

Table 3. *Puckering parameters for the fused rings*

	A	B	C
q_1 (Å)	0.102 (6)	0.652 (5)	0.042 (2)
ϕ_1 (°)	140 (3)	12.6 (5)	
q_2 (Å)		-0.056 (5)	
Q_2 (Å)		0.654 (5)	
θ (°)		94.9 (5)	

methyl group of the ethoxycarbonyl moiety lies almost on the perpendicular axis of the *p*-chlorophenyl ring at 3.85 (1) Å from the least-squares plane. This feature may be correlated with the unusual chemical shift of the methyl protons ($\delta = 0.85$). This shielding effect is due to the diamagnetic anisotropy of the aromatic ring facing the methyl group. These observations assured us that the conformation of the system remains substantially unchanged in CDCl_3 solution.

Intermolecular distances shorter than the sum of the van der Waals radii are found for $\text{Cl}\cdots\text{Cl}(-x, -y, -z) = 3.154$ (4) Å and for $\text{C}(32)\cdots\text{O}(11)(0.5-x, y-0.5, 1-z) = 3.091$ (4) Å.

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Structure of 1-Adamantanylammonium Trinitromethide

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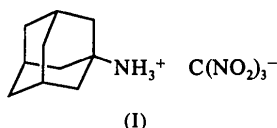
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Abstract. $\text{C}_{11}\text{H}_{18}\text{N}_4\text{O}_6$, $M_r = 302.3$, orthorhombic, *Pnma*, $a = 23.802$ (9), $b = 8.431$ (3), $c = 7.166$ (2) Å, $V = 1438.0$ (8) Å³, $Z = 4$, D_m (floatation) = 1.37 (5), $D_x = 1.396$ g cm⁻³, m.p. 464 (1) K, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å (graphite monochromator), $\mu = 1.234$ cm⁻¹, $F(000) = 640$, $T = 293$ K, final $R = 0.048$ for 860 reflections with $I > 3\sigma(I)$. Both the adamantanylammonium cation and trinitromethide anion

possess mirror symmetry. The cation is linked to three trinitromethide anions by six N–H \cdots O hydrogen bonds through the three ammonium hydrogens.

Introduction. There is considerable interest in the synthesis and chemistry of high density energetic materials (Alster, Iyer & Marchand, 1983/1984). The adamantane skeleton and nitro groups are attractive

ingredients for the preparation of high-density energetic materials. The crystal structure of 2,2-dinitroadamantane has been reported previously (George & Gilardi, 1983). We now report the crystal structure of the title compound (I).



Experimental. Yellowish crystal formed from a 1:1 mixture of saturated potassium trinitromethide and (I) dissolved in minimum amount of water; $0.4 \times 0.35 \times 0.1$ mm rectangular plate; Enraf-Nonius CAD-4 diffractometer; monochromated Mo radiation; cell parameters from 25 reflections ($7.5 < \theta < 14.2^\circ$); θ - 2θ scan, $\theta = 1.03$ - $8.24^\circ \text{ min}^{-1}$; 96 steps over the θ range of $1.5(1.2^\circ + 0.35^\circ \tan \theta)$, processed with a modified Lehmann-Larsen profile analysis procedure (Lehmann & Larsen, 1974; Ammon, 1986); seven standards (33I, I3Z, I4Z, 443, 060, 12,0,0, 221) measured at 200 data intervals; 1601 data (includes standards and systematically absent reflections) measured from $\theta = 2$ to 25° ; $h, k, l = 0$ to 28, 0 to 10, 0 to 8; 1356 unique; 860 with $I > 3\sigma(I)$; average change in standard intensities of 0.6% with a range of -0.9 to 3.9%. TEXSAN (1987) program system on DEC Micro-VAX II computer; *Pnma* from systematic absences and $N(z)$ test (using 1356 reflections); MITHRIL direct methods (Gilmore, 1983); full-matrix least-squares refinement with C, N, O anisotropic and H isotropic (adamantane H's initially positioned from C-atom framework, ammonium H's located in difference map); minimization of $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$; secondary-extinction parameter [method of Zachariasen (1968)] refined; empirical absorption correction determined from systematic differences between F_o and F_c [method of Walker & Stuart (1983)], min. and max. corrections of 0.660 and 1.199; final S, R and wR are 2.19, 0.048 and 0.061, respectively; max. shift/e.s.d. 0.02; min. and max. values in the final difference map -0.211 and $0.176 \text{ e } \text{\AA}^{-3}$. Atomic coordinates are listed in Table 1.*

Discussion. An ORTEP (Johnson, 1965) drawing is shown in Fig. 1; bond lengths and angles are listed in Table 2. Both the adamantanylammonium and trinitromethide ions have mirror symmetry. In the anion, the C8-N2-O1-O2 moiety is on the crystallographic

