between non-H atoms involve O(23)···C(3) [3·259 (5) Å] and O(24)···C(19) [3·184 (5) Å]; the closest such contact between non-H and H atoms is 2·45 (6) Å for both O(23)···H(3*b*) and O(24)···H(19*c*).

A packing diagram viewed down **b** is available as supplementary material.

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2,3-Dihydro-1,4-diazepinium Picrate, $C_5H_9N_2^+.C_6H_2N_3O_7^-$

BY GEORGE FERGUSON, BARBARA L. RUHL AND TADEUSZ WIECKOWSKI

*Chemistry Department, University of Guelph, Guelph, Ontario, Canada N*1*G* 2*W*1

AND DOUGLAS LLOYD AND HAMISH MCNAB*

*Department of Chemistry, Purdie Building, University of St. Andrews, St. Andrews, Fife KY*16 9*ST, Scotland*

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Abstract. $M_r = 366{\cdot}8$, monoclinic, $P2_1/c$, $a = 11{\cdot}042\ (3)$, $b = 8{\cdot}224\ (3)$, $c = 15{\cdot}113\ (3)$ Å, $\beta = 92{\cdot}40\ (2)°$, $V = 1371{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}58$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}70926$ Å, $\mu = 1{\cdot}3$ cm^{-1}, $F(000) = 672$, $T = 293$ K, final $R = 0{\cdot}042$ for 1336 observed data. The crystal structure contains discrete diazepinium cations and picrate anions linked in chains by N—H···O hydrogen bonds [2·898 (3), 2·777 (3) Å]. The cation contains a five-membered delocalized 1,5-diazapentadienium chain [N(4),C(5),C(6),C(7),N(1); mean C—C 1·382 (8), mean C—N 1·306 (9) Å] in a helical conformation with N(1) −0·059 (3) and N(4) 0·062 (3) Å from the five-atom plane; the methylene atoms C(2) and C(3) are −0·399 (3) and +0·444 (3) Å respectively from this plane. The picrate ring plane is planar but the nitro groups are inclined at 37·5 (3) and 25·6 (3)° (*ortho*) and 1·9 (3)° (*para*) to the ring. The picrate dimensions are consistent with significant contributions from a resonance form with an essentially normal C=O bond.

Introduction. The 2,3-dihydro-1,4-diazepinium cation, present in compound (1), is of chemical interest (Lloyd, Cleghorn & Marshall, 1974; Lloyd, 1975; Lloyd & McNab, 1978) because it possesses a delocalized

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* Present address: Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, Scotland.

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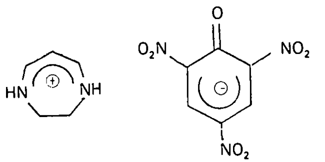
vinamidinium system (Lloyd & McNab, 1976) which is noteworthy because of its stability and tendency to take part in substitution reactions, and also because in this case the geometry of this system is relatively fixed since it is held in a ring. Chemical studies suggest that its reactions may be influenced markedly by small changes in the geometry and conformation brought about by substituent atoms or groups. For this reason a series of studies on the conformation of variously substituted 2,3-dihydro-1,4-diazepinium rings has been initiated and we report here the crystal and molecular structure of the title compound (1) containing the unsubstituted cation. Crystals of the corresponding perchlorate salt proved quite unsuitable for this and several related structure analyses, whereas the picrate salts have all yielded suitable crystals (Ruhl, Ferguson, Parvez & Wieckowski, 1983).



(1)

