shortening of the terminal bonds by some 0·04 Å might be explained by a localization of electronic charge at the two ends of the Se$_5^{2-}$ chain. The covalent radii of Se and Br differ by about this, and Se$^-$ is isoelectronic with Br. Our results do not conflict with this interpretation. Whereas the two terminal angles, Se(1)—Se(2)—Se(3) and Se(3)—Se(4)—Se(5), in [PPh$_4$]$_2$[Se$_5$] are very similar to those found in the other Se$_5^{2-}$ units (Table 3), the internal Se(2)—Se(3)—Se(4) angle, 110·59 (7)°, is at least 4° larger than that found in Rb$_2$Se$_5$, 104·5 (6) (Böttcher, 1979), Cs$_2$Se$_5$, 104·6 (4) (Kretschmann & Böttcher, 1985), [Cs(18-crown-6)]$_2$[Se$_5$], 106·6 (2) (Brese, Randall & Ibers, 1987), Fe$_2$Se$_2$(Se$_5$)$_2^{2-}$, 103·35 (7) (Strasdeit, Krebs & Henkel, 1984), and V$_2$Se$_{13}^{2-}$, 103·4 (1)° (Chau, Wardle & Ibers, 1987). The torsional angles in the present Se$_5^{2-}$ chain are 77·32 (8) and 89·16 (7)°. These are different from those of 75·0 and 67·1° found in Rb$_2$Se$_5$ (Böttcher, 1979).

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trans-2-Dimethylamino-3-*p*-nitrophenyl-1,4-diphenyl-3,4-dihydro-1-azetium Perchlorate

By Peter F. Lindley and Adrial R. Walton

Department of Crystallography, Birkbeck College, Malet St, London WC1E 7HX, England

and Gerhard V. Boyd and George A. Nicolaou

Department of Chemistry, King's College, Campden Hill, London W8 7AH, England

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Abstract. C$_{23}$H$_{22}$N$_3$O$_2^+$.ClO$_4^-$, $M_r = 471{\cdot}4$, triclinic, $P\bar{1}$, $a = 8{\cdot}168\ (6)$, $b = 8{\cdot}644\ (6)$, $c = 16{\cdot}609\ (12)$ Å, $\alpha = 100{\cdot}03\ (4)$, $\beta = 92{\cdot}58\ (3)$, $\gamma = 101{\cdot}40\ (3)°$, $U = 1128\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}388$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}70926$ Å, $\mu = 0{\cdot}170$ mm^{-1}, $F(000) = 492$, $T = 293\ (1)$ K, $R(F) = 0{\cdot}083$ for 3903 significant reflections. Within the planar four-membered ring the bond lengths are N(1)—C(2) 1·329 (7), C(2)—C(3) 1·508 (15), C(3)—C(4) 1·507 (8) and C(4)—N(1) 1·463 (14) Å. The exocyclic C—N linkage, 1·302 (11) Å, has considerable double-bond character; the H atoms at C(3) and C(4) have a *trans* configuration.

Introduction. 1-Substituted 2-dialkylamino-1-azetium salts are produced from α-chloroenamines and Schiff's bases (De Poortere, Marchand-Brynaert & Ghosez, 1974). We have found that, in a related reaction, the action of phosphorus oxychloride on a mixture of the dimethylamide (I) of an arylacetic acid or phenoxyacetic acid and a Schiff's base (II) in refluxing chloroform results in the formation of 1-azetium salts, which were isolated as perchlorates (III). Only one of the two possible geometrical isomers was obtained in each of the eleven reactions carried out. The products showed C=N$^+$ absorptions at 1710 cm^{-1}. In the ^{1}H NMR spectra the signals of the protons of the dimethylamino groups appeared as two singlets, which indicates substantial double-bond character of the exocyclic C—N linkage [*cf.* (III*A*)]. The protons attached to C(3) and C(4) resonated as doublets with coupling constants of 1·0 Hz or less, but assignment of *cis* or *trans* geometry was uncertain because the Karplus equation (Sternhell, 1969) does not hold for strained molecules. One of the salts, the perchlorate (III*a*), was therefore submitted to X-ray analysis, which

