# An X-ray Crystallographic Study of 1,2,5- and 1,3,5-Triazapentadienium Salts, $C_6H_{14}N_3^+.ClO_4^-$, $C_6H_{14}N_3^+.ClO_4^-$, $C_6H_{14}N_3^+.C_6H_2N_3O_7^-$

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**Abstract.** The structures of 1,1,5,5-tetramethyl-1,3,5-triazapentadienium perchlorate (2*a*), 1,1,5,5-tetramethyl-1,2,5-triazapentadienium perchlorate (3*a*), and the corresponding picrate (3*b*) were determined with Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å. Compound (2*a*): $M_r = 228$, $Cc$, $a = 8.022$ (1), $b = 18.583$ (2), $c = 7.512$ (2) Å, $\beta = 103.97$ (2)°, $U = 1087$ Å$^3$, $Z = 4$, $D_x = 1.39$ g cm$^{-3}$, $\mu = 3.5$ cm$^{-1}$, $F(000) = 480$, $T = 293$ K, $R = 0.045$ for 656 observed reflections. Compound (3*a*): $M_r = 228$, $P2_1$, $a = 10.638$ (10), $b = 7.015$ (9), $c = 15.087$ (12) Å, $\beta = 99.77$ (10)°, $U = 1110$ Å$^3$, $Z = 4$, $D_x = 1.36$ g cm$^{-3}$, $\mu = 3.5$ cm$^{-1}$, $F(000) = 480$, $T = 293$ K, $R = 0.058$ for 1135 observed reflections. Picrate salt (3*b*): $M_r = 356$, $P\bar{1}$, $a = 8.374$ (1), $b = 9.485$ (1), $c = 11.756$ (3) Å, $\alpha = 66.895$ (22), $\beta = 75.504$ (14), $\gamma = 82.577$ (15)°, $U = 831$ Å$^3$, $Z = 2$, $D_x = 1.36$ g cm$^{-2}$, $\mu = 1.2$ cm$^{-1}$, $F(000) = 372$, $T = 293$ K, $R = 0.054$ for 1542 observed reflections. The cations show an all-*trans* planar structure: the bond lengths and angles are interpreted in terms of lone-pair and non-bonded interactions.

**Introduction.** The effect of the replacement of CH groups in delocalized systems by nitrogen atoms has most often been studied with cyclic model compounds. The comparison of pyridine with benzene is a classic example (Mootz & Wussow, 1981). From a structural point of view, the incorporation of two relatively short C—N bonds into the cyclic structure causes significant distortion, especially of the bond angles, but the role of the nitrogen atom itself remains unclear. In this paper, we examine some *acyclic* delocalized systems, and have chosen the electron-rich 1,5-diazapentadienium group (1) as the basis for the investigation. The terminal nitrogen atoms contribute two electrons to the six-$\pi$-electron framework, and so the two possible aza analogues are the symmetrical 1,3,5-triazapentadienium cation (2) and the unsymmetrical 1,2,5-triazapentadienium cation (3).

X-ray crystal structure data for the parent system are available for the two N-substituted examples (1*a*) (Matthews, Stenkamp & Colman, 1973) and (1*b*) (Zedler & Kulpe, 1970) though corresponding results for the triaza system (2) have been reported only for examples with multiple polar substituents [*e.g.* (4)]
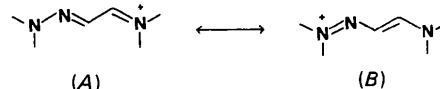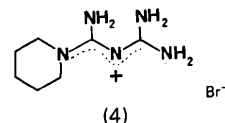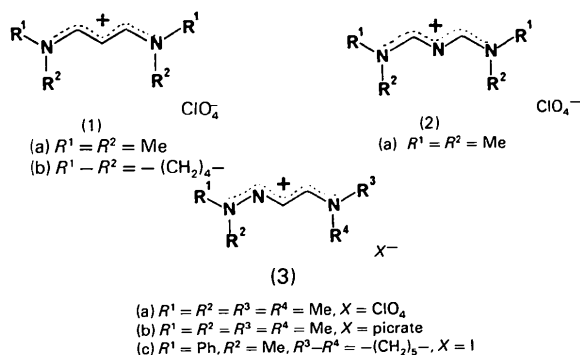


(Handa & Saha, 1973). While this present work was in progress the structure of the aryl derivative (3*c*) was reported (Nagel & Allmann, 1981), though in that case the inherent asymmetry of the delocalized system may be affected by the asymmetry of the substituents. In contrast, the present work is restricted to the 1,1,5,5-tetramethyl derivatives (2*a*) (Gold, 1960), (3*a*) (McNab, 1978) and (3*b*) (McNab, 1978). The picrate (3*b*) was investigated because of some disorder in the structure of the perchlorate (3*a*), and it also allows an assessment of the effect of the counterion on the overall structure.

