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6-Bromo-2,3-dihydro-5,7-dimethyl-1,4-diazepinium Picrate and 6-Bromo-2,3-dihydro-1,4-diazepinium Picrate

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Abstract. (1) $C_7H_{12}BrN_2^+.C_6H_2N_3O_7^-$, $M_r = 432{\cdot}2$, triclinic, $P\bar{1}$, $a = 7{\cdot}760\,(3)$, $b = 9{\cdot}139\,(2)$, $c = 12{\cdot}262\,(4)$ Å, $\alpha = 100{\cdot}24\,(2)$, $\beta = 98{\cdot}32\,(3)$, $\gamma = 93{\cdot}63\,(3)^\circ$, $V = 843\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}70926$ Å, $\mu = 24{\cdot}6$ cm^{-1}, $F(000) = 436$, $T = 294$ K, $R = 0{\cdot}039$, $wR = 0{\cdot}046$ for 2045 observed data. (2) $C_5H_8BrN_2^+.C_6H_2N_3O_7^-$, $M_r = 404{\cdot}1$, monoclinic, $C2/c$, $a = 21{\cdot}501\,(6)$, $b = 10{\cdot}685\,(4)$, $c = 13{\cdot}255\,(5)$ Å, $\beta = 90{\cdot}47\,(2)^\circ$, $V = 3045\,(3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}76$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}70926$ Å, $\mu = 27{\cdot}2$ cm^{-1}, $F(000) = 1616$, $R = 0{\cdot}044$, $wR = 0{\cdot}046$ for 1562 observed data. Both crystal structures contain discrete diazepinium cations and picrate anions which are linked by N—H···O hydrogen bonds to form centrosymmetric tetrameric rings in (1) (N···O 2·779–3·166 Å) and infinite chains in (2) (N···O 2·863–3·020 Å). The seven-membered ring of each cation contains a five-membered delocalized 1,5-diazapentadienium chain [N—C—C—C—N; mean C—C 1·413 (6), mean C—N 1·306 (5) Å in (1), mean C—C 1·390 (7), mean C—N 1·304 (7) Å in (2)] in a helical conformation. The picrate ring dimensions in both (1) and (2) are consistent with significant contributions from a resonance form with an essentially normal C═O bond.

Introduction. Interest in the 2,3-dihydro-1,4-diazepinium cation has centred on the delocalized nature of its 1,5-diazapentadienium, or vinamidinium, system and on its 'quasi-aromatic' character (Lloyd & Marshall, 1964, 1971). Because of this character, it was suprising that the Br atom of the 6-bromo-5,7-dimethyl derivative (1) underwent ready nucleophilic displacement (Lloyd & Marshall, 1958; Gorringe, Lloyd, Wasson, Marshall & Duffield, 1969). The unmethylated derivative (2) was found not to take part in such reactions, and rationalization of these reactions has invoked steric crowding between the geminal bromo and methyl groups in (1) (Lloyd, McNab & Marshall, 1975) which would be absent in (2). X-ray analyses of the bromo compounds (1) and (2) were therefore desirable to allow us to compare them with each other and with the corresponding 6-hydrogeno-5,7-dimethyl analogue (Ferguson, Marsh, Lloyd & Marshall, 1980). The 1,4-diazepinium picrate derivatives were obtained from the corresponding bases by reaction with picric acid in acetone (Lloyd & McNab, 1989).

Experimental. (1) Yellow crystals, 0·30 × 0·20 × 0·35 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 reflections with θ in range $10 < \theta < 15^\circ$ used to determine lattice parameters; for data collection $2 < \theta < 25^\circ$ (h -9 to 9, k -10 to 10, l 0 to 14), ω–2θ scans, ω-scan width $(0{\cdot}60 + 0{\cdot}35\tan\theta)^\circ$; intensities of three reflections monitored every 2 h of exposure time showed no significant decay; Lorentz, polarization and

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absorption corrections (maximum and minimum transmission coefficients 0·6257 and 0·5330 respectively). 2946 unique reflections, 2045 (69·4%) 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.