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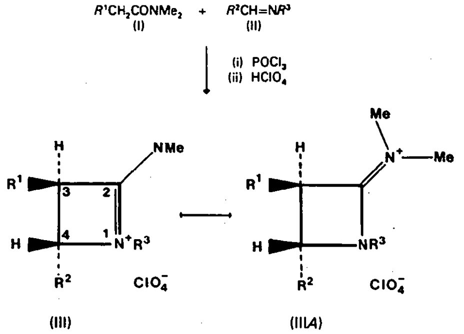
showed it to be the *trans* isomer; the other salts are presumed to have the same configuration.



a: *R*1 = *p*-$O_2NC_6H_4$,*R*2 = *R*3 = Ph
b: R^1 = *p*-$MeOC_6H_4$, R^2 = R^3 = Ph
c: R^1 = PhO, R^2 = R^3 = Ph
d: R^1 = 1-naphthyl, R^2 = R^3 = Ph
e: R^1 = *p*-ClC_6H_4, R^2 = R^3 = Ph
f: R^1 = 3,4-$(MeO)_2C_6H_3$, R^2 = R^3 = Ph
g: R^1 = R^2 = R^3 = Ph
h: R^1 = *p*-$MeOC_6H_4$, R^2 = *p*-$O_2NC_6H_4$, R^3 = Me
i: R^1 = 1-naphthyl, R^2 = *p*-$O_2NC_6H_4$, R^3 = Me
j: R^1 = R^3 = Ph, R^2 = *p*-$MeOC_6H_4$
k: R^1 = *p*-MeC_6H_4, R^2 = *p*-$O_2NC_6H_4$, R^3 = Me

Experimental. Phosphorus oxychloride (4·8 g, 1·3 mol. equiv.) was slowly added to an ice-cold solution of *N*,*N*-dimethyl-*p*-nitrophenylacetamide (5·0 g) and benzylideneaniline (4·35 g, 1 mol. equiv.) in chloroform (40 ml), and the resulting solution was heated under reflux until infrared spectroscopy showed the reaction complete. The cooled solution was poured onto cracked ice containing 60% perchloric acid (5 ml, *ca* 2 mol. equiv.), the precipitated product collected and recrystallized from acetonitrile/ethyl acetate. Yield: 8·83 g (78%), m.p. 495·2–496·7 K, ν_{max} 1710, 1600 and 1100 (*br*) cm^{-1}, δ (TFA-d) 8·38 (*d*, 2H, $J = 9$Hz) and 7·75 (*d*, 2H, $J = 9$Hz) (*p*-$O_2NC_6H_4$), 7·4 (*br s*, 10H 2 × Ph), 5·5 (*d*, 1H, $J = 1$Hz) and 5·17 (*d*, 1H, $J = 1$Hz) (benzylic protons), 3·19 (*s*, 3H, N-Me), and 3·17 (*s*, 3H, N-Me). Found: C 58·16, H 4·66, N 8·33; $C_{23}H_{22}ClN_3O_6$ requires C 58·53, H 4·71, N 8·61%.) The remaining compounds, (III*b*–*k*) inclusive, were prepared in a similar manner; analytical details have been deposited.*

Details of data collection and structure refinement are listed in Table 1. Space-group information and preliminary unit-cell dimensions obtained from precession photographs. Intensity data collected with a Hilger & Watts Y290 diffractometer; graphite-monochromated Mo *Kα* radiation; $\omega/2\theta$ step scans; stationary background mode. Four reference reflections measured every 50 reflections and data scaled to their intensity sum by linear interpolation. Lp and empirical absorption corrections (North, Phillips & Mathews, 1968) to all data.

Table 1. *Details of data collection and structure refinement*

Crystal dimensions (mm)	0·07 × 0·50 × 1·37
Scan parameters and step size	Stationary background mode: Peak 60 steps of 0·01°; Background count 6 s each side of peak
Cell parameter determination: number and θ range (°) of reflections	21; 12–15
Absorption correction; max. variation in transmission	6·5%
Max. $(\sin\theta)/\lambda$ (Å^{-1})	0·596
Range *h*	−4, 10
k	−10, 10
l	−16, 20
Standard *hkl*: number and variation in intensity sum	4; 4·1%
Number of intensity measurements	6098
Number of unique reflections	4106
Merging *R* for equivalent *hkl*	0·013
Number of unobserved reflections [$F < 5\sigma(F)$]	203
Final residuals:	
R	0·083
wR	0·099
Weighting scheme	$1/[\sigma^2(F) + 0{\cdot}0002F^2]$
Maximum shift/e.s.d. in final cycle of refinement	0·743
Max. and min. height in final difference Fourier synthesis (e Å^{-3})	0·45; −0·38
Scattering factors	*International Tables for X-ray Crystallography* (1974)