**Experimental.** (2*a*) Crystal $0.2 \times 0.2 \times 0.35$ mm, 12 zero level and 4 upper level reflections for measuring lattice parameters, 2200 reflections, layers *hk*0 through *hk*8, Stoe two-circle diffractometer (no standard reflections measured), $2\theta_{max} = 50°$, 950 unique reflections, 656 observed, $I > 2.5\sigma(I)$, no absorption correction, direct methods (Main, Lessinger, Woolfson, Germain & Declercq, 1977), refinement with *SHELX* (Sheldrick,

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1976); in final cycles of full-matrix least-squares refinement on $F$, all non-hydrogen atoms anisotropic, H atoms in calculated positions with C—H 1·08 Å, methyl groups refined as rigid groups, H atoms in each group constrained to have the same isotropic thermal parameter, H atoms attached to C(2) and C(4) refined with isotropic temperature factors constrained to be equal; 142 parameters refined in the final cycle; ratio of largest shift to estimated standard deviation was 0·01, the largest peak on a difference Fourier map corresponded to less than 0·25 e Å⁻³; unit weights gave an even distribution of variance in $|F|$ analysed in ranges of $|F|$ and $\sin\theta$, $wR = 0·043$, $R = 0·045$, scattering factors from *SHELX*.

(3a) Crystal 0·15 × 0·2 × 0·35 mm, 12 zero level and 4 upper level reflections for measuring lattice parameters, layers $h0l$ through $h8l$, Stoe two-circle diffractometer (no standard reflections measured), 2118 unique reflections, $2\theta_{max} = 50°$, 1135 observed, $I > 2·5\sigma(I)$, no absorption correction; a recognizable fragment was obtained with *MULTAN* (Main *et al.*, 1977). There are two crystallographically unrelated molecules in the unit cell, each lying almost exactly on the plane at $y = \frac{1}{4}$, as do the chlorine atoms of the perchlorate anions. Two possible models were examined corresponding to space groups $P2_1$ and $P2_1/m$; the latter imposes a molecular mirror plane through both cations. The best model in $P2_1/m$ required drastically disordered $ClO_4^-$ ions and methyl groups and converged (refinement on $F$) with $R = 0·067$. The $P2_1$ model gave a rather better convergence with much less disorder with a final $R = 0·058$. H atoms were input in calculated positions. Methyl groups were refined as rigid groups with C—H = 1·08 Å and H—C—H = 109·5° (single isotropic temperature factor for the three atoms). Both perchlorate ions were rotationally disordered and refinement was facilitated by constraining the Cl—O distance to be 1·37 ± 0·03 Å. In the final cycles, all non-hydrogen atoms were refined anisotropically. A unit weighting scheme was found to give a relatively even distribution of variance in $|F|$ analysed in ranges of both $|F|$ and $\sin\theta$; $wR = 0·057$, 288 parameters refined; in final cycle no shift was greater than 0·6 times its e.s.d., highest residual peaks on a final difference map were less than 0·5 e Å⁻³ and were close to the disordered perchlorate ions, scattering factors from *SHELX*.