(2) Yellow crystals, 0·18 × 0·15 × 0·33 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 reflections with θ in range $10 < \theta < 15°$ used to determine lattice constants; for data collection $2 < \theta < 27°$ (h −27 to 27, k 0 to 13, l 0 to 16), ω–2θ scans, ω-scan width $(0{\cdot}70 + 0{\cdot}35\tan\theta)°$; intensities of three reflections monitored every 1·5 h of exposure time showed no significant variation; Lorentz, polarization and absorption corrections (maximum and minimum transmission coefficients 0·7009 and 0·5828 respectively). 3311 unique reflections, 1562 with $I > 3\sigma(I)$; there were very few reflections with $\theta > 20°$ hence the relatively low (47·2%) observed:total reflection ratio.

Both structures were solved by the heavy-atom method; refinement was by full-matrix least-squares calculations on F with anisotropic thermal parameters; one nitro group in (1) had its O atoms disordered over two sites. Coordinates for all H atoms were located from difference syntheses and included with idealized geometry (C—H, N—H, 0·95 Å) and an overall isotropic temperature factor. For (1) at convergence $R = 0{\cdot}039$, $wR = 0{\cdot}046$ for 2045 observed data; $w = 1/(\sigma F_o^2 + 0{\cdot}0031F_o^2)$, maxima 0·5 e Å^{-3} in the vicinity of the disordered NO_2 group, maximum shift/e.s.d. = 0·27 for U_{12} of O2, mean shift/e.s.d. = 0·03. For (2) at convergence $R = 0{\cdot}044$, $wR = 0{\cdot}046$ for 1562 observed data, $w = 1/(\sigma^2F + 0{\cdot}0005F_o^2)$, maxima 0·8 e Å^{-3} close to the Br atom in the final difference map, maximum shift/e.s.d. = 0·05 for x of N1, mean shift/e.s.d. = 0·02. Atomic scattering factors were from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Computer programs used included *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP*II (Johnson, 1976). Final fractional coordinates with equivalent isotropic temperature factors are in Table 1. Table 2 contains molecular dimensions.* Views (Johnson, 1976) of the ions of (1) and (2) are in Figs. 1 and 2.

