P_+(\mathbf{h}) > 0{\cdot}95$ was used in assigning phases, where $P_+(\mathbf{h})$ is the probability that the sign associated with $E_{\mathbf{h}}$ is positive. After 29 signs had been determined correctly, an incorrect sign was obtained. As a consequence, 26 of the first 67 signs determined were incorrect. This gave rise to E maps which did not contain the entire structure. In one E map, however, a partial structure of the triphenylphosphine group was discerned. This partial structure was used as a basis for phasing by changing to the noncentric space group, $P1$, and using the tangent formula in the manner described by Karle (1968). The two molecules of the unit cell were thus developed in $P1$; a center of symmetry

Table 2. *Fractional coordinates and thermal parameters with standard deviations in parentheses*

	x	y	z	B 11	B 22	B 33	B 12	B 13	B 23
PHOS	0.2318(1)	0.3010(1)	0.7845(1)	2.69(5)	2.10(5)	1.92(5)	-0.50(4)	0.91(4)	0.25(4)
C(1)	0.0812(4)	0.3983(4)	0.7970(4)	2.92(17)	2.83(17)	2.37(17)	-0.51(14)	1.24(14)	0.51(14)
C(2)	-0.0055(5)	0.3478(4)	0.7973(5)	3.81(21)	3.93(21)	2.84(21)	-0.85(17)	1.32(17)	0.60(17)
C(3)	-0.1207(5)	0.4197(5)	0.8170(5)	3.74(24)	4.74(24)	3.88(24)	-0.24(19)	2.02(20)	1.12(19)
C(4)	-0.1478(6)	0.5402(5)	0.8357(6)	3.86(25)	4.55(25)	3.79(25)	0.05(20)	1.72(20)	1.10(20)
C(5)	-0.0626(5)	0.5896(5)	0.8316(5)	4.55(23)	3.56(23)	3.74(23)	-0.04(19)	1.97(19)	0.75(19)
C(6)	0.0511(5)	0.5194(4)	0.8119(5)	3.56(20)	2.69(20)	2.98(20)	-0.02(16)	1.43(16)	0.53(16)
C(7)	0.2693(4)	0.3232(3)	0.6625(4)	3.26(16)	2.74(16)	2.57(16)	-0.85(13)	1.36(13)	0.27(13)
C(8)	0.1935(4)	0.4132(4)	0.5934(4)	4.54(18)	3.10(18)	2.52(18)	-1.17(15)	1.19(15)	0.49(15)
C(9)	0.2318(5)	0.4286(4)	0.5058(5)	5.37(22)	4.66(22)	3.21(22)	-1.82(18)	1.78(18)	0.67(18)
C(10)	0.3433(6)	0.3534(5)	0.4843(6)	6.02(25)	6.03(25)	4.18(26)	-2.22(21)	2.56(21)	0.62(20)
C(11)	0.4183(5)	0.2620(5)	0.5522(6)	5.41(25)	5.70(25)	4.90(25)	-1.37(20)	3.20(21)	0.86(20)
C(12)	0.3819(5)	0.2480(4)	0.6420(5)	4.05(21)	4.31(21)	3.99(21)	-0.98(17)	2.07(17)	0.62(17)
C(13)	0.3676(4)	0.3380(3)	0.9387(4)	3.62(17)	3.20(17)	2.48(17)	-1.06(13)	1.17(14)	0.43(13)
C(14)	0.3581(4)	0.4513(4)	1.0149(5)	4.67(20)	3.73(20)	3.25(20)	-1.63(16)	1.27(16)	0.20(16)
C(15)	0.4662(5)	0.4800(5)	1.1279(5)	5.81(25)	5.14(25)	3.63(25)	-2.77(20)	0.78(21)	0.09(20)
C(16)	0.5838(5)	0.3942(5)	1.1638(6)	4.82(26)	6.07(26)	4.19(26)	-2.47(21)	0.46(21)	1.51(21)
C(17)	0.5935(5)	0.2811(5)	1.0896(5)	3.64(23)	5.77(24)	4.33(23)	-1.64(19)	0.48(19)	1.65(19)
C(18)	0.4858(5)	0.2533(4)	0.9764(5)	3.34(20)	4.31(20)	3.85(20)	-0.86(16)	0.94(16)	1.01(16)