(3b) Crystal 0·2 × 0·3 × 0·3 mm, 25 reflections with 20 < 2θ < 30° for measuring lattice parameters, CAD-4 diffractometer, 2884 unique reflections, $\theta \le 25°$, $0 < h < 9, -11 < k < 11, -14 < l < 14$, 1542 observed, $I > 2·5\sigma(I)$, no absorption correction, 2 standard reflections varied <1%; high-angle reflections weak indicating probable disorder; direct methods (Sheldrick, 1976), refinement on $F$, non-hydrogen atoms anisotropic, H atoms located in difference Fourier maps and refined, H atoms on the same methyl group constrained to have the same isotropic temperature factor (which was refined); weighting scheme which gave the best

analysis of variance in range of $|F|$ was $w = 1/[\sigma^2(F) + 0·00044 F^2]$; in final cycle 281 parameters refined, $R = 0·054$ ($wR = 0·067$), ratio of largest shift to e.s.d. was 0·01, largest peaks in the final difference Fourier map were about 0·25 e Å⁻³ and were near the $NO_2$ groups in the picrate ion. The large anisotropic thermal terms for the $NO_2$ oxygen atoms are consistent with a slight rotational disorder about the N—C bond. Scattering factors from *SHELX*.

**Discussion.** Positional parameters for non-hydrogen atoms are given in Tables 1, 2 and 3.* Bond lengths, angles, and torsion angles for all cations are given in Table 4, and projections of the cations of each structure into their best planes are shown in Fig. 1.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38520 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates of atoms with e.s.d.'s for compound (2a)*

$U_{eq} = \frac{1}{3}$ trace **U**.

|       | $x$          | $y$          | $z$          | $U_{eq}(Å^2)$ |
|-------|--------------|--------------|--------------|---------------|
| Cl    | 0·11430      | 0·63354 (11) | 0·00259      | 0·0574        |
| O(1)  | −0·0305 (10) | 0·3222 (4)   | 0·4330 (13)  | 0·0993        |
| O(2)  | 0·2235 (12)  | 0·3266 (6)   | 0·6466 (15)  | 0·1415        |
| O(3)  | 0·0709 (12)  | 0·4280 (4)   | 0·5899 (13)  | 0·1068        |
| O(4)  | 0·2040 (16)  | 0·3789 (7)   | 0·3757 (15)  | 0·1963        |
| C(11) | −0·3196 (14) | 0·6797 (5)   | 0·2103 (14)  | 0·0635        |
| C(12) | −0·0495 (12) | 0·6723 (5)   | 0·4538 (14)  | 0·0664        |
| N(1)  | −0·1953 (9)  | 0·6346 (4)   | 0·3353 (9)   | 0·0487        |
| C(2)  | −0·2074 (12) | 0·5644 (5)   | 0·3319 (13)  | 0·0503        |
| N(3)  | −0·3376 (9)  | 0·5304 (3)   | 0·2222 (10)  | 0·0477        |
| C(4)  | −0·3389 (12) | 0·4598 (4)   | 0·2396 (11)  | 0·0452        |
| N(5)  | −0·4649 (10) | 0·4214 (3)   | 0·1456 (9)   | 0·0518        |
| C(51) | −0·6198 (11) | 0·4539 (5)   | 0·0222 (13)  | 0·0631        |
| C(52) | −0·4674 (15) | 0·3432 (4)   | 0·1707 (16)  | 0·0768        |

Table 2. *Fractional coordinates of atoms with e.s.d.'s for compound (3a)*

Unprimed atoms are in molecule 1, primed atoms in molecule 2.
$U_{eq} = \frac{1}{3}$ trace **U**.

|        | $x$           | $y$          | $z$          | $U_{eq}(Å^2)$ |
|--------|---------------|--------------|--------------|---------------|
| Cl(1)  | −1·31734 (21) | −0·25        | −0·05065 (15)| 0·0691        |
| O(1)   | −1·2469 (15)  | −0·4090 (21) | −0·0643 (12) | 0·1677        |
| O(2)   | −1·3320 (13)  | −0·282 (3)   | 0·0368 (5)   | 0·1927        |
| O(3)   | −1·2607 (14)  | −0·0874 (15) | −0·0815 (7)  | 0·0854        |
| O(4)   | −1·4397 (7)   | −0·271 (4)   | −0·1011 (8)  | 0·2075        |
| Cl(2)  | −0·70953 (21) | −0·2547 (11) | 0·59831 (16) | 0·0700        |
| O(5)   | −0·6330 (11)  | −0·278 (4)   | 0·5357 (7)   | 0·1997        |
| O(6)   | −0·6707 (16)  | −0·3787 (22) | 0·6650 (9)   | 0·1997        |
| O(7)   | −0·7437 (18)  | −0·0793 (16) | 0·6272 (11)  | 0·1707        |
| O(8)   | −0·8249 (13)  | −0·316 (4)   | 0·5618 (14)  | 0·3207        |
| C(11)  | −1·3243 (9)   | −0·247 (4)   | 0·7004 (7)   | 0·0775        |
| C(12)  | −1·2653 (13)  | −0·276 (5)   | 0·5433 (7)   | 0·1259        |
| N(1)   | −1·2277 (8)   | −0·261 (3)   | 0·6444 (5)   | 0·0708        |
| N(2)   | −1·1052 (9)   | −0·251 (3)   | 0·6759 (6)   | 0·0800        |
| C(3)   | −1·0621 (9)   | −0·252 (3)   | 0·7634 (6)   | 0·0599        |
| C(4)   | −0·9317 (11)  | −0·257 (3)   | 0·7857 (7)   | 0·0619        |
| N(5)   | −0·8667 (7)   | −0·255 (3)   | 0·8665 (6)   | 0·0651        |
| C(51)  | −0·9264 (11)  | −0·261 (5)   | 0·9482 (7)   | 0·1012        |
| C(52)  | −0·7228 (8)   | −0·247 (4)   | 0·8838 (7)   | 0·0767        |

