of the propyl derivative are $a' = 8·502$, $b' = 8·234$, $c' = 17·494$ Å, $\alpha' = 78·41$, $\beta' = 84·96$ and $\gamma' = 61·24°$, which were obtained by exchanging the axes $a \rightarrow -b'$, $b \rightarrow -a'$, $c \rightarrow -c'$. The $a \times b$ dimension for the butyl derivative (65·7 Å^2) is larger than the 61·4 Å^2 found for the propyl derivative, while the (001) interplanar distance (16·9 Å) is slightly smaller than the 17·1 Å found for the propyl derivative. Thus, exchange of the propyl group by the butyl group causes the tilt of the dodecyl chain from the (001) plane to change from 52 to 53°. This small change reflects a similar packing form of dodecyl chains; a triclinic subcell assuming the a_s axis parallel to the long-chain axis has similar dimensions $a_s = 2·54$ (1), $b_s = 4·35$ (4), $c_s = 4·90$ (4) Å, $\alpha_s = 66·5$ (6), $\beta_s = 88·2$ (4) and $\gamma_s = 77·4$ (4)°. The short intermolecular C···C contacts are 3·888 (1) Å for C(17)···C(18) and 3·899 (1) Å for C(12)···C(16).

The Br ions and water molecules form an isolated anionic group in a square shape. The Br···O hydrogen-bond distances are 3·410 (1) and 3·414 (1) Å, and the Br···O···Br and O···Br···O angles are 112·9 (3) and 67·1 (2)°. In comparison with the propyl derivative, the Br···O distances are long and the Br···O···Br angle is open. The anionic group is surrounded by cationic ammonium groups with shortest O···N distance 4·443 (1) Å and Br···N distances 4·233 (1) Å.

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Structure of 1,4-Cubanediyldiammonium Bis(trinitromethanide)*

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Abstract. $C_8H_{12}N_2^+.2CN_3O_6^-$, $M_r = 436·27$, monoclinic, $C2/m$, $a = 14·298$ (2), $b = 8·408$ (1), $c = 7·354$ (2) Å, $\beta = 103·42$ (2)°, $V = 859·9$ (5) Å^3, $Z = 2$, $D_x = 1·68$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å (graphite monochromator), $\mu = 1·66$ cm^{-1}, $F(000) = 448$, $T = 293$ K, final $R = 0·039$ for 672 reflections with $I \geq 3\sigma(I)$. The cubanediyldiammonium cation and trinitromethanide anion have $2/m$ and m crystallographic symmetries, respectively. The cation is linked to six trinitromethanide anions, three at each end, by a total of 12 N—H···O hydrogen bonds through the six cation H atoms. The cubane cage has a local threefold axis of symmetry along the long axis (N1···N1) of the cation and undergoes a large librational motion, 17° r.m.s. amplitude, about this axis.

Introduction. There is a continued interest in the synthesis and chemistry of cubane derivatives because of the potential of cubane as a molecular template for the formation of high-density energetic materials (Alster & Iyer, 1983–1988). In the case of octanitrocubane, various estimates of the crystal density have been in the 1·99–2·10 g cm^{-3} range. The crystal structures of several nitrocubanes are known at this time; only that of 1,4-dinitrocubane has been published (Eaton, Ravi Shanka, Price, Pluth, Gilbert, Alster & Sandus, 1984; Umrigar, Vaz, Kirschenheuter, Griffin, Majeste, Klein, Stevens, Gilbert, Alster, Sandus & Legendre, 1988). The

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* Cubane is pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane.

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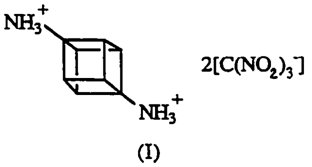
trinitromethanide anion is of interest as a constituent of energetic materials. We have published recently the structure of 1-adamantylammonium trinitromethanide (Ammon, Choi, Bashir-Hashemi, Moriarty & Khosrowshahi, 1989), and now report the crystal structure of the title compound (I) which combines a cubane-based cation and the trinitromethanide anion. (I) can be prepared and handled without encountering any serious safety problems.