Experimental. Yellow crystals, 0·25 × 0·09 × 0·38 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 reflections with θ in range $10 < \theta < 15°$ used for measuring lattice constants; for data collection $2 < \theta < 25°$ (h 0 to 14, k 0 to 10, l −19 to 19), ω–2θ scans, ω-scan width $(0{\cdot}60 + 0{\cdot}35\tan\theta)°$; intensities of three reflections monitored every 100 min of exposure time showed no significant variation; Lp corrections, 3126 unique reflections, 1336 with $I > 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S - B)]^2$, S = scan count and B = time-averaged background count; there were very few reflections with $\theta > 20°$ hence the relatively low (42%) observed:total reflection ratio; absorption correction not considered necessary. Structure solved with the aid of *MULTAN*80 segment (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) of the *NRC Crystal Structure Package* (Gabe, Larson, Wang & Lee, 1981). Refinement by block-diagonal least-squares calculations on F, non-H atoms allowed anisotropic vibration, H atoms (from difference syntheses) refined isotropically. Final $R = 0{\cdot}042$, $R_w = 0{\cdot}032$ for 1336 observed data, $R = 0{\cdot}119$ for all data, $w = 1/\sigma^2(F)$, $S = 3{\cdot}17$, maxima $\pm 0{\cdot}1$ e Å^{-3} in final difference map, max. parameter shift/e.s.d. = 0·05 for x of N(4), mean shift/e.s.d. = 0·01; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Other computer programs used included *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP*II (Johnson, 1976).

Table 1. *Final fractional coordinates and the mean* B_{iso} (Å^2) [$= \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$ *for non-*H *atoms and* $8\pi^2 U_{iso}$ *for* H *atoms*] *for* $C_5H_9N_2^+.C_6H_2N_3O_7^-$ *with e.s.d.'s in parentheses*

	x	y	z	B_{iso}
O(1)	0·2081 (2)	0·1521 (3)	0·6142 (1)	4·2 (1)
O(2)	0·2621 (2)	0·3674 (4)	0·4846 (1)	6·8 (2)
O(3)	0·1599 (2)	0·2948 (4)	0·3689 (1)	6·8 (2)
O(4)	−0·2743 (2)	0·3102 (3)	0·4039 (2)	5·6 (2)
O(5)	−0·3461 (2)	0·1845 (3)	0·5168 (1)	5·5 (2)
O(6)	−0·0804 (2)	0·0265 (3)	0·7593 (1)	5·8 (2)
O(7)	0·0988 (2)	−0·0515 (3)	0·7267 (1)	6·1 (2)
N(1)	0·3981 (2)	0·1183 (3)	0·1640 (2)	3·7 (2)
N(4)	0·6300 (2)	0·0278 (3)	0·2798 (2)	3·7 (2)
N(12)	0·1717 (2)	0·3107 (4)	0·4492 (2)	4·2 (2)
N(14)	−0·2621 (2)	0·2408 (3)	0·4753 (2)	4·2 (2)
N(16)	0·0052 (2)	0·0255 (3)	0·7101 (2)	4·1 (2)
C(2)	0·5102 (3)	0·0455 (4)	0·1374 (2)	4·0 (2)
C(3)	0·6204 (3)	0·1016 (4)	0·1930 (2)	3·6 (2)
C(5)	0·5434 (3)	0·0240 (4)	0·3354 (2)	3·8 (2)
C(6)	0·4245 (3)	0·0767 (4)	0·3227 (2)	4·1 (2)
C(7)	0·3635 (3)	0·1253 (4)	0·2459 (2)	3·9 (2)
C(11)	0·1020 (3)	0·1724 (4)	0·5847 (2)	3·0 (2)
C(12)	0·0726 (2)	0·2534 (4)	0·5017 (2)	2·9 (2)
C(13)	−0·0429 (3)	0·2758 (4)	0·4665 (2)	3·3 (2)
C(14)	−0·1386 (3)	0·2193 (4)	0·5132 (2)	3·2 (2)
C(15)	−0·1216 (3)	0·1428 (4)	0·5939 (2)	3·2 (2)
C(16)	−0·0053 (3)	0·1170 (4)	0·6269 (2)	3·0 (2)
H(N1)	0·348 (3)	0·180 (4)	0·120 (2)	7·9 (10)
H(N4)	0·702 (2)	−0·016 (3)	0·296 (2)	5·7 (8)
H(21)	0·517 (2)	0·075 (3)	0·074 (2)	4·9 (8)
H(22)	0·505 (2)	−0·075 (3)	0·140 (2)	4·9 (7)
H(31)	0·620 (2)	0·218 (3)	0·198 (2)	3·8 (7)
H(32)	0·697 (2)	0·070 (3)	0·162 (1)	3·6 (7)
H(5)	0·567 (3)	−0·023 (4)	0·398 (2)	8·6 (10)
H(6)	0·377 (3)	0·088 (4)	0·377 (2)	6·7 (9)
H(7)	0·283 (2)	0·163 (3)	0·250 (2)	5·0 (8)
H(13)	−0·050 (2)	0·327 (3)	0·411 (1)	3·2 (6)
H(15)	−0·189 (2)	0·102 (3)	0·622 (1)	3·1 (6)

