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Structure of 1-(*p*-Nitrobenzylidineamino)guanidinium Chloride

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Abstract. $C_8H_{10}N_5O_2^+.Cl^-$, $M_r = 243·67$, monoclinic, $P2_1/c$, $a = 8·406$ (2), $b = 11·490$ (4), $c = 11·510$ (2) Å, $\beta = 101·89$ (2)°, $V = 1087·7$ (5) Å^3, $Z = 4$, $D_x = 1·49$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0·70926$ Å, $\mu = 3·48$ cm^{-1}, $T = 293$ K, $F(000) = 504$, final $R = 0·056$ for 1965 observations. Ionic/hydrogen bonds between the chloride ion and the guanidinium groups as well as stacking interactions involving the guanidinium and phenyl groups maintain the crystalline structure. The separation of planes of stacked guanidinium groups is 3·72 (14) Å, and of phenyl planes is 3·46 (26) Å.

Introduction. ADP-ribosylation* is an enzyme-mediated transfer of the ADP-ribose group of NAD$^+$ to an appropriate acceptor. Reactions of ADP-ribosylation fall into two broad categories:

$$\text{Acceptor} + n\text{NAD}^+ \xrightarrow[\text{poly(ADP-ribose) polymerase}]{\text{DNA}} \text{Acceptor(ADP-ribose)}_n + n\text{Nicotinamide} + n\text{H}^+ \quad (1)$$

$$\text{Acceptor} + \text{NAD}^+ \xrightarrow[\text{ADP-ribosyl transferase}]{} \text{Acceptor-ADP-ribose} + \text{Nicotinamide} + \text{H}^+ \quad (2)$$

Poly-ADP-ribosylation (reaction 1) may play a role in the synthesis, transcription and repair of DNA. The polymerase for poly-ADP-ribosylation requires DNA for activity. In fact, breaks in single- or double-stranded DNA enhance polymerase activity [for a review, see Purnell, Stone & Whish (1980)]. Mono-ADP-ribosylation (reaction 2) is involved in the mechanism of cholera toxin, diphtheria toxin and heat-labile enterotoxin from *Escherichia coli*. The A_1 subunit of cholera toxin, for instance, catalyzes the ADP-ribosylation of L-arginine (Moss & Vaughan, 1977). Cassel & Pfeuffer (1978) have evidence for the ADP-ribosylation by cholera toxin of the GTP binding protein from a preparation of solubilized adenylate cyclase. Finally, Goff (1974) has demonstrated ADP-ribosylation of an arginine residue in RNA polymerase of *E. coli* following infection with *T*4 phage.

The mechanism of transfer reactions involving the title compound is of interest to investigators studying the broader problem of ADP-ribosylation of macromolecules. Soman, Tomer & Graves (1983) assayed for the activity of ADP-ribosyl transferases by using 1-(*p*-nitrobenzylidineamino)guanidinium chloride as an acceptor of the ADP-ribosyl group. The kinetics of the transfer reaction could be sensitive to the tautomeric form of the guanidinium group as well as to its state of protonation. Structures of the title compound under conditions of high and low pH will provide information relevant to current speculation on the mechanism of transfer reactions. We report, here, the structure of the salt, 1-(*p*-nitrobenzylidineamino)guanidinium chloride.