Table 2 (cont.)

| | $x$ | $y$ | $z$ | $U_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| C(11') | −1·0021 (13) | −0·279 (4) | 0·3801 (9) | 0·1104 |
| C(12') | −1·1444 (9) | −0·226 (4) | 0·2302 (11) | 0·1083 |
| N(1') | −1·0180 (8) | −0·259 (3) | 0·2836 (7) | 0·0889 |
| N(2') | −0·9219 (7) | −0·257 (3) | 0·2371 (5) | 0·0662 |
| C(3') | −0·8031 (8) | −0·246 (4) | 0·2811 (6) | 0·0511 |
| C(4') | −0·7146 (8) | −0·242 (3) | 0·2234 (7) | 0·0514 |
| N(5') | −0·5927 (6) | −0·259 (3) | 0·2475 (5) | 0·0573 |
| C(51') | −0·5274 (10) | −0·254 (4) | 0·3413 (7) | 0·0827 |
| C(52') | −0·5080 (11) | −0·271 (4) | 0·1771 (8) | 0·0819 |

Table 3. *Fractional coordinates of atoms with e.s.d.'s for compound* (3b)

*P* indicates atoms in the picrate ion.

$U_{eq} = \frac{1}{3}\text{trace } \mathbf{U}.$

| | $x$ | $y$ | $z$ | $U_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| C(1P) | 0·2826 (5) | 0·5313 (5) | 0·8307 (4) | 0·0664 |
| C(2P) | 0·1766 (5) | 0·6646 (5) | 0·8285 (3) | 0·0626 |
| C(3P) | 0·1084 (4) | 0·7001 (5) | 0·9333 (4) | 0·0619 |
| C(4P) | 0·1394 (4) | 0·6043 (4) | 1·0493 (3) | 0·0574 |
| C(5P) | 0·2378 (5) | 0·4729 (5) | 1·0608 (4) | 0·0620 |
| C(6P) | 0·3072 (4) | 0·4431 (4) | 0·9561 (4) | 0·0627 |
| O(1P) | 0·3430 (4) | 0·4914 (4) | 0·7393 (3) | 0·1093 |
| N(2P) | 0·1338 (6) | 0·7685 (5) | 0·7106 (4) | 0·0906 |
| O(21P) | 0·0214 (7) | 0·8602 (5) | 0·7149 (4) | 0·1391 |
| O(22P) | 0·2135 (5) | 0·7606 (5) | 0·6106 (3) | 0·1314 |
| N(4P) | 0·0717 (4) | 0·6432 (5) | 1·1589 (4) | 0·0834 |
| O(41P) | 0·0901 (4) | 0·5484 (5) | 1·2622 (3) | 0·1140 |
| O(42P) | −0·0005 (5) | 0·7653 (5) | 1·1447 (3) | 0·1295 |
| N(6P) | 0·4133 (6) | 0·3029 (6) | 0·9733 (5) | 0·1090 |
| O(61P) | 0·3549 (8) | 0·1845 (6) | 1·0559 (5) | 0·1763 |
| O(62P) | 0·5437 (5) | 0·3122 (5) | 0·8991 (5) | 0·1690 |
| C(11) | 0·3512 (8) | −0·1240 (6) | 1·2974 (5) | 0·0951 |
| C(12) | 0·6467 (7) | −0·0685 (7) | 1·1933 (6) | 0·0960 |
| N(1) | 0·4955 (4) | −0·0398 (4) | 1·2742 (3) | 0·0690 |
| N(2) | 0·4937 (4) | 0·0709 (4) | 1·3121 (3) | 0·0643 |
| C(3) | 0·3591 (5) | 0·1105 (4) | 1·3804 (3) | 0·0563 |
| C(4) | 0·3752 (5) | 0·2332 (4) | 1·4116 (3) | 0·0588 |
| N(5) | 0·2629 (4) | 0·2945 (3) | 1·4771 (3) | 0·0571 |
| C(51) | 0·0965 (6) | 0·2389 (6) | 1·5304 (5) | 0·0790 |
| C(52) | 0·2952 (7) | 0·4319 (6) | 1·4943 (5) | 0·0908 |