(I)

Experimental. Yellowish crystal, 0·3 × 0·35 × 0·4 mm irregular shape; Enraf–Nonius CAD-4 diffractometer; cell parameters from 25 reflections in the range $4·65 < \theta < 12·81°$; θ–2θ scan, scan speed of $8·24°\ \text{min}^{-1}$; 96 steps over the θ range of $1·5(0·80 + 0·35\tan\theta)°$; on-line intensity profile analysis (Grant & Gabe, 1978), points in profile taken at *ca* 0·01° intervals; nine standards measured at 1 h crystal X-ray exposure intervals; 1911 data measured (includes standards and systematically absent reflections); $\theta = 2$–$25°$; $h, k, l = -16$ to 16, 0 to 9, -8 to 8; 811 unique data, $R_{\text{int}} = 0·016$ for averaged reflections; 672 data with $I \geq 3\sigma(I)$; 0·05% average change in standard intensities with a range of $-1·8$ to 3·1%; *TEXSAN* (1987) crystallographic program system on Digital Equipment Corporation MicroVAXII computer; *C*2/*m* space group from systematic absences and *N*(*z*) test; structure solution by the *MITHRIL* direct-methods (Gilmore, 1983) subprogram; structure refinement by full-matrix least squares with anisotropic temperature factors for C, N, O and isotropic terms for H (cubane H atoms initially positioned from C-atom framework, ammonium H atoms from a difference electron density map); minimization of $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$; secondary-extinction parameter (Zachariasen, 1968) refined, extinction coefficient = $0·27(3) \times 10^{-5}$; no absorption correction; final *S*, *R* and *wR* of 2·46, 0·039 and 0·054, respectively; maximum shift/e.s.d. = 0·38; minimum and maximum values in the final difference map of $-0·19$ and $0·21\ \text{e}\ \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are listed in Table 1.* Figs. 1–3 were drawn with the *ORTEP* (Johnson, 1965) subprogram in the *TEXSAN* package; labeling with the *PLOTMD* program (Luo, Ammon & Gilliland, 1989).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
O1	0·7973 (1)	0·3427 (2)	0·1951 (2)	4·61 (8)
O2	0·8589 (1)	0·2364 (2)	0·4639 (2)	5·02 (8)
O3	0·8414 (2)	½	0·7592 (3)	5·6 (1)
O4	0·9765 (2)	½	0·6960 (4)	7·8 (2)
N1	0·8287 (2)	0	0·1206 (4)	3·1 (1)
N2	0·8326 (1)	0·3554 (2)	0·3654 (2)	3·43 (8)
N3	0·8913 (2)	½	0·6494 (3)	3·5 (1)
C1	0·9193 (2)	0	0·0585 (4)	2·6 (1)
C2	0·9498 (2)	0·1280 (4)	−0·0617 (5)	6·2 (1)
C3	1·0201 (3)	0	0·1839 (5)	6·1 (2)
C4	0·8446 (2)	½	0·4508 (4)	3·2 (1)
H1	0·916 (2)	0·213 (4)	−0·102 (4)	8·0 (8)
H2	1·034 (4)	0	0·330 (7)	9 (1)
H3	0·778 (3)	0	0·030 (6)	5 (1)
H4	0·825 (2)	0·084 (4)	0·186 (4)	5·3 (6)

Discussion. An *ORTEP* (Johnson, 1965) drawing is shown in Fig. 1; bond lengths and angles are listed in Table 2. The cubanediyldiammonium cation has 2/*m* symmetry, with a mirror plane through the H3—N1—C1—C3—H2 moiety. Each cation is linked to six trinitromethanide anions by a total of 12 strong N—H···O-type hydrogen bonds through the two ammonium substituents. Each $—NH_3^+$ is associated with six of these contacts, and each anion is linked to three cations. There are three crystallographically different hydrogen bonds, N1—H3···O1, N1—H4···O1 and N1—H4···O2 (bond parameters are given in Table 3.). The hydrogen bonds extending from each end of the cation form infinite two-dimensional nets. In effect, the cations are suspended between the two hydrogen-bond nets by the two ammonium groups at the diagonal corners of the cubane cage as illustrated in Fig. 2.

The cubane moiety has cubic symmetry within experimental error. One can envision that the cubane cage is held in the crystal mainly by the two ammonium end points of the axis [by the $NH_3^+\cdots C(NO_2)_3^-$ hydrogen bonds] and that there is relatively little hindrance to rotation about the axis. The shortest intermolecular distances that involve the cubane H atoms (H1 and H2) are 2·74, 2·88 and 2·91 Å for H···O, H···H and H···C, respectively. The *ORTEP* drawing (Fig. 3) of the cation viewed down the long-axis direction illustrates the effects of thermal motion about the axis. The thermal-ellipsoid data for the cubanediyldiammonium cation were used in a rigid-body analysis by the method of Schomaker & Trueblood (1968). The agreement between the observed atomic thermal parameters and the corresponding parameters based on the rigid-body analy-

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52282 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sis was excellent, with an r.m.s. deviation of 0·0025 Å^2 for the mean U_{ij} of 0·063 Å^2. The principal axes of the translation and libration tensors were found to be 0·043 (1) 0·0 0·006 (1)/0·006 (1) 0·023 (1) 0·0/0·006 (1) 0·0 0·032 (1) Å^2 and 205 (3) 0·0 −0·043 (1)/−0·043 (1) 5 (1) 0·0/−0·043 (1) 0·0 102 (3)°^{2}, respectively, based on the orthogonal axes of $b \times c$, b and c. The librational motion is extremely anisotropic with r.m.s. amplitudes for the three principal axes of 17·4, 2·2 and 2·0°, respectively. The orientation of the 17·4° principal axis is within 3° of the long cationic axis (N1···N1). The C—C bond lengths corrected for libration are included in Table 2 (in parentheses).