Table 1. *Positional and equivalent isotropic thermal parameters with their e.s.d.'s*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq} (Å^2)
(1)				
Br	0·1892 (1)	0·4340 (1)	0·4231 (1)	5·7 (1)
N1	0·3987 (4)	0·6515 (4)	0·7391 (3)	4·3 (2)
C2	0·3960 (7)	0·5641 (5)	0·8267 (4)	5·1 (3)
C3	0·4767 (6)	0·4216 (5)	0·7985 (4)	4·9 (2)
N4	0·3563 (4)	0·3103 (4)	0·7199 (3)	4·5 (2)
C5	0·2737 (5)	0·3254 (4)	0·6228 (3)	4·1 (2)
C6	0·2809 (4)	0·4585 (4)	0·5798 (3)	3·9 (2)
C7	0·3479 (5)	0·6062 (4)	0·6311 (3)	4·1 (2)
C51	0·1735 (7)	0·1825 (6)	0·5545 (4)	6·3 (3)
C71	0·3599 (7)	0·7276 (6)	0·5645 (4)	6·3 (3)
O1	0·3848 (5)	0·1045 (4)	0·1353 (4)	6·7 (2)
C11	0·2800 (5)	−0·0036 (4)	0·0878 (4)	4·3 (2)
C12	0·1998 (4)	−0·1076 (4)	0·1489 (2)	3·8 (2)
C13	0·0791 (5)	−0·2231 (4)	0·0988 (3)	3·7 (2)
C14	0·0307 (5)	−0·2520 (4)	−0·0163 (3)	3·5 (2)
C15	0·1001 (5)	−0·1630 (4)	−0·0827 (3)	3·7 (2)
C16	0·2195 (5)	−0·0438 (4)	−0·0320 (4)	4·1 (2)
N12	0·2474 (4)	−0·0829 (4)	0·2698 (2)	5·9 (3)
O2	0·4017 (5)	−0·0502 (9)	0·3115 (4)	7·5 (5)
O3	0·1405 (7)	−0·1251 (11)	0·3251 (3)	8·7 (8)
O21	0·2627 (28)	0·0471 (6)	0·3215 (5)	15·1 (16)
O31	0·2277 (25)	0·1882 (8)	0·3176 (4)	12·8 (14)
N14	−0·0963 (4)	−0·3752 (3)	−0·0683 (3)	4·1 (2)
O4	−0·1797 (4)	−0·4375 (3)	−0·0095 (3)	4·9 (2)
O5	−0·1148 (5)	−0·4156 (4)	−0·1709 (3)	6·3 (2)
N16	0·2812 (5)	0·0470 (4)	−0·1064 (4)	5·7 (2)
O6	0·2335 (5)	0·0106 (5)	−0·2064 (4)	7·8 (3)
O7	0·3827 (5)	0·1597 (4)	−0·0668 (4)	7·9 (3)
(2)				
Br	0·3077 (1)	0·3156 (1)	0·3359 (1)	5·2 (1)
N1	0·1723 (2)	0·3402 (4)	0·1228 (4)	3·6 (3)
C2	0·1296 (3)	0·4433 (5)	0·1359 (4)	3·6 (3)
C3	0·1003 (2)	0·4436 (5)	0·2389 (4)	3·4 (3)
N4	0·1408 (2)	0·4957 (4)	0·3158 (3)	3·2 (3)
C5	0·1973 (3)	0·4567 (5)	0·3330 (4)	3·3 (3)
C6	0·2298 (2)	0·3650 (5)	0·2794 (4)	3·2 (3)
C7	0·2158 (3)	0·3103 (5)	0·1877 (5)	3·4 (3)
O1	0·3723 (2)	0·2268 (3)	0·0740 (3)	3·2 (2)
C11	0·4049 (2)	0·3224 (5)	0·0865 (4)	2·5 (3)
C12	0·3805 (2)	0·4483 (5)	0·0783 (4)	2·9 (3)
C13	0·4135 (3)	0·5552 (5)	0·0959 (4)	3·1 (3)
C14	0·4763 (3)	0·5457 (5)	0·1194 (4)	3·2 (3)
C15	0·5045 (3)	0·4296 (5)	0·1265 (4)	3·2 (3)
C16	0·4709 (3)	0·3225 (5)	0·1113 (4)	2·7 (3)
N12	0·3155 (2)	0·4638 (4)	0·0500 (4)	3·6 (3)
O2	0·2920 (2)	0·3926 (4)	−0·0112 (3)	4·3 (3)
O3	0·2863 (2)	0·5516 (4)	0·0874 (4)	5·8 (3)
N14	0·5134 (3)	0·6577 (5)	0·1327 (4)	4·3 (4)
O4	0·4885 (3)	0·7591 (4)	0·1194 (4)	5·7 (3)
O5	0·5683 (2)	0·6448 (5)	0·1572 (4)	5·8 (3)
N16	0·5049 (2)	0·2068 (4)	0·1165 (4)	3·9 (4)
O6	0·5603 (2)	0·2129 (5)	0·1264 (7)	10·4 (6)
O7	0·4791 (2)	0·1079 (4)	0·1090 (4)	5·7 (3)

For (1), atoms O2, O3, O21 and O31 are disordered O atoms on N12, with occupancies 0·6, 0·6, 0·4 and 0·4, respectively.

Discussion. In the cations (Fig. 1) the bond lengths of the N4,C5,C6,C7,N1 system [mean C—C 1·413 (6), mean N—C 1·306 (5) Å for (1), mean C—C 1·390 (7), mean N—C 1·304 (7) Å for (2)] (Table 2) are consistent with fully delocalized vinamidinium systems, with the mean C—C distance for (1) just significantly longer than the mean of the corresponding bonds in (2), and in the 6-hydrogeno-5,7-dimethyl analogue [mean C—C 1·391 (4) Å] (Ferguson *et al.*, 1980); this supports the rationalization of the different reactivity towards nucleophiles of the two bromo compounds by Lloyd *et al.* (1975).