Experimental. Crystals of the title compound (provided by Dr Soman, Department of Biochemistry and Biophysics, Iowa State University) grew as yellow prisms from a solution of HCl/ethanol. The specimen for data collection measured 0·70 × 0·68 × 0·35 mm. Unit-cell parameters derived from setting angles of 15 reflections with $30 < 2\theta < 35°$. Data over one quadrant ($-13 \leq h \leq 13$, $0 \leq k \leq 17$, $0 \leq l \leq 17$) was collected on a Syntex $P2_1$ diffractometer to $2\theta = 60°$ [$(\sin\theta/\lambda)_{\max} = 0·704$ Å^{-1}] using 2θ–θ scans. Of the total 3481 reflections, 162 were extinct, 139 were redundant ($R_{\text{int}} = 0·049$), 1412 had intensities with $I < 3\sigma(I)$, leaving 1768 reflections with intensities above three standard deviations. Intensities of six standard reflections ($20 < 2\theta < 56°$) indicated no measurable decay. The transmission factors based on an empirical absorption correction (North, Phillips & Mathews, 1968) varied from 0·975 to 1·000. *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) gave the locations of all non-H atoms. The H atoms were located by inspection of a difference map. We used 1965 structure factors to 0·6 Å^{-1} in $\sin\theta/\lambda$ in the weighted refinement [$w = 1/\sigma^2(F)$] of the positions and thermal tensors of non-H atoms and the positions and isotropic thermal parameters of H atoms. Scattering factors came from the *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). The highest and lowest peaks in the final difference map were 0·26 and $-0·24$ e Å^{-3}. The final statistics of refinement were $(\Delta/\sigma)_{\max} = 0·03$, $R = 0·056$, $wR = 0·051$ and $S = 1·3018$. All calculations were done on a VAX 11/780 computer using programs developed in the group of R. A. Jacobson (Karcher, 1981; Powell & Jacobson, 1980; Lapp & Jacobson, 1979).

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* Abbreviations used: ADP, adenosine 5′-diphosphate; NAD$^+$, nicotinamide adenine diphosphate.

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Discussion. Fractional coordinates and average isotropic temperature factors are in Table 1;* Fig. 1 shows the atom-numbering scheme and Fig. 2 a stereoview along the *b* axis. The near equivalence of bond lengths (Table 2) of N to C of the guanidinium group [average length 1·320 (2) Å] and the near equivalence of bond lengths of C to C of the phenyl ring [average length, 1·379 (1) Å] indicate extensive electronic resonance in these moieties. Atoms fall into either the plane of the phenyl ring [C(6), C(7), C(8), C(9), C(10), C(11), C(12), N(13); root-mean-square deviation from planarity, 0·0067 Å] or the plane of the guanidinium group [N(1), N(2), C(3), N(4), N(5); root-mean-square deviation from planarity, 0·0015 Å]. Guanidinium groups stack along the *a* axis with a planar separation of 3·72 (14) Å. Even stronger stacking interactions occur between C(10)—C(12$^{\mathrm{i}}$), C(11)—C(11$^{\mathrm{i}}$) and C(12)—C(10$^{\mathrm{i}}$)* of the phenyl groups. The separation of planes of stacked phenyl groups is 3·46 (26) Å. The chloride ion, Cl(16), binds to four H atoms of three molecules of 1-(*p*-nitrobenzylidineamino)guanidinium chloride (Table 3); the second and third molecules are related respectively to the first by the glide operation [atom H(18$^{\mathrm{ii}}$)] and by the symmetry operation $\frac{3}{2}-x$, $-\frac{1}{2}+y$, $2-z$ [atom H(21$^{\mathrm{iii}}$)]. Crystals of the title compound slowly decompose into an amorphous powder upon exposure to air. In view of the proximity of four exchangeble protons to each chloride ion and the anomalously low pK_a (approximately 7·0; personal communication: D. J. Graves) of the guanidinium group, deterioration of crystals may be a consequence of the formation and volatilization of HCl from the crystal.