C(19)	0.2427(4)	0.1522(4)	0.7568(4)	3.13(16)	2.28(17)	2.63(17)	-0.44(13)	1.16(14)	0.51(13)
C(20)	0.2248(4)	0.0784(4)	0.6296(4)	2.80(17)	2.52(17)	2.36(17)	-0.42(13)	0.90(14)	0.50(13)
N(21)	0.1392(4)	0.1107(4)	0.5176(4)	3.17(17)	2.19(17)	2.24(17)	-0.63(14)	0.97(14)	0.21(14)
C(22)	0.1365(5)	0.0399(4)	0.3899(5)	3.06(20)	2.37(20)	2.46(20)	-0.24(16)	1.16(17)	0.45(16)
C(23)	0.2440(6)	0.0111(5)	0.3589(6)	3.43(25)	4.12(25)	3.40(25)	-0.47(20)	1.57(20)	0.72(20)
C(24)	0.2407(6)	-0.0597(6)	0.2355(6)	4.61(28)	4.76(28)	3.37(28)	-0.89(22)	1.86(23)	0.37(23)
C(25)	0.1269(6)	-0.0950(5)	0.1460(6)	5.21(26)	3.18(26)	2.78(26)	-0.79(21)	1.92(22)	0.09(21)
C(26)	0.0171(6)	-0.0632(5)	0.1757(6)	4.30(25)	3.87(25)	3.33(25)	-1.43(20)	1.65(21)	0.18(20)
C(27)	0.0222(5)	0.0050(5)	0.2992(5)	3.75(23)	3.15(22)	2.89(23)	-1.22(18)	1.25(19)	0.17(18)
C(28)	0.2830(4)	0.0970(4)	0.8640(4)	3.34(18)	2.93(19)	2.44(18)	-0.56(15)	1.06(15)	0.69(15)
O(29)	0.3157(4)	-0.0078(3)	0.8575(4)	5.54(16)	2.71(17)	3.61(16)	-0.42(13)	1.86(13)	1.13(13)
O(30)	0.2747(3)	0.1750(3)	0.9749(3)	3.90(14)	3.07(14)	2.39(14)	-0.48(11)	1.22(11)	0.71(11)
C(31)	0.3347(6)	0.1291(5)	1.0938(6)	5.99(28)	5.45(28)	2.50(29)	-0.19(23)	1.21(23)	1.91(23)
C(32)	0.3044(4)	-0.0468(4)	0.6169(4)	3.62(19)	2.72(18)	2.53(18)	-0.37(15)	1.24(15)	0.57(14)
O(33)	0.4218(3)	-0.0737(3)	0.6440(3)	3.31(16)	3.66(14)	3.51(15)	-0.11(12)	1.24(12)	0.89(12)
O(34)	0.2289(3)	-0.1201(3)	0.5681(3)	4.05(14)	2.43(14)	3.68(14)	-0.66(11)	1.58(11)	0.39(11)
C(35)	0.2934(6)	-0.2443(5)	0.5508(6)	6.43(28)	2.04(28)	7.22(28)	-0.11(22)	3.75(23)	0.58(23)
N(36)	0.0471(4)	0.2188(4)	0.5267(4)	3.15(19)	2.58(19)	2.70(19)	-0.22(15)	0.98(15)	0.51(15)
C(37)	-0.0120(5)	0.2587(5)	0.4173(5)	3.35(23)	2.43(23)	3.49(24)	-0.38(18)	1.13(20)	0.45(19)
N(38)	-0.0745(5)	0.3025(5)	0.3268(6)	5.11(25)	3.43(25)	4.14(26)	-0.13(20)	1.17(22)	1.49(21)
CLOR	0.1199(2)	-0.1792(1)	-0.0088(1)	8.38(9)	5.82(7)	3.47(5)	-2.40(7)	3.38(6)	-1.21(5)
H(2)	0.014	0.261	0.784						
H(3)	-0.143	0.384	0.817						
H(4)	-0.228	0.591	0.852						
H(5)	-0.084	0.676	0.843						
H(6)	0.111	0.555	0.808						
H(8)	0.112	0.466	0.607						
H(9)	0.179	0.494	0.458						
H(10)	0.370	0.365	0.420						
H(11)	0.498	0.207	0.536						
H(12)	0.436	0.184	0.692						
H(14)	0.274	0.512	0.984						
H(15)	0.460	0.561	1.183						
H(16)	0.661	0.415	1.244						
H(17)	0.677	0.219	1.117						
H(18)	0.494	0.172	0.922						
H(23)	0.324	0.040	0.423						
H(24)	0.319	-0.085	0.211						
H(26)	-0.065	-0.089	0.110						
H(27)	-0.056	0.029	0.323						
H(31)	0.431	0.094	1.114						
H(31)	0.292	0.068	1.080						
H(31)	0.323	0.194	1.170						
H(35)	0.360	-0.263	0.638						
H(35)	0.338	-0.265	0.489						
H(35)	0.226	-0.290	0.514						