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j \times 10^3$ (Å^2).

	x	*y*	*z*	U_{eq}
Cl(1)	0·7380 (1)	0·4114 (1)	0·3360 (1)	63 (1)
O(11)	0·8267 (4)	0·4356 (5)	0·2674 (2)	102 (2)
O(12)	0·6599 (8)	0·5384 (6)	0·3596 (4)	174 (3)
O(13)	0·8487 (7)	0·3891 (9)	0·3982 (3)	177 (4)
O(14)	0·6106 (6)	0·2781 (5)	0·3108 (4)	157 (3)
N(1)	0·7794 (3)	0·2632 (3)	0·6918 (2)	46 (1)
C(11)	0·7534 (4)	0·1426 (3)	0·6186 (2)	46 (1)
C(12)	0·8455 (4)	0·1659 (4)	0·5537 (2)	59 (1)
C(13)	0·8167 (6)	0·0445 (5)	0·4834 (2)	76 (2)
C(14)	0·7008 (6)	−0·0962 (5)	0·4822 (3)	74 (2)
C(15)	0·6151 (5)	−0·1160 (4)	0·5486 (3)	69 (2)
C(16)	0·6360 (4)	0·0030 (4)	0·6183 (2)	55 (1)
C(2)	0·8023 (3)	0·4223 (3)	0·7105 (2)	44 (1)
N(21)	0·7850 (3)	0·5313 (3)	0·6675 (2)	47 (1)
C(22)	0·8291 (5)	0·7006 (4)	0·7061 (2)	62 (1)
C(23)	0·7243 (5)	0·4970 (4)	0·5817 (2)	62 (1)
C(3)	0·8373 (4)	0·4325 (4)	0·8014 (2)	46 (1)
C(31)	0·7219 (4)	0·5098 (4)	0·8554 (2)	46 (1)
C(32)	0·5509 (4)	0·4852 (5)	0·8296 (2)	66 (1)
C(33)	0·4477 (5)	0·5625 (6)	0·8758 (2)	73 (2)
C(34)	0·5111 (4)	0·6642 (4)	0·9478 (2)	57 (1)
C(35)	0·6750 (5)	0·6887 (5)	0·9765 (2)	63 (1)
C(36)	0·7808 (4)	0·6099 (4)	0·9287 (2)	53 (1)
N(37)	0·3984 (5)	0·7500 (5)	0·9958 (2)	77 (2)
O(38)	0·2505 (5)	0·7194 (5)	0·9721 (2)	111 (2)
O(39)	0·4564 (5)	0·8424 (5)	1·0588 (2)	118 (2)
C(4)	0·8031 (4)	0·2422 (4)	0·7786 (2)	48 (1)
C(41)	0·9363 (4)	0·1572 (4)	0·7971 (2)	48 (1)
C(42)	1·0783 (4)	0·1621 (5)	0·7521 (2)	63 (1)
C(43)	1·1973 (5)	0·0805 (5)	0·7698 (3)	73 (2)
C(44)	1·1836 (5)	−0·0084 (5)	0·8314 (3)	70 (2)
C(45)	1·0468 (6)	−0·0132 (5)	0·8760 (2)	70 (2)
C(46)	0·9226 (5)	0·0682 (4)	0·8590 (2)	59 (1)

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* Analytical details for compounds (III*b*–*k*) inclusive, together with lists of structure amplitudes, anisotropic thermal parameters for non-hydrogen atoms, H-atom coordinates, and bond lengths and angles for the ClO_4^- anion for (III*a*) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44729 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