(2a)          (3a), molecule 1
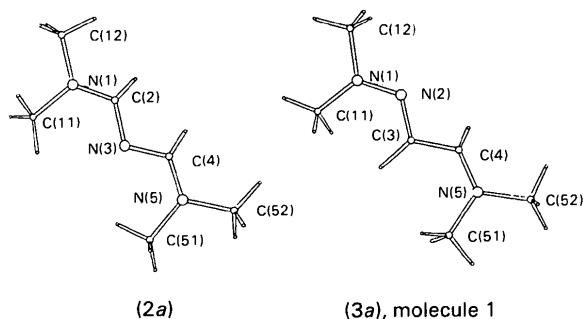
(3a), molecule 2          (3b)

Fig. 1. Projections, into their best planes, of the cations of (2a), (3a), and (3b).

In structure (2a), there are no statistically significant differences in length between chemically equivalent C—N bonds, though as expected the N—methyl bonds are significantly longer than the other N—C bonds in the cation. One bond angle at each N atom is less than 117°. The non-methyl hydrogen atoms of the cation have a root-mean-square deviation of 0·05 Å from their

Table 4. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

| Atoms (2a) | (2a) | (3a) Molecule 1 | (3a) Molecule 2 | (3b) | Atoms (3a) and (3b) |
|---|---|---|---|---|---|
| C(11)–N(1) | 1·458 (11) | 1·440 (15) | 1·443 (18) | 1·444 (8) | C(11)–N(1) |
| C(12)–N(1) | 1·467 (11) | 1·514 (13) | 1·464 (14) | 1·447 (6) | C(12)–N(1) |
| N(1)–C(2) | 1·308 (12) | 1·311 (12) | 1·335 (13) | 1·289 (6) | N(1)–N(2) |
| C(2)–N(3) | 1·324 (11) | 1·322 (12) | 1·326 (11) | 1·316 (5) | N(2)–C(3) |
| N(3)–C(4) | 1·319 (10) | 1·371 (14) | 1·387 (14) | 1·381 (7) | C(3)–C(4) |
| C(4)–N(5) | 1·298 (11) | 1·295 (13) | 1·292 (11) | 1·290 (5) | C(4)–N(5) |
| N(5)–C(51) | 1·487 (11) | 1·480 (14) | 1·467 (11) | 1·451 (6) | N(5)–C(51) |
| N(5)–C(52) | 1·466 (11) | 1·510 (11) | 1·507 (15) | 1·462 (8) | N(5)–C(52) |
| C(11)–N(1)–C(12) | 116·0 (7) | 120·2 (9) | 120·6 (11) | 119·1 (4) | C(11)–N(1)–C(12) |
| C(11)–N(1)–C(2) | 121·6 (7) | 123·2 (8) | 124·2 (9) | 123·4 (3) | C(11)–N(1)–N(2) |
| C(12)–N(1)–C(2) | 122·2 (7) | 116·5 (9) | 115·0 (11) | 117·2 (4) | C(12)–N(1)–N(2) |
| N(1)–C(2)–N(3) | 122·1 (8) | 121·1 (10) | 119·2 (8) | 121·4 (3) | N(1)–N(2)–C(3) |
| C(2)–N(3)–C(4) | 115·9 (7) | 114·2 (10) | 112·2 (8) | 114·8 (4) | N(2)–C(3)–C(4) |
| N(3)–C(4)–N(5) | 121·1 (7) | 125·9 (10) | 125·3 (9) | 127·2 (4) | C(3)–C(4)–N(5) |
| C(4)–N(5)–C(51) | 122·7 (7) | 123·2 (8) | 123·9 (9) | 122·8 (4) | C(4)–N(5)–C(51) |
| C(4)–N(5)–C(52) | 120·5 (7) | 121·8 (9) | 119·9 (8) | 120·8 (3) | C(4)–N(5)–C(52) |
| C(51)–N(5)–C(52) | 116·6 (7) | 115·0 (8) | 116·1 (7) | 116·3 (4) | C(51)–N(5)–C(52) |
| C(11)–N(1)–C(2)–N(3) | −3·7 (15)* | 9 (4) | −9 (4) | 3·0 (5)* | C(11)–N(1)–N(2)–C(3) |
| C(12)–N(1)–C(2)–N(3) | −178·7 (9) | −174 (2) | 166 (2) | 176·4 (4) | C(12)–N(1)–N(2)–C(3) |
| N(1)–C(2)–N(3)–C(4) | −176·4 (9) | 175 (2) | −179 (2) | −178·7 (3) | N(1)–N(2)–C(3)–C(4) |
| C(2)–N(3)–C(4)–N(5) | 176·5 (9) | 178 (2) | −169 (2) | 179·9 (4) | N(2)–C(3)–C(4)–N(5) |
| N(3)–C(4)–N(5)–C(51) | −3·9 (14) | 5 (4) | −11 (4) | 0·6 (6) | C(3)–C(4)–N(5)–C(51) |
| N(3)–C(4)–N(5)–C(52) | −178·0 (9) | −176 (2) | 174 (2) | −175·3 (4) | C(3)–C(4)–N(5)–C(52) |