Table 1. *Atom coordinates* (× 10⁴) *with e.s.d.'s in parentheses and average temperature factors* (Å² × 10³)

$U_{\mathrm{av}} = \langle U_{ll} \rangle$, where U_{ll} are the diagonal components of the tensor associated with a temperature factor of the form $\exp(-2\pi^2\sum\sum U_{ij}a_i^*a_j^*h_ih_j)$.

	x	y	z	U_{av}
N(1)	8181 (3)	−2296 (2)	10587 (2)	53
N(2)	8171 (3)	−3938 (2)	9459 (2)	54
C(3)	8546 (3)	−2838 (2)	9673 (2)	40
N(4)	9273 (2)	−2232 (2)	8940 (2)	44
N(5)	9723 (2)	−2805 (2)	8013 (1)	41
C(6)	10093 (3)	−2161 (2)	7217 (2)	41
C(7)	10599 (2)	−2688 (2)	6194 (2)	37
C(8)	10440 (3)	−2068 (2)	5142 (2)	45
C(9)	10808 (3)	−2560 (2)	4145 (2)	46
C(10)	11406 (3)	−3680 (2)	4238 (2)	42
C(11)	11650 (3)	−4306 (2)	5282 (2)	43
C(12)	11222 (3)	−3811 (2)	6259 (2)	41
N(13)	11795 (3)	−4222 (2)	3186 (2)	56
O(14)	11243 (3)	−3821 (2)	2224 (2)	91
O(15)	12635 (3)	−5091 (2)	3315 (2)	89
Cl(16)	6160·7 (8)	−4462·3 (5)	11566·2 (5)	51

Table 2. *Bond distances* (Å) *and angles* (°)

N(1)—C(3)	1·312 (3)	C(9)—C(10)	1·377 (3)
N(2)—C(3)	1·313 (3)	C(11)—C(10)	1·378 (3)
C(3)—N(4)	1·336 (3)	C(12)—C(11)	1·373 (3)
N(4)—N(5)	1·372 (3)	C(7)—C(12)	1·389 (3)
N(5)—C(6)	1·266 (3)	C(10)—N(13)	1·458 (3)
C(6)—C(7)	1·463 (3)	O(14)—N(13)	1·201 (3)
C(8)—C(7)	1·387 (3)	O(15)—N(13)	1·214 (3)
C(8)—C(9)	1·370 (3)		
N(1)—C(3)—N(2)	121·4 (2)	C(8)—C(9)—C(10)	117·5 (2)
N(1)—C(3)—N(4)	118·2 (2)	C(9)—C(10)—C(11)	122·8 (2)
N(2)—C(3)—N(4)	120·4 (2)	C(9)—C(10)—N(13)	118·4 (2)
C(3)—N(4)—N(5)	118·5 (2)	C(11)—C(10)—N(13)	118·8 (2)
N(4)—N(5)—C(6)	115·5 (2)	C(12)—C(11)—C(10)	118·7 (2)
N(5)—C(6)—C(7)	119·7 (2)	C(7)—C(12)—C(11)	120·0 (2)
C(6)—C(7)—C(8)	119·9 (2)	C(10)—N(13)—O(14)	119·4 (2)
C(6)—C(7)—C(12)	120·7 (2)	O(14)—N(13)—O(15)	122·2 (2)
C(8)—C(7)—C(12)	119·4 (2)	O(15)—N(13)—C(10)	118·4 (2)
C(7)—C(8)—C(9)	121·4 (2)		

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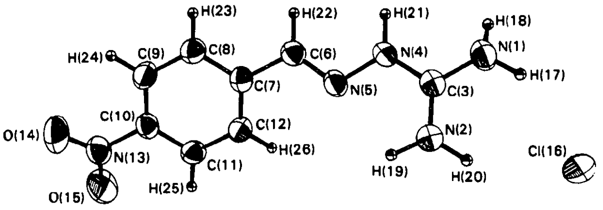

Fig. 1. *ORTEP* (Johnson, 1970) drawing showing the atom-numbering scheme. Ellipsoids represent a 50% probability level.

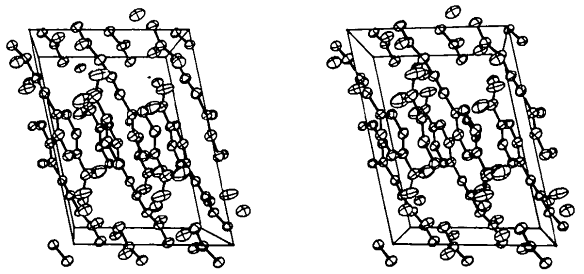

Fig. 2. Stereoview along the *b* axis depicting the molecular packing. The positive *a* axis lies along the horizontal.