The seven-membered rings of the cations in (1) and (2) have very similar conformations and have approximate twofold symmetry, with the twofold

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* Lists of structure factors, calculated hydrogen coordinates, anisotropic thermal parameters, mean-plane data and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52657 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular dimensions*

(*a*) Bond lengths (Å) for (1)

Cation

Br	C6	1·918 (3)	N4	C5	1·302 (5)
N1	C2	1·450 (5)	C5	C6	1·410 (6)
N1	C7	1·309 (5)	C5	C51	1·518 (6)
C2	C3	1·488 (6)	C6	C7	1·415 (6)
C3	N4	1·452 (5)	C7	C71	1·496 (6)

Anion

O1	C11	1·238 (5)	C16	N16	1·448 (5)
C11	C12	1·471 (5)	N12	O2	1·228 (5)
C11	C16	1·449 (6)	N12	O3	1·230 (5)
C12	C13	1·359 (5)	N12	O21	1·233 (6)
C12	N12	1·448 (5)	N12	O31	1·225 (6)
C13	C14	1·380 (5)	N14	O4	1·224 (4)
C14	C15	1·386 (5)	N14	O5	1·231 (4)
C14	N14	1·438 (5)	N16	O6	1·208 (6)
C15	C16	1·377 (5)	N16	O7	1·235 (5)

(*b*) Bond angles (°)

Cation

C2	N1	C7	127·5 (3)	Br	C6	C5	114·3 (3)
N1	C2	C3	111·4 (3)	Br	C6	C7	114·3 (3)
C2	C3	N4	111·5 (4)	C5	C6	C7	131·4 (3)
C3	N4	C5	126·7 (3)	N1	C7	C6	124·5 (3)
N4	C5	C6	124·5 (3)	N1	C7	C71	113·7 (4)
N4	C5	C51	113·9 (3)	C6	C7	C71	121·7 (3)
C6	C5	C51	121·5 (3)				

Anion

O1	C11	C12	122·9 (4)	C15	C16	N16	115·7 (3)
O1	C11	C16	125·6 (4)	C12	N12	O2	118·9 (4)
C12	C11	C16	111·5 (3)	C12	N12	O3	118·5 (4)
C11	C12	C13	123·8 (3)	C12	N12	O21	117·5 (8)
C11	C12	N12	118·3 (3)	C12	N12	O31	118·7 (9)
C13	C12	N12	117·9 (3)	O2	N12	O3	120·8 (4)
C12	C13	C14	120·0 (3)	O21	N12	O31	121·2 (12)
C13	C14	C15	121·2 (3)	C14	N14	O4	119·3 (3)
C13	C14	N14	119·5 (3)	C14	N14	O5	118·3 (3)
C15	C14	N14	119·3 (3)	O4	N14	O5	122·4 (3)
C14	C15	C16	118·9 (4)	C16	N16	O6	119·4 (4)
C11	C16	C15	124·5 (3)	C16	N16	O7	119·6 (4)
C11	C16	N16	119·8 (3)	O6	N16	O7	121·1 (4)

(*c*) Short contact and hydrogen-bond geometry (Å and °) for (1)

Br···O5^{i}	3·035 (3)		
	N···O	H···O	N—H···O
N1—H···O1^{ii}	2·779 (6)	1·94	146
N4—H···O6^{iii}	3·166 (6)	2·23	169
N4—H···O7^{iii}	3·152 (6)	2·47	128

Symmetry code: (i) $-x,-y,-z$; (ii) $1-x,1-y,1-z$; (iii) $x,y,1+z$.

(*d*) Bond lengths (Å) for (2)

Cation

Br	C6	1·904 (5)	C3	N4	1·447 (7)
N1	C2	1·445 (7)	N4	C5	1·303 (6)
N1	C7	1·305 (7)	C5	C6	1·400 (7)
C2	C3	1·508 (8)	C6	C7	1·380 (8)

Anion

O1	C11	1·249 (6)	C15	C16	1·367 (7)
C11	C12	1·448 (7)	C16	N16	1·438 (7)
C11	C16	1·454 (7)	N12	O2	1·219 (6)
C12	C13	1·364 (7)	N12	O3	1·235 (6)
C12	N12	1·454 (7)	N14	O4	1·221 (7)
C13	C14	1·387 (8)	N14	O5	1·229 (7)
C14	C15	1·384 (7)	N16	O6	1·199 (6)
C14	N14	1·448 (7)	N16	O7	1·197 (6)