* In these cases, symmetry-related molecules will have the opposite hand.

best plane. Each methyl hydrogen atom is within 2·5 to 2·8 Å of a perchlorate oxygen atom. Cations stack along **c**, with a separation of 3·706 (2) Å, which is probably too large for any cooperative stacking effect.

In (3a), there are no statistically significant differences in bond lengths between the two crystallographically independent ions. The only marked differences are between N—methyl-carbon bond lengths which range from 1·44 (2) to 1·51 (1) Å. All other corresponding C—C, C—N and N—N bonds are within about one standard deviation of one another and lie within the expected ranges for a partially delocalized system. Bond angles are also consistent between the two molecules. Noteworthy here are the narrow central N—C—C angles of 114·2 (10) and 112·2 (8)°. There is also, as in (2a), one significantly narrow angle at each of the methyl-substituted nitrogen atoms. The non-hydrogen atoms have a root-mean-square deviation from their best planes of 0·05 and 0·09 Å for the two ions. The ions are essentially coplanar with a dihedral angle of 4 (1)° between the two best planes. The cations lie in sheets perpendicular to the $2_1$ screw axis with an intersheet separation of $b/2 = 3·51$ (1) Å. This suggests that there may be a cooperative stacking effect as found for example in base stacking in B-DNA in which the interbase separation is 3·4 Å (Wing et al., 1980). The chlorine atoms of the perchlorate ions also lie in these planes and each of the eight crystallographically independent methyl groups has O···C contacts of between 2·9 and 3·3 Å.

The bond lengths and angles of the cation of (3b) are consistent with those of (3a) and show the same narrow angle at C(3). The carbon and nitrogen atoms of the cation chain are coplanar with a r.m.s. deviation of 0·007 Å from their best plane. This rises to 0·05 Å if the terminal methyl carbons are included. All 16 hydrogen atoms were located and refined, giving C—H bond lengths between 0·88 and 1·01 Å with e.s.d.'s of about 0·05 Å. Both of the protons on the delocalized system, H(3) and H(4), lie in the plane of the cation.