Table 1. Atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
O1	0.0594 (2)	$\frac{1}{4}$	0.2604 (5)	5.6 (2)
O2	0.1361 (2)	$\frac{1}{4}$	0.4165 (6)	6.7 (2)
O3	0.0223 (1)	0.4081 (3)	0.8119 (3)	4.5 (1)
O4	0.0623 (1)	0.5130 (2)	0.5696 (3)	4.6 (1)
N1	-0.0531 (2)	$\frac{1}{4}$	0.0846 (7)	3.3 (2)
N2	0.0856 (2)	$\frac{1}{4}$	0.4053 (5)	3.8 (2)
N3	0.0456 (1)	0.3953 (3)	0.6579 (4)	3.3 (1)
C1	-0.1115 (2)	$\frac{1}{4}$	0.0056 (5)	2.6 (2)
C2	-0.1541 (3)	$\frac{1}{4}$	0.1628 (8)	5.4 (3)
C3	-0.2129 (2)	$\frac{1}{4}$	0.0793 (8)	6.1 (3)
C4	-0.2218 (2)	0.1055 (6)	-0.0353 (8)	6.6 (2)
C5	-0.1794 (2)	0.1036 (5)	-0.1927 (7)	6.3 (2)
C6	-0.1195 (2)	0.1042 (5)	-0.1127 (7)	5.4 (2)
C7	-0.1861 (3)	$\frac{1}{4}$	-0.3104 (9)	7.0 (4)
C8	0.0537 (2)	$\frac{1}{4}$	0.5763 (6)	3.4 (2)
H1A	-0.047 (2)	0.326 (5)	0.157 (5)	7 (1)
H1B	-0.027 (2)	$\frac{1}{4}$	-0.001 (6)	4 (1)
H2	-0.144 (2)	0.349 (5)	0.223 (6)	9 (1)
H3	-0.240 (3)	$\frac{1}{4}$	0.173 (8)	8 (2)
H4A	-0.263 (2)	0.114 (5)	-0.088 (5)	8 (1)
H4B	-0.214 (2)	0.004 (6)	0.040 (7)	10 (1)
H5	-0.184 (2)	0.011 (6)	-0.253 (6)	9 (1)
H6A	-0.092 (2)	0.104 (5)	-0.219 (5)	7 (1)
H6B	-0.113 (2)	0.013 (5)	-0.045 (6)	7 (1)
H7A	-0.222 (2)	$\frac{1}{4}$	-0.364 (6)	5 (1)
H7B	-0.157 (3)	$\frac{1}{4}$	-0.411 (7)	8 (1)

mirror plane; the C8-N3-O3-O4 plane is almost perpendicular (85.8°) to the mirror plane. Bond lengths and angles in the anion exhibit an interesting pattern. For example, the in-mirror-plane values of N2-O1 = 1.212 (5), N2-O2 = 1.205 (5), C8-N2 = 1.442 (5) Å compared with the out-of-plane values of N3-O2 = 1.239 (3), N3-O4 = 1.243 (3), C8-N3 = 1.371 (3) Å clearly show the effects of π -electron delocalization in the out-of-plane O₂N-C-NO₂ fragment. This accords with the intermolecular H-bonding pattern (Fig. 1, Table 3) of close contacts between the cation and out-of-plane nitro-group oxygen atoms (O3 and O4), and suggests that the out-of-plane fragment supports the majority of the negative charge in the anion. The C8-N2 = 1.442 (5) and C8-N3 = 1.371 (3) Å distances illustrate the presence of conjugation in the out-of-plane O₂N-C8-NO₂ moiety, and the absence of conjugation between C8 and the in-plane nitro group. Differences of this type are expected from the orthogonality of the two possible π -orbital systems.

The C-N-O internal angles in the out-of-plane O₂N-C-NO₂ moiety are somewhat enlarged. This is probably due to intra-anion repulsion between the mirror-symmetry-related O3 atoms. Additionally, the enlarged N3-C8-N3' angle of $126.6(4)^\circ$ reflects this repulsive interaction.

A search of the Cambridge Structure Database revealed six structures containing the trinitromethide anion, three with univalent metal cations, and three with organic cations. Only one of these structures, that

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51371 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of iodomethyltriphenylphosphonium trinitromethide (Scherfise, Weller & Dehnicke, 1985), has been determined with sufficient accuracy for meaningful comparison with (I). All of the determinations, however, show the overall structural feature in the anion of one C—NO₂ plane approximately normal to the other O₂N—C—NO₂ plane. Although the C—N distances in the phosphonium structure of 1.362 (7), 1.394 (8) and 1.410 (8) Å do not show the dramatic difference found in (I), the trend of a shorter C—N and longer N—O distances in the same C—NO₂ is observed.