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* Lists of anisotropic thermal parameters, H-atom coordinates, bond angles and distances involving H atoms, least-squares planes, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43154 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The symmetry operations are as follows: (i) $2-x$, $-1-y$, $1-z$; (ii) $x-\frac{1}{2}$, $y-\frac{1}{2}$, z; (iii) $\frac{3}{2}-x$, $-\frac{1}{2}+y$, $2-z$.

Table 3. *Hydrogen-bonding distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Donor	H	Acceptor	*D*—H	H···*A*	*D*···*A*	Angle
Intermolecular						
N(1)	H(18^{i})	Cl(16)	0·91 (3)	2·38 (3)	3·240 (2)	157 (2)
N(4)	H(21^{iii})	Cl(16)	0·88 (3)	2·39 (3)	3·240 (2)	162 (2)
Intramolecular						
N(1)	H(17)	Cl(16)	0·84 (2)	2·58 (2)	3·340 (2)	150 (2)
N(2)	H(20)	Cl(16)	0·89 (3)	2·47 (3)	3·280 (2)	152 (3)

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4-Methyl-1,2,6-triphosphatricyclo[2.2.1.$0^{2,6}$]heptane

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Abstract. $C_5H_9P_3$, $M_r = 162{\cdot}05$, hexagonal, $R\bar{3}$, $a = 9{\cdot}281\,(1)$, $c = 15{\cdot}386\,(2)$ Å, $V = 1147{\cdot}7\,(2)$ Å^3, $Z = 6$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 6{\cdot}7$ cm^{-1}, $F(000) = 504$, room temperature, final $R = 0{\cdot}043$ for 563 reflections (including five unobserved). The molecule consists of three P atoms which form a regular triangle [P—P: 2·200 (1) Å] and the organic group [P—C: 1·851 (2) Å]. Literature data of bond lengths and bond angles are in good agreement with our results. In the crystal the molecules are held together by van der Waals forces.

Introduction. The title compound is especially suited for the study of phosphorus bonding because the molecule possesses a single P_3 unit. The electronic structure was calculated on the basis of its photoelectron spectrum (Gleiter, Köppel, Hofmann, Schmidt & Ellermann, 1985). Here we describe the solid-state structure determined by X-ray analysis. The analogous Sb compound was reported recently (Ellermann, Köck & Burzlaff, 1985).

Experimental. Colourless crystals recrystallized from heptane. Spherical crystal, $r = 0{\cdot}21\,(2)$ mm, Philips PW 1100 diffractometer (graphite monochromator, Mo $K\alpha$ radiation), ω–2θ scans, scan width: $(1{\cdot}000 + 0{\cdot}345\tan\theta)°$, 38 reflections ($15{\cdot}6 < \theta < 18{\cdot}3°$) used in least-squares program *GIVER* (Krogmann, 1966) for refinement of lattice parameters; spherical absorption correction applied: $\mu R = 0{\cdot}14\,(1)$, absorption correction factor $A = 1{\cdot}225\,(1)$; max. $(\sin\theta)/\lambda = 0{\cdot}640$ Å^{-1}, index range h 0→11, k −10→9, l 0→19; six standard reflections used for control of stability (intensity variation: 0·3%), 3354 reflections measured, after averaging equivalents 563 reflections remained [including 5 unobserveds with $I \leq 3\sigma(I)$], $R_{\rm int} = 0{\cdot}013$; structure solved by Patterson techniques, subsequent Fourier map revealed all C atoms and all H atoms found in a difference Fourier map; least squares based on F and weights $w = 1/\sigma^2(|F_o|)$; final cycles refined

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