The picrate ion of (3b) shows marked distortions from benzene geometry (Jones & Kennard, 1977; Bernstein, Regev & Herbstein, 1980). Bond lengths and angles are summarized in Table 5. The numbering system is given in Fig. 2. The major distortions of the ring occur at C(1), where the in-ring angle of 110·9 (4)° is compensated by the adjacent angles at C(2) and C(6) of 124·0 (3) and 126·2 (2)°. The r.m.s. deviation of the carbon atoms from the best plane of the ring is 0·010 Å and this increases to 0·017 Å if the nitrogen and oxygen substituent atoms are included in the plane calculation. The nitro groups are significantly tilted out of the ring plane. The interplanar angles are 13·9 (4)° at C(2), 7·3 (4)° at C(4), and 49·4 (5)° at C(6). This twist, which has been observed in other picrates (Jones & Kennard, 1977; Bernstein et al., 1980), may be related to the distinctive ion pairing in the crystal, shown in Fig. 2. The planes of anion and cation are mutually perpendicular [dihedral angle

88 (1)°] with the short contacts shown. The large twist at C(6) allows O(61) to interact with both N(1) and N(2) of the cation chain.

As previously found for (1), the delocalized systems in (2) and (3) are almost planar, and adopt the all-*trans* configuration. These results confirm previous speculation based in part on spectroscopic data (McNab, 1978).

Four bonding types are involved in the conjugation, *viz* terminal C—N bonds, central C—N bonds, C—C bonds, and N—N bonds. Average values of these parameters are given in Table 6, along with model comparisons with aromatic compounds. In general, the bond lengths found in the cations (1)–(3) are shorter than in the corresponding aromatic, *i.e.* C—C bonds are shorter than in benzene, C—N bonds are shorter than in pyridine, *etc.* It is possible that this effect is due to an increase in bond order caused by six $\pi$ electrons being delocalized over four bonds.

Table 5. *Bond lengths (Å) and angles (°) for the picrate anion of (3b)*

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·443 (6) | C(6)—C(1)—C(2) | 110·9 (4) |
| C(2)—C(3) | 1·372 (5) | C(1)—C(2)—C(3) | 124·0 (3) |
| C(3)—C(4) | 1·377 (5) | C(2)—C(3)—C(4) | 119·5 (4) |
| C(4)—C(5) | 1·382 (6) | C(3)—C(4)—C(5) | 120·6 (4) |
| C(5)—C(6) | 1·344 (6) | C(4)—C(5)—C(6) | 118·8 (3) |
| C(6)—C(1) | 1·434 (5) | C(5)—C(6)—C(1) | 126·2 (2) |
| C(1)—O(1) | 1·246 (6) | C(6)—C(1)—O(1) | 122·6 (4) |
| C(2)—N(2) | 1·451 (5) | C(2)—C(1)—O(1) | 126·4 (3) |
| N(2)—O(21) | 1·223 (7) | C(1)—C(2)—N(2) | 119·8 (4) |
| N(2)—O(22) | 1·202 (6) | C(3)—C(2)—N(2) | 116·2 (4) |
| C(3)—H(3) | 0·89 (5) | C(2)—N(2)—O(21) | 118·5 (4) |
| C(4)—N(4) | 1·439 (6) | C(2)—N(2)—O(22) | 119·1 (4) |
| N(4)—O(41) | 1·228 (5) | O(21)—N(2)—O(22) | 122·3 (4) |
| N(4)—O(42) | 1·205 (6) | C(3)—C(4)—N(4) | 119·7 (4) |
| C(5)—H(5) | 0·92 (5) | C(5)—C(4)—N(4) | 119·7 (3) |
| C(6)—N(6) | 1·474 (6) | C(4)—N(4)—O(41) | 117·6 (4) |
| N(6)—O(61) | 1·221 (7) | C(4)—N(4)—O(42) | 118·6 (3) |
| N(6)—O(62) | 1·204 (6) | O(41)—N(4)—O(42) | 123·8 (4) |
| | | C(5)—C(6)—N(6) | 116·6 (4) |
| | | C(1)—C(6)—N(6) | 117·2 (4) |
| | | C(6)—N(6)—O(61) | 116·6 (5) |
| | | C(6)—N(6)—O(62) | 117·6 (4) |
| | | O(61)—N(6)—O(62) | 125·5 (6) |
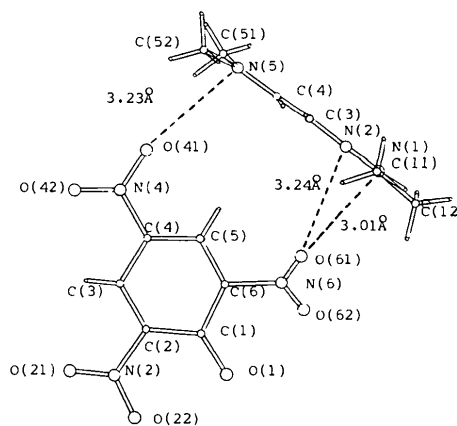