The thermal parameters are of the form $T = \exp\left[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right]$.

The B_{ij}'s are in Å^2 units.

Hydrogen atoms were assigned the same anisotropic thermal parameters as the adjacent carbon atom.

was then apparent, and the origin was appropriately shifted.

It was determined that if four symbols had been used instead of three, the determination could have proceeded satisfactorily with the more restrictive criterion, $P_+(\mathbf{h}) > 0{\cdot}975$. All of the interactions satisfying

Table 3. *Observed and calculated structure factors for* $C_{31}H_{25}ClN_3O_4P$

The columns are the index k, $|F_o| \times 10$, and $F_c \times 10$.

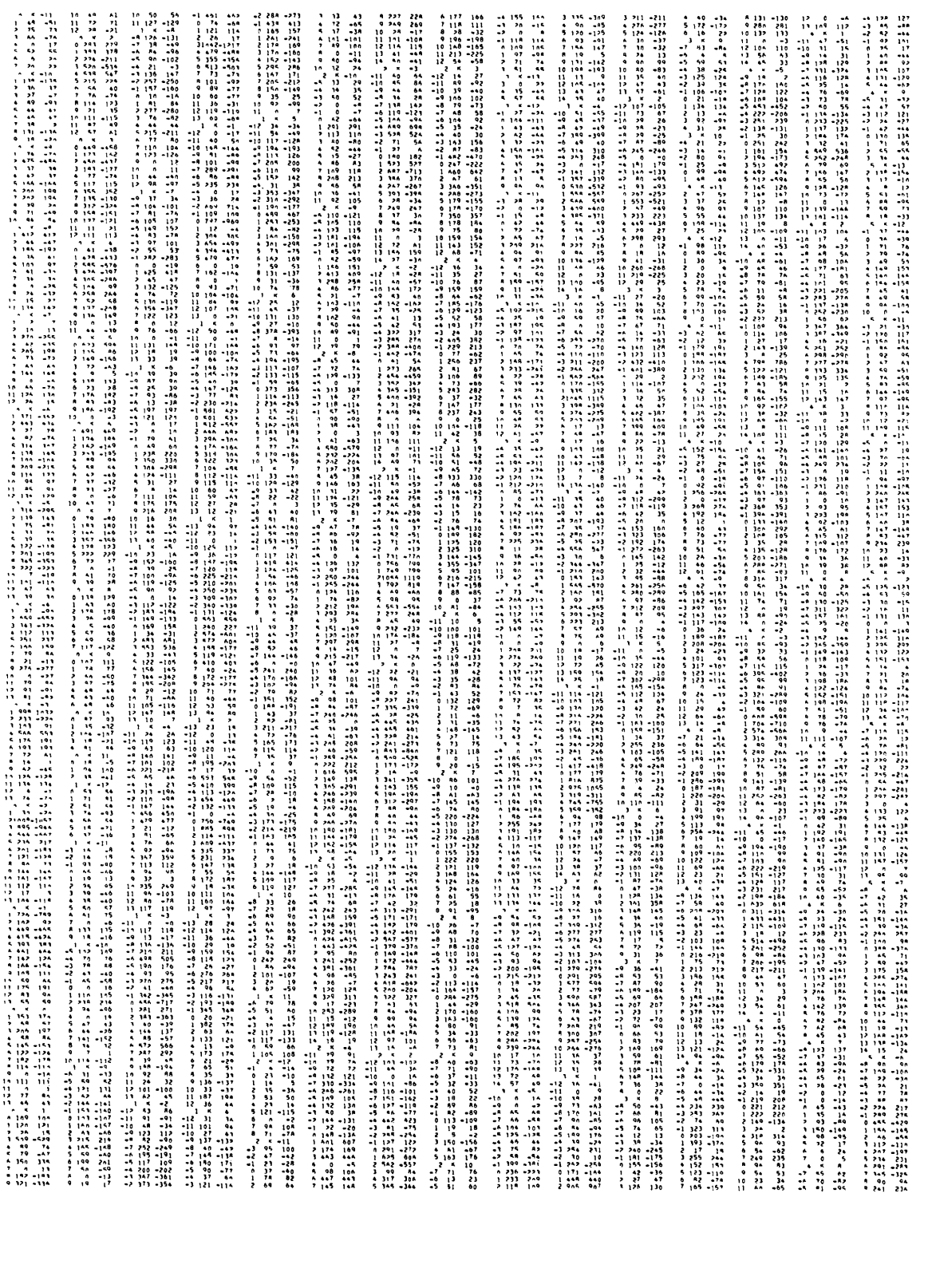
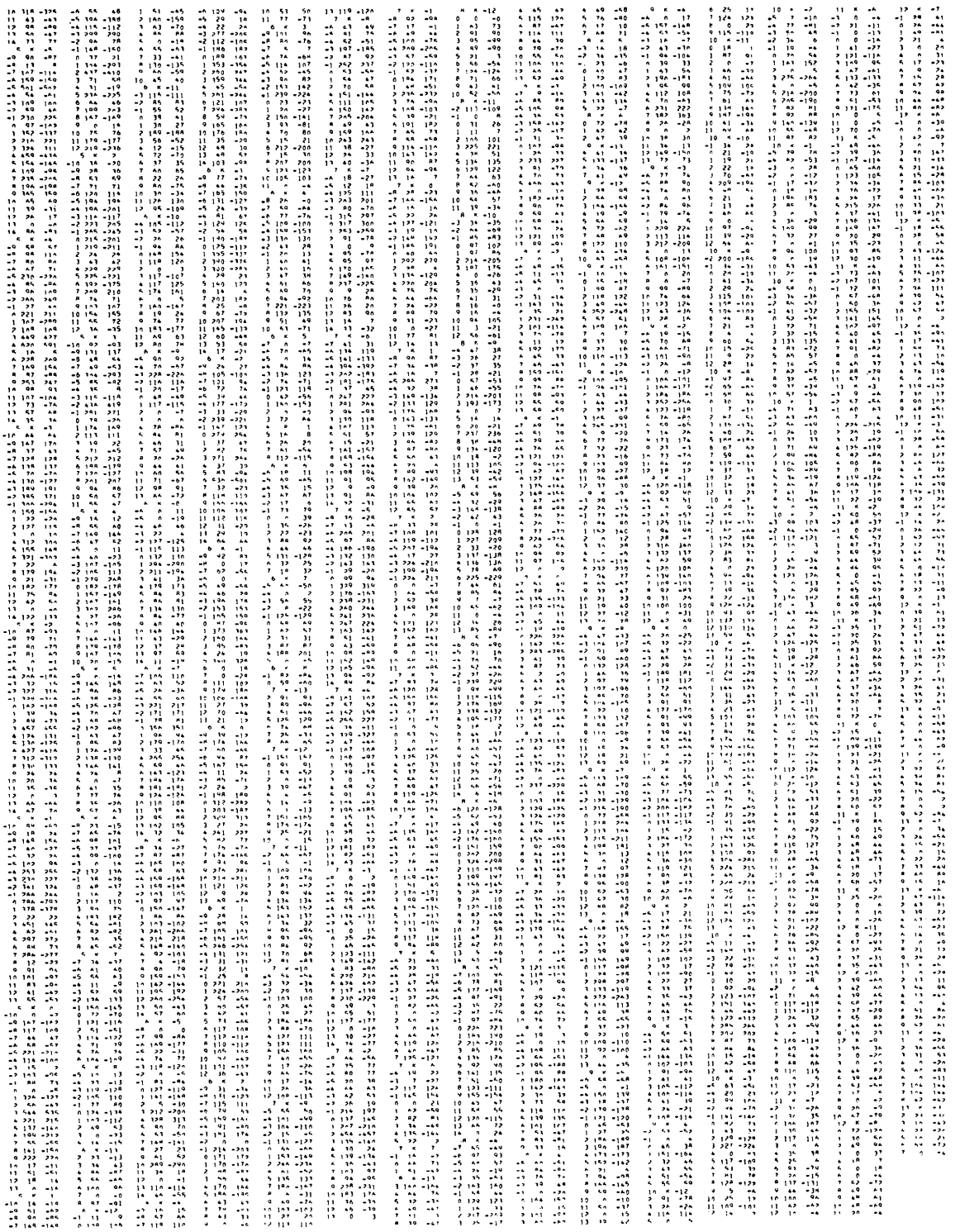