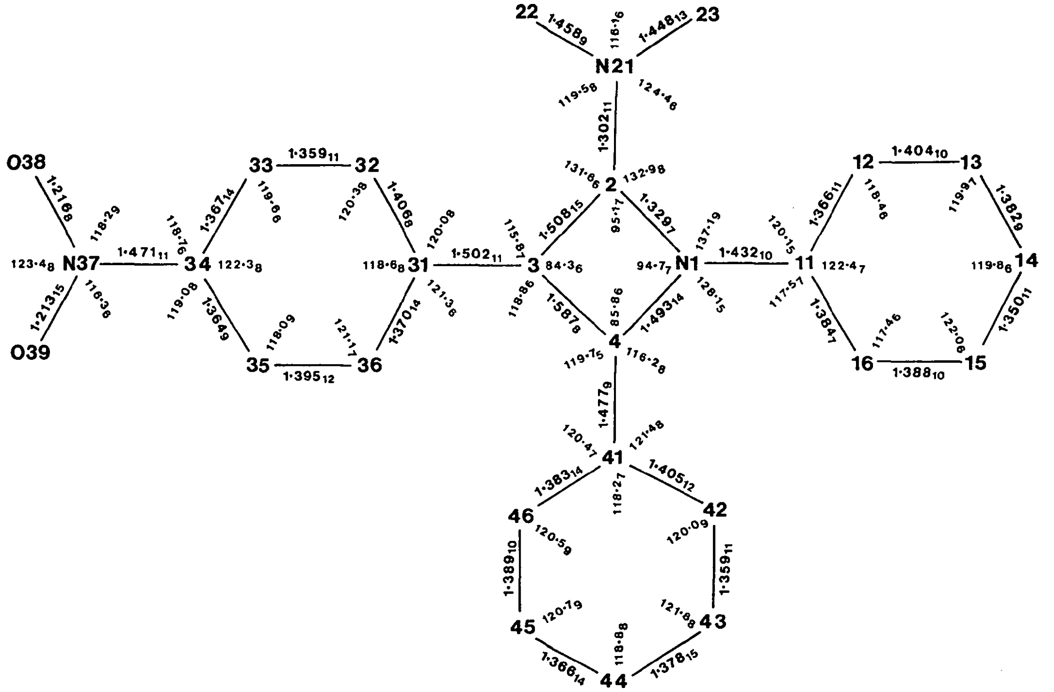

Fig. 1. Schematic diagram of the cation showing the atomic numbering together with the bond lengths (Å) and angles (°) with their corresponding estimated standard deviations.

Structure solved by direct methods (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using *SHELX*76 (Sheldrick, 1976). H atoms located from difference Fourier syntheses and subsequently fixed in positions with idealized geometry and assumed C—H separations of 1·0 Å; isotropic thermal parameters for all H atoms assigned as 0·1 Å^2. All major computations performed on the Birkbeck College VAX 11/750 or on the Amdahl computer at University of London Computer Centre.

Discussion. Fractional coordinates are given in Table 2. Fig. 1 is a schematic diagram of the azetium cation showing the atomic numbering and the bond lengths and angles together with their corresponding estimated standard deviations. Fig. 2 is a stereo drawing (Motherwell & Clegg, 1978) of the molecule and clearly shows the *trans* substituents at C(3) and C(4).

The four-membered heterocyclic ring is planar within experimental error with a maximum displacement of −0·013 (8) Å for C(3). The endocyclic N(1)—C(2) and exocyclic C(2)—N(21) bond lengths, 1·329 (7) and 1·302 (11) Å respectively, indicate electron delocalization over these three atomic centres in agreement with the ^{1}H NMR spectra. The strain within the heterocyclic ring is partially alleviated by an increase of the C(3)—C(4) bond length to 1·587 (8) Å, compared with the expected value of 1·535 Å for a single sp^3—sp^3 C—C bond (Pauling, 1960).

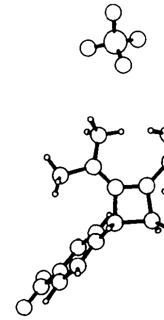

Fig. 2. Perspective view of the cation.

The phenyl substitutents at N(1) and C(4) are both planar within experimental error and are inclined at dihedral angles of −45·1 (4) and −73·5 (4)° to the least-squares plane through the heterocyclic ring. The phenyl ring at C(3) is also planar, making a dihedral angle of 78·4 (3)° with the four-membered ring, but the NO$_2$ moiety is tilted out of this plane in order to reduce steric hindrance with the adjacent ring H atoms; the dihedral angle between the plane of the NO$_2$ group and the phenyl ring is 3·1 (2)°.