Discussion. Final fractional coordinates* with mean isotropic temperature factors are in Table 1. Table 2 contains molecular dimensions. Fig. 1 has views of the cation and anion with our numbering scheme. Fig. 2 shows the molecular packing.

The crystal structure contains diazepinium cations and picrate anions linked in chains along the **a** direction by N—H···O [N(1)···O(1^{i}) 2·898 (3), N(4)···O(1^{ii}) 2·777 (3) Å] hydrogen bonds. The cations are stacked in the **b** direction by operation of a twofold screw axis (Fig. 2). The picrate anions are associated in pairs about inversion centres with an interplanar spacing of 3·56 Å; other inter-ion contacts correspond to normal van der Waals interactions.

In the diazepinium cation (Fig. 1) the bond lengths of the N(4),C(5),C(6),C(7),N(1) system [mean C—C 1·382 (8), mean C—N 1·306 (9) Å] (Table 2) are consistent with a fully delocalized system and these atoms define a portion of a helix with N(4) 0·062 (3), C(5) −0·079 (3), C(6) 0·003 (3), C(7) 0·073 (3) and N(1) −0·059 (3) Å from the best plane through them.

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, mean-plane data, selected torsion angles and bond lengths involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39510 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

These displacements correspond to torsion angles N(4)—C(5)—C(6)—C(7) 9·8 (3) and C(5)—C(6)—C(7)—N(1) 7·9 (3)°. The remaining two atoms of the seven-membered ring are −0·399 (3) [C(2)] and +0·444 (3) Å [C(3)] from the plane of the delocalized atoms, corresponding to an N(1)—C(2)—C(3)—N(4) torsion angle of 75·8 (3)°. The cation thus has approximate twofold symmetry, with the twofold axis passing through C(6) and the C(2)—C(3) mid-point. The ring valency angles at the N and sp^2-hybridized C atoms have been increased from the normal 120° to a mean value of 127·2 (3)° (Table 2). The sp^3-hybridized C atoms have N—C—C angles close to those anticipated [mean value 113·4 (3)°].

The six-membered ring of the picrate anion (Fig. 1) is essentially planar [mean displacement 0·008 (3) Å] and its dimensions [C(11)—O(1) 1·247 (3), C(11)—C(12) and C(11)—C(16) mean 1·445 (4), other C—C ring bonds mean 1·376 (4) Å] are consistent with a major contribution from a resonance form as shown in (1) with the negative charge constrained to lie in the ring and an essentially normal C=O carbonyl group. Similar observations have been made in other picrate ions (*e.g.* Palenik, 1972; Ferguson, Kaitner, Lloyd & McNab, 1984).

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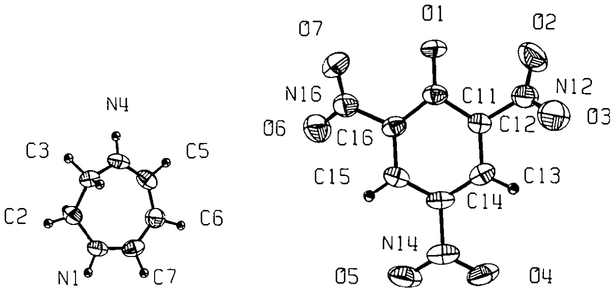

Fig. 1. The cation and anion in $C_5H_9N_2^+.C_6H_2N_3O_7^-$ with our numbering scheme.