Table 3 (*cont.*)



this criterion were valid, and a set of more than 100 phases could be obtained without any errors; this set leads to a direct, full structure determination in $P\bar{1}$. The solution is also trivial if the modified $B_{3,0}$ formula (Karle, 1970) is used; if all of the interactions for which $P_+(\mathbf{h}) > 0{\cdot}90$ are examined, the cosine invariants of three are negative; the modified $B_{3,0}$ formula identifies these three atypical relationships. One of these three

interactions was the one which led the initial phase determination astray.

The coordinates and thermal parameters of the 40 non-hydrogen atoms were refined using the full-matrix least-squares refinement program of Busing, Martin & Levy (1962). The quantity minimized was $\sum w(|F_o|-|F_c|)^2$. Relative weights were assigned according to the formula $1/w=1{\cdot}0+(|F_o|/25)^2$, which was derived from a statistical examination of the discrepancies. Isotropic refinement led to an R value of 0·14. In order to perform an anisotropic refinement on the 40 heavier atoms, it was necessary that the refinement be carried out in large blocks. Twelve atoms were refined each time, and the chlorine atom, for which anisotropic vibration was apparent, was included in each cycle of partial refinement. The R value calculated for *all* data decreased to 0·095. At this stage, most of the hydrogen atoms were not sharply indicated by a difference map. However, the positions of all the hydrogen atoms could be predicted with little change of major error. Assuming a bond length of 1·0 Å and tetrahedral or trigonal geometry, hydrogen atom positions were calculated and added to the list of atomic parameters and assigned the same anisotropic thermal factor as the adjacent carbon atom. This addition, with no further refinement, led to an R value of 0·065 based on all 4577 data. The observed and calculated structure factors are listed in Table 3 and the atomic parameters of the atoms are listed in Table 2.