In the adamantanylammonium cation, N1, C1, C2, C3 and C7 are positioned on the mirror plane. C—C bond lengths range from 1.484 (6) to 1.538 (5) Å and the bond angles 107.8 (5) to 110.4 (3)°. The ammonium cation is strongly linked to four adjacent trinitromethide anions by six N—H...O type hydrogen bonds (Fig. 1, Table 3).

An attempt was made to refine the crystal structure in the non-centrosymmetric space group, *Pn*2₁*a*, to confirm the crystal symmetry. Least-squares refinement of an initial model deliberately distorted to break the mirror symmetry in *Pnma* converged to *R* = 0.042, *wR* = 0.051. The resulting structure showed substantial distortions [*e.g.* C3—C4 = 1.32 (1) Å] with considerably larger *e.s.d.*'s due to the increased number of parameters (from 150 to 262). All of the atom pairs related by the pseudo-mirror symmetry in the non-centrosymmetric structure showed high correlation coefficients (greater than 50%) in the refinement. Furthermore, the averaged values of *x* and *z* coordinates of the pseudo-mirror symmetric pairs were essentially identical to those of the centrosymmetric structure. Therefore, it is concluded that the crystal symmetry is *Pnma*.

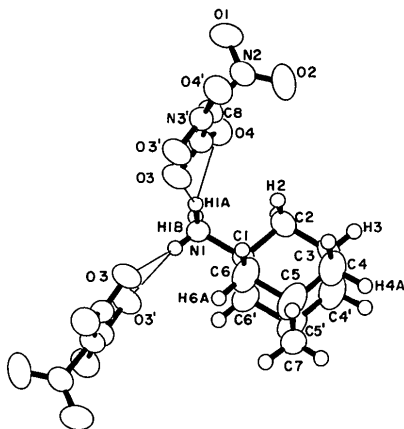


Fig. 1. ORTEP drawing of adamantanylammonium cation, and two of the three nearest trinitromethide anions linked by N—H...O hydrogen bonds. A third anion is related by mirror symmetry to the H1A-linked anion; it is not shown here for clarity. The contact distances are given in Table 3.

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

O1—N2	1.212 (5)	C2—C3	1.523 (8)
O2—N2	1.205 (5)	C3—H3	0.93 (6)
O3—N3	1.239 (3)	C3—C4	1.484 (6)
O4—N3	1.243 (3)	C4—H4B	1.03 (5)
N1—H1A	0.84 (4)	C4—H4A	1.06 (5)
N1—H1B	0.87 (5)	C4—C5	1.513 (7)
N1—C1	1.501 (6)	C5—H5	0.90 (5)
N2—C8	1.442 (5)	C5—C7	1.503 (5)
N3—C8	1.371 (3)	C5—C6	1.538 (5)
C1—C6	1.505 (4)	C6—H6B	0.92 (4)
C1—C2	1.515 (7)	C6—H6A	1.01 (4)
C2—H2	0.97 (4)	C7—H7A	0.93 (5)
		C7—H7B	1.01 (6)
O2—N2—O1	124.9 (4)	C1—C2—C3	108.8 (5)
O2—N2—C8	118.0 (4)	C4—C3—C4	110.3 (6)
O1—N2—C8	117.1 (4)	C4—C3—C2	110.4 (3)
O3—N3—O4	121.8 (3)	C3—C4—C5	109.1 (4)
O3—N3—C8	121.4 (3)	C7—C5—C4	109.8 (4)
O4—N3—C8	116.8 (3)	C7—C5—C6	107.8 (5)
N1—C1—C6	109.2 (3)	C4—C5—C6	109.9 (4)
N1—C1—C6	109.2 (3)	C1—C6—C5	109.2 (3)
N1—C1—C2	109.8 (4)	C5—C7—C5	110.4 (5)
C6—C1—C6	109.5 (5)	N3—C8—N3	126.6 (4)
C6—C1—C2	109.6 (3)	N3—C8—N2	115.9 (2)

Table 3. N—H...O hydrogen-bond parameters

The symmetry relationships for the O atoms are shown in parentheses.

	N—H(Å)	H...O(Å)	N...O(Å)	N—H...O (°)	ADC of O
N1—H1B...O3(i)	0.87 (5)	2.23 (4)	2.968 (5)	143 (4)	55401
N1—H1A...O3(ii)	0.84 (4)	2.33 (4)	3.067 (3)	147 (3)	56602
N1—H1A...O4(ii)	0.84 (4)	2.41 (4)	3.191 (4)	155 (4)	56602

(i) *x*, *y*, $-1 + z$; (ii) $-x$, $-\frac{1}{2} + y$, $-1 - z$.

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