(*e*) Bond angles (°) for (2)

Cation

C2	N1	C7	124·0 (5)	Br	C6	C5	115·8 (5)
N1	C2	C3	112·4 (5)	Br	C6	C7	114·5 (4)
C2	C3	N4	112·7 (4)	C5	C6	C7	129·6 (5)
C3	N4	C5	123·7 (4)	N1	C7	C6	128·8 (5)
N4	C5	C6	127·1 (5)				

Table 2 (*cont.*)

Anion

C12	C11	C16	111·6 (4)	C11	C16	N16	120·3 (5)
C12	C11	O1	123·2 (5)	C15	C16	N16	116·4 (5)
C16	C11	O1	125·2 (5)	C12	N12	O2	119·6 (5)
C11	C12	C13	125·3 (5)	C12	N12	O3	118·3 (5)
C11	C12	N12	118·2 (4)	O2	N12	O3	122·1 (5)
C13	C12	N12	116·5 (5)	C14	N14	O4	118·4 (6)
C12	C13	C14	118·8 (5)	C14	N14	O5	117·8 (6)
C13	C14	C15	120·4 (5)	O4	N14	O5	123·8 (5)
C13	C14	N14	120·1 (5)	C16	N16	O6	117·6 (5)
C15	C14	N14	119·5 (5)	C16	N16	O7	121·3 (5)
C14	C15	C16	120·6 (5)	O6	N16	O7	121·1 (5)
C11	C16	C15	123·2 (5)				

(*f*) Short contact and hydrogen-bond geometry (Å and °) for (2)

Br···O6^{i}	3·080 (5)		
	N···O	H···O	N—H···O
N1—H···O1^{ii}	2·863 (7)	2·02	147
N1—H···O2^{ii}	2·997 (7)	2·25	135
N4—H···O1^{iii}	2·884 (7)	1·99	156
N4—H···O7^{iii}	3·020 (7)	2·35	128

Symmetry code: (i) $1-x,y,0{\cdot}5-z$; (ii) $0{\cdot}5-x,0{\cdot}5-y,-z$; (iii) $0{\cdot}5-x,0{\cdot}5+y,0{\cdot}5-z$.

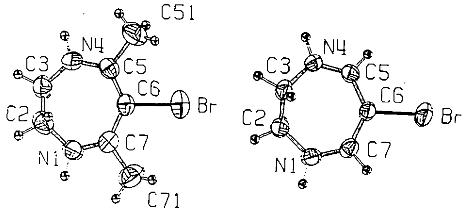


Fig. 1. The $C_7H_{12}BrN_2^+$ (left) and $C_5H_8BrN_2^+$ (right) cations with our numbering scheme. Thermal ellipsoids are at the 50% probability level.

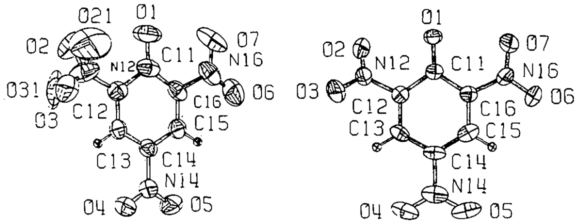
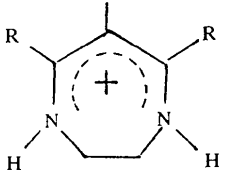


Fig. 2. The $C_6H_2N_3O_7^-$ anions in (1) (left) and in (2) (right) with our numbering scheme. Thermal ellipsoids are at the 50% probability level.