Discussion

The configuration of molecule (III) is shown in the stereodiagram, Fig. 1. Structural diagrams (III*a*) and (III*b*) imply that the chain connecting the phosphorus atom and the cyanamide anion should exhibit bond distances between normal single and double bond values. If the electron delocalization occurs to a significant extent, the chain would also be expected to be planar or nearly planar. Even though steric interactions cause a large out-of-plane torsion in the chain, it is evident that the bond lengths are affected by delocalization (see Fig. 2). The P–C(19) distance of 1·753 (8) Å is between the predicted P–C single and double bond values of 1·87 and 1·67 Å (Pauling, 1960); the adjacent C(19)–C(20) and C(20)–N(21) bonds also have lengths which are between the expected single and double bond values for

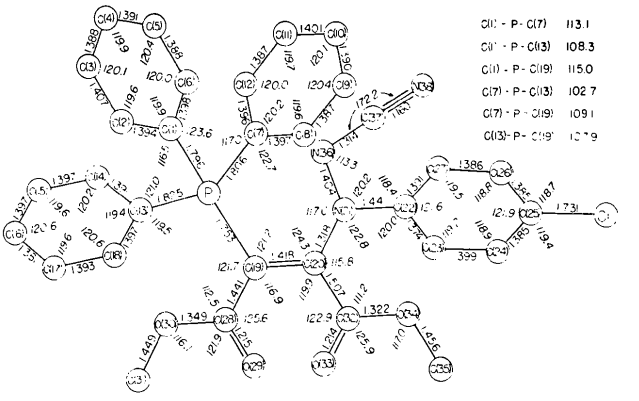


Fig. 2. Bond lengths, angles, and the numbering scheme presented on a schematic drawing of the zwitterion. Estimated standard deviations are 0·005 Å for the P–C distances and are from 0·007 to 0·009 Å for other distances. Angular standard deviations range from 0·4 to 0·7°.

C–C and C–N. There is a torsion of 37° about the C(19)–C(20) bond. This rotation can relieve nonbonded repulsions between the P atom and the two N atoms, N(21) and N(36). The P···N(36) distance in this molecule is only 2·88 Å, whereas the van der Waals separation for P···N is estimated to be about 3·4 Å. The P···N(21) distance is somewhat longer, 3·20 Å. Other short intramolecular distances in (III) are listed in Table 5. In the similar but less crowded molecule (IV), the torsion about the bond equivalent to C(19)–C(20) in (III) is 15·5° (calculated from the coordinates of Mak & Trotter, 1965).

Table 4. *Torsion angles*

P–C(19)–C(20)–N(21)	−37·1°
C(19)–C(20)–N(21)–N(36)	−10·2
C(20)–N(21)–N(36)–C(37)	+163·8
C(7)–P–C(19)–C(20)	−25·1
C(13)–P–C(19)–C(20)	−136·0
C(1)–P–C(19)–C(20)	103·1
C(20)–C(19)–C(28)–C(29)	+8·0
C(19)–C(20)–C(32)–C(33)	−69·3
C(19)–C(28)–O(30)–C(31)	−169·5
C(20)–C(32)–O(34)–C(35)	−179·9
C(20)–N(21)–C(22)–C(23)	−60·8

The methyl ester group containing O(29) is approximately coplanar with the PC(19)C(20) moiety with a

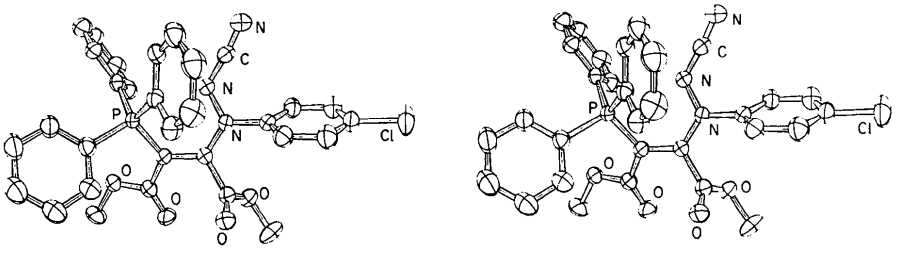


Fig. 1. A stereo-illustration of the zwitterion.