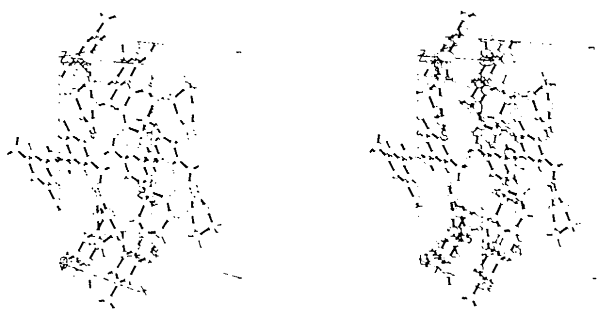

Fig. 2. A stereoview of the crystal structure of $C_5H_9N_2^+.C_6H_2N_3O_7^-$.

Table 2. *Interatomic distances* (Å), *bond angles* (°), *and hydrogen-bond geometry*

(*a*) Bond lengths

Anion

O(1)—C(11)	1·247 (3)	N(14)—C(14)	1·468 (4)
O(2)—N(12)	1·206 (3)	N(16)—C(16)	1·466 (4)
O(3)—N(12)	1·222 (3)	C(11)—C(12)	1·446 (4)
O(4)—N(14)	1·223 (3)	C(11)—C(16)	1·443 (4)
O(5)—N(14)	1·231 (4)	C(12)—C(13)	1·373 (4)
O(6)—N(16)	1·227 (3)	C(13)—C(14)	1·376 (4)
O(7)—N(16)	1·229 (4)	C(14)—C(15)	1·378 (4)
N(12)—C(12)	1·456 (4)	C(15)—C(16)	1·376 (4)

Cation

N(1)—C(2)	1·447 (4)	C(2)—C(3)	1·521 (4)
N(1)—C(7)	1·312 (4)	C(5)—C(6)	1·388 (5)
N(4)—C(3)	1·445 (4)	C(6)—C(7)	1·376 (4)
N(4)—C(5)	1·299 (4)		

(*b*) Bond angles

Anion

O(2)—N(12)—O(3)	122·3 (3)	N(12)—C(12)—C(11)	118·4 (2)
O(2)—N(12)—C(12)	120·6 (2)	N(12)—C(12)—C(13)	116·9 (3)
O(3)—N(12)—C(12)	117·1 (3)	C(11)—C(12)—C(13)	124·7 (3)
O(4)—N(14)—O(5)	124·6 (2)	C(12)—C(13)—C(14)	118·5 (3)
O(4)—N(14)—C(14)	117·8 (3)	N(14)—C(14)—C(13)	118·7 (3)
O(5)—N(14)—C(14)	117·7 (3)	N(14)—C(14)—C(15)	119·3 (3)
O(6)—N(16)—O(7)	122·9 (3)	C(13)—C(14)—C(15)	122·0 (3)
O(6)—N(16)—C(16)	118·8 (3)	C(14)—C(15)—C(16)	118·8 (3)
O(7)—N(16)—C(16)	118·3 (3)	N(16)—C(16)—C(11)	120·3 (2)
O(1)—C(11)—C(12)	123·0 (3)	N(16)—C(16)—C(15)	115·5 (3)
O(1)—C(11)—C(16)	125·2 (3)	C(11)—C(16)—C(15)	124·2 (3)
C(12)—C(11)—C(16)	111·8 (2)		

Cation

C(2)—N(1)—C(7)	124·6 (3)	N(4)—C(5)—C(6)	128·3 (3)
N(1)—C(2)—C(3)	113·2 (3)	C(5)—C(6)—C(7)	129·3 (3)
C(2)—C(3)—N(4)	113·6 (3)	C(6)—C(7)—N(1)	129·1 (3)
C(3)—N(4)—C(5)	124·7 (3)		

(*c*) Hydrogen-bond geometry

	N···O (Å)	N—H (Å)	H···O (Å)	N—H···O (°)
N(1)—H···O(1^{i})	2·898 (3)	0·99 (3)	2·07 (3)	140 (3)
N(4)—H···O(1^{ii})	2·777 (3)	0·90 (3)	1·99 (3)	145 (3)

The superscripts refer to the equivalent positions: (i) $x, \frac{1}{2}+y, -\frac{1}{2}+z$; (ii) $1-x, -y, 1-z$.

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