In the crystal (Fig. 3) the cations are arranged in rows so that alternate pairs of C(1)–phenyl and C(3)–nitrophenyl substituents run parallel to one another; the closest approach distances are C(14) to C(16) (at 1−x, y, 1−z), 3·445 (5) Å, and C(36) to

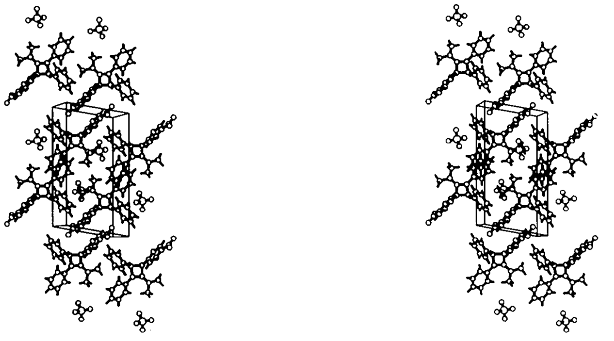

Fig. 3. Stereo drawing of the unit-cell contents, viewed approximately perpendicular to the *bc* plane.

O(38) (at $1+x$, y, z), 3·770 (6) Å respectively. The perchlorate anions are accommodated between these rows in proximity to N(21) with a closest approach, N(21) to O(2) (at $1-x$, $1-y$, $1-z$), of 3·559 (8) Å. However, none of the intermolecular distances is significantly shorter than the sum of the corresponding van der Waals radii.

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Structure of Glycine *cyclo*-Tetraphosphate

By M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel

Laboratoire de Cristallographie associé à l'Université Scientifique Technologique et Mèdicale de Grenoble, Centre National de la Recherche Scientifique, 166X, 38042 Grenoble CEDEX, France

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Abstract. $(NH_3CH_2COOH)_4P_4O_{12}$, $4C_2H_6NO_2^+.$-$P_4O_{12}^{4-}$, $M_r = 620{\cdot}18$, triclinic, $P\bar{1}$, $a = 7{\cdot}988\ (5)$, $b = 8{\cdot}449\ (5)$, $c = 9{\cdot}739\ (5)$ Å, $\alpha = 111{\cdot}64\ (5)$, $\beta = 105{\cdot}27\ (5)$, $\gamma = 99{\cdot}40\ (5)°$, $V = 564\ (2)$ Å^3, $Z = 1$, $D_x = 1{\cdot}826$ Mg m^{-3}, $\lambda(\text{Ag}\ K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}239$ mm^{-1}, $F(000) = 320$, $T = 295$ K, final $R = 0{\cdot}025$ for 3393 unique reflexions. The title compound is the first example of an amino acid *cyclo*-tetraphosphate. In its atomic arrangement the non-acidic cyclic phosphoric group $(P_4O_{12})^{4-}$ is interconnected by hydrogen bonds to eight different $(C_2H_6NO_2)^+$ groups. A complete hydrogen-bond scheme is reported.

Introduction. As part of a systematic investigation of amino acid phosphates we previously reported chemical preparations and crystal structures of glycine monophosphate and glycine *cyclo*-triphosphate (Averbuch-Pouchot, Durif & Guitel, 1988). In the present work we describe the first amino acid *cyclo*-tetraphosphate: $(gly)_4.P_4O_{12}$.

Experimental. Crystals of glycine *cyclo*-tetraphosphate were prepared by a metathesis reaction deriving from that described by Boullé (1941) for the preparation of water-soluble inorganic *cyclo*-triphosphates: the silver *cyclo*-triphosphate monohydrate being replaced by the silver *cyclo*-tetraphosphate $Ag_4P_4O_{12}$. To a slurry in water of the sparingly soluble silver *cyclo*-tetraphosphate is slowly added an aqueous solution of glycine hydrochloride in stoichiometric ratio 1:4. The reaction is

$$Ag_4P_4O_{12} + 4(NH_3CH_2COOH)Cl \rightarrow 4AgCl + (NH_3CH_2COOH)_4P_4O_{12}.$$

After about two hours of mechanical stirring the insoluble silver chloride is eliminated by filtration. The resulting aqueous solution is then kept at room temperature. After some days of evaporation, colorless flat prisms of glycine *cyclo*-tetraphosphate appear in the solution. Crystal size: 0·29 × 0·35 × 0·24 mm. Density not measured. Philips PW1100 diffractometer, graphite

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