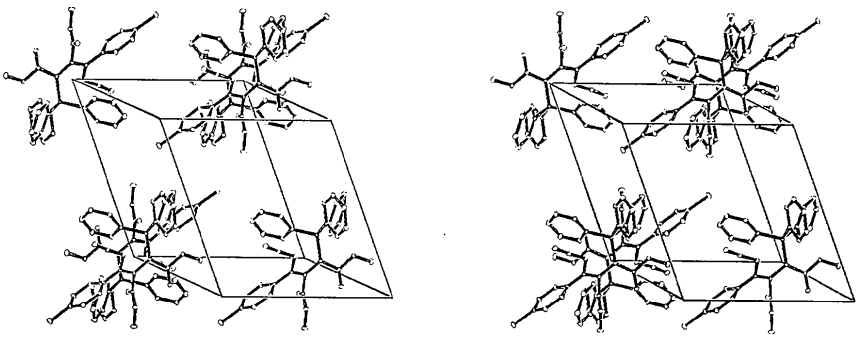


Fig. 3. A stereo packing diagram. Two centrosymmetric pairs of molecules are shown, and also two isolated molecules. A unit cell is superimposed with **c** horizontal, **b** almost vertical, and **a** directed into the paper.

twist of only 8° about the C(19)–C(28) bond, while the methyl ester group containing O(33) is rotated by −69° about the C(20)–C(32) bond, Table 4. The twist of one of the methyl ester groups results in a separation of 3·03 Å between O(29) and O(33). The loss of conjugation occasioned by the large twist of the methyl ester containing O(33) is reflected in the difference between the C(19)–C(28) distance of 1·441 Å and the C(20)–C(32) distance of 1·507 Å. A similar twist of one of the methyl ester groups occurs also in molecule IV.

Table 5. *Short intramolecular distances*

The distances listed are between atoms which are separated by at least two intervening bonded atoms.

	Separation (Å)	Van der Waals approach (Å)
P·····N(36)	2·88	3·4
P·····O(30)	2·92	3·3
P·····N(21)	3·20	3·4
N(36)···C(19)	2·76	3·2
N(36)···C(7)	2·90	3·2
C(23)···C(32)	3·04	3·4
C(23)···C(20)	3·07	3·4
C(13)···O(30)	2·88	3·1

Molecules (III) and (IV) differ in comparable bond lengths occurring along the P···N(38) chain. These differences are qualitatively consistent with the different structural formulae, (III*a*+III*b*) and (IV). However, no individual difference can be considered significant when compared with the relatively large combined standard deviations (±0·04 or ±0·05 Å). The standard deviations quoted in this determination (see Fig. 2) are derived from the estimated atomic positional standard deviations calculated during the last refinement cycle for that atom. An independent check on their magnitude is available from the large number of chemically equivalent bonds. If the 24 carbon–carbon bonds of the four benzene rings are considered equivalent, the distribution of their distances indicates $\langle r_{CC}\rangle = 1{\cdot}392$ Å and $\sigma_r = 0{\cdot}007$ Å. The σ_r values estimated from the least-squares calculations range from 0·007 to 0·009 Å for the benzene ring distances.

The packing in the crystal is shown in Fig. 3. As can be seen from Table 6, the closest intermolecular approaches are of the same magnitude as van der Waals separations.

Table 6. *Nearest intermolecular distances*

	Separation	Van der Waals approach
C(6)····N(38″)	3·33 Å	3·2 Å
C(8)····N(38)″	3·30	3·2
Cl·····N(38′)	3·35	3·3
Cl·····C(26′)	3·64	3·5
Cl·····C(17‴)	3·61	3·5
C(11)···O(33‴)	3·38	3·1
C(17)···O(29‴)	3·39	3·1
C(31)···O(33‴)	3·16	3·3
C(35)···C(37′)	3·60	3·6

The parameters of the atoms in this table are related to the parameters listed in Table 2 by the transformations:

′	$-x, -y, -z$
″	$-x, 1{\cdot}0-y, 1{\cdot}0-z$
‴	$1{\cdot}0-x, -y, 1{\cdot}0-z$

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