Fig. 2. Numbering system and ion pairing for the ions in (3b). E.s.d.'s are 0·01 Å.

Table 6. *Average bond lengths* (Å) *in cations* (1)–(3)
*and related model systems*

| Compound | C$\doteq$N Terminal | C$\doteq$N Central | C$\doteq$C | N$\doteq$N |
|---|---|---|---|---|
| (1a)[a] | 1·308 | — | 1·381 | — |
| (2a) | 1·303 | 1·322 | — | — |
| (3a) | 1·294 | 1·324 | 1·379 | 1·323 |
| (3b) | 1·290 | 1·316 | 1·381 | 1·289 |
| Benzene[b] | — | — | 1·397 | — |
| Pyridine[c] | — | 1·336 | 1·378, 1·381 | — |
| Pyridazine[d] hydrochloride | — | 1·314 | 1·377, 1·406 | 1·334 |

References: (a) Matthews *et al.* (1973); (b) Bacon, Curry & Wilson (1964); (c) Mootz & Wussow (1981); (d) Ottersen (1975).

The observed trends in the bond angles within the delocalized systems of compounds (2)–(3) may be explained in terms of non-bonded interactions and lone-pair repulsions. Thus the narrow angle at the central nitrogen atom of (2a) [115·9 (7)°], which is similar to that of pyridine (116·6°) (Mootz & Wussow, 1981), is presumably due to lone-pair effects. The angle at N(2) of structures (3a) and (3b), weighted mean 120·6 (6)°, is rather wider, and this may be caused by competing effects of lone-pair repulsions, and of non-bonded interactions between the 1-(Z)-methyl group [C(11)] and the central hydrogen atom, H(3). Relief of non-bonded interactions between the central hydrogen atom and the 5-(Z)-methyl group of (3a) and (3b) [C(51)] probably explains the exceptionally wide angle [weighted mean 126·7 (6)°] at C(4) and the narrow angle [114·2 (10)°] at the central carbon of these structures. In the latter case, the absence of a hydrogen atom at the 2-position allows the hydrogen attached to C(4) to move closer to N(2).

The angles subtended by the N-methyl groups at the terminal nitrogen atoms also follow trends which can be rationalized on the basis of non-bonded interactions.

Thus the angle between the (Z)-methyl group, C(11) or C(51), and the chain is always >120°, but the effect is less pronounced in (2a) which has no central hydrogen atom. Similarly, the absence of a hydrogen at position 2 in (3) allows a much smaller angle between the (E)-methyl group, C(12), and the chain.

Earlier spectroscopic data (McNab, 1978) had suggested that structure (A) was the predominant canonical form of the unsymmetrical cation (3). A comparison of C—N and C—C bond lengths within the series (1)–(3) shows that such non-equivalence has a negligible effect on the structure, and that the cation is best represented as a fully delocalized system.

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# Structure d'Agents Mutagènes. II. Le Méthoxy-8 Nitro-2 Naphto[2,1-b]furanne, C₁₃H₉NO₄

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**Abstract.** $M_r = 243·2$, $P2_1/c$, $a = 9·400$ (3), $b = 10·945$ (3), $c = 10·738$ (4) Å, $\beta = 97·80$ (2)°, $V = 1094·5$ Å$^3$, $Z = 4$, $D_m = 1·48$, $D_x = 1·476$ g cm$^{-3}$, Cu $K\bar{\alpha}$, $\lambda = 1·54184$ Å, $\bar{\mu} = 9·5$ cm$^{-1}$, $F(000) = 504$, $T = 298$K, $R = 0·056$ for 1159 reflections. This is an isomer of the 7-methoxy analog (R 7000), the most effective mutagenic agent, to which it is very similar as far as geometrical parameters are concerned.