axis passing through Br, C6 and the C2—C3 midpoint. In (1) the vinamidinium atoms define a portion of a helix with torsion angles N4—C5—C6—C7 −11·3 (4)° and C5—C6—C7—N1 −9·8 (4)°. The remaining two atoms of the seven-membered ring are −0·409 (5) (C2) and +0·488 (5) Å (C3) from the plane of the delocalized atoms [torsion angle N1—C2—C3—N4 −79·5 (4)°]. The Br atom is only 0·076 (4) Å out of the plane of the delocalized 1,5-diazapentadienium chain while methyl carbons C51 and C71 are displaced from this plane by −0·367 (6) and +0·357 (6) Å respectively. Intramolecular overcrowding also causes the angles C6—C5—C51 and C6—C7—C71 [mean 121·6 (3)°] to be greater than N4—C5—C51 and N1—C7—C71 [mean 113·8 (3)°]. In (2) the vinamidinium atoms define a portion of a helix with torsion angles N4—C5—C6—C7 −12·7 (6)° and C5—C6—C7—N1 −8·3 (6)°. The remaining two atoms of the seven-membered ring are −0·394 (5) (C2) and +0·491 Å (C3) from the plane of the delocalized atoms, corresponding to an N1—C2—C3—N4 torsion angle of −80·0 (6)°. The Br atom is −0·082 (2) Å from the plane of the delocalized chain.

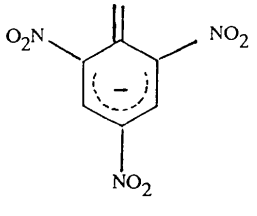
In both (1) and (2) the distances in the N—CH_2—CH_2—N moieties [mean C—N 1·451 (5) (1), 1·446 (7) (2), C—C 1·488 (6) (1), 1·508 (8) Å (2)], the C—Br distances [1·918 (3) (1), 1·904 (5) Å (2)], and the excyclic C—C distances in (1) [mean 1·507 (6) Å] are within the normal ranges (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The ring valency angles at N and sp^2-hybridized C atoms have been increased from the normal 120° to a mean value of 126·9 (3)° in (1) and 126·6 (3)° in (2) (Table 2); angles involving sp^2-hybridized C atoms [mean 111·5 (4) in (1), 112·5 (5)° in (2)] are close to those expected.

The six-membered rings of the picrate anions (Fig. 2) in (1) and (2) are essentially planar and their dimensions [for (1) C11—O1 1·238 (5), C11—C12 and C11—C16 mean 1·460 (6), other C—C ring bonds mean 1·376 (5) Å; for (2) C11—O1 1·249 (6), C11—C12 and C11—C16 mean 1·451 (7), other C—C ring bonds mean 1·376 (7) Å] are consistent with a major contribution from a resonance form as shown below 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, 1983; Ferguson, Ruhl, Wieckowski, Lloyd & McNab, 1984). Only one of the nitro groups in the anion of (1) and two in the anion of (2) are approximately coplanar with the relevant picrate ring; the out-of-plane rotations are undoubtedly associated with packing and hydrogen-bond considerations.



(1) R = CH_3

(2) R = H



The crystal structure of (1) contains discrete 6-bromo-2,3-dihydro-5,7-dimethyl-1,4-diazepinium cations and picrate anions linked to form tetrameric rings in which centrosymmetrically related pairs of cations and anions are linked by bifurcated N—H···O hydrogen bonds [N1···O1^{i} 2·779 (6), N4···O6^{ii} 3·166 (6) and N4···O7^{ii} 3·153 (6) Å]. There is also a short inter-ion contact between the bromine and a nitro O atom [Br···O5 3·035 (4) Å]. The picrate anions are associated in pairs about the origin with an interplanar separation of 3·34 Å, and are stacked along the **a** direction. Other inter-ion contacts correspond to normal van der Waals interactions.

The crystal structure of (2) contains discrete cations and anions linked to form infinite chains by bifurcated N—H···O hydrogen bonds [N1···O1^{i} 2·863 (7), N1···O2^{i} 2·997 (7), N4···O1^{ii} 2·884 (7) and N4···O7^{ii} 3·020 (7) Å]. There is also a short inter-ion contact between the bromine and a nitro O atom [Br···O6 3·080 (6) Å]. The picrate anions do not overlap fully and are stacked along the **c** direction by operation of inversion centres and twofold axes with interplanar separations of 3·28 Å; other inter-ion contacts correspond to normal van der Waals interactions.

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