The 1·52 Å average of the observed C—C bond lengths in (I) is apparently shorter than distances in other cubane derivatives (see Table 3). The shortening may be attributed to the intense libration of the cubane cage. Correction of the distances for rigid-body libration gives a mean bond length of 1·57 Å, in reasonable agreement with other cubane derivatives (no corrections for libration).

The rigid-body motions of the anion also were analyzed by the same procedure with **T**, **L** and **S** (screw motion was included because of the lack of

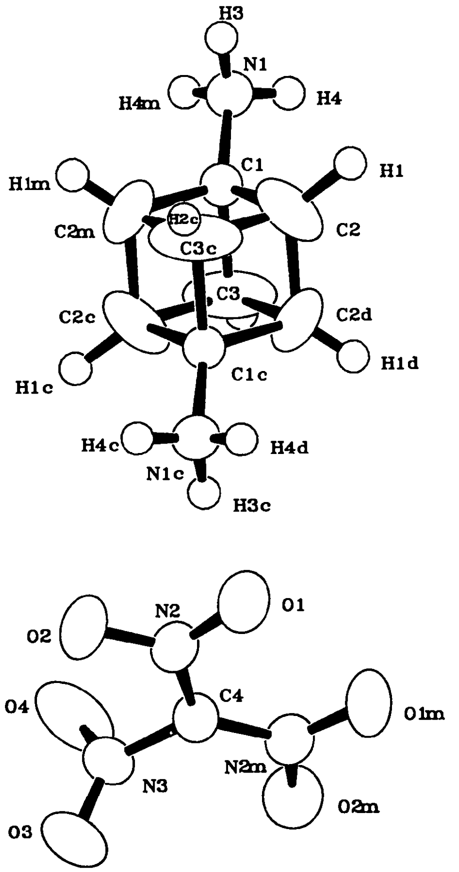

Fig. 1. *ORTEP* drawing of (I) with 50% probability ellipsoids for C, N and O. The cubanediyldiammonium cation and trinitromethanide anion have 2/*m* and *m* crystallographic symmetries, respectively. The unique atoms are designated with a letter and number as in C1. The lower-case letters *c*, *m* and *d* indicate atoms related by the center, mirror and dyad symmetry operations to the original set. For example, C1*c* is related to C1 by a center of symmetry. A label for atom H2, linked to C3, has been omitted for clarity.

Table 2. *Intramolecular distances* (Å) *and angles* (°) *and hydrogen-bond parameters with e.s.d.'s in parentheses*

The designations *c*, *m* and *d* refer to atoms produced by center, mirror and dyad symmetry operations. The bond lengths corrected for librational motion are given within parentheses.

O1	N2	1·242 (2)		N3	C4	1·458 (4)	
O2	N2	1·242 (2)		C1	C2	1·519 (3)	(1·566)
O3	N3	1·195 (3)		C1	C3	1·520 (4)	(1·572)
O4	N3	1·187 (3)		C2	H1	0·87 (4)	
N1	H4	0·86 (3)		C2	C2*d*	1·511 (6)	(1·561)
N1	H3	0·86 (4)		C2	C3*c*	1·527 (4)	(1·573)
N1	C1	1·470 (4)	(1·472)	C3	H2	1·05 (5)	
N2	C4	1·361 (2)					

H4	N1	H4*m*	109 (4)	C2*m*	C1	C3	89·6 (2)
H4	N1	H3	106 (2)	H1	C2	C2*d*	125 (2)
H4	N1	C1	110 (2)	H1	C2	C1	125 (2)
H4*m*	N1	H3	106 (2)	H1	C2	C3*c*	126 (2)
H4*m*	N1	C1	110 (2)	C2*d*	C2	C1	90·6 (2)
H3	N1	C1	114 (3)	C2*d*	C2	C3*c*	89·7 (2)
O2	N2	O1	121·1 (2)	C1	C2	C3*c*	90·1 (2)
O2	N2	C4	117·5 (2)	H2	C3	C1	123 (3)
O1	N2	C4	121·4 (2)	H2	C3	C2*d*	126 (1)
O4	N3	O3	122·6 (3)	H2	C3	C2*c*	126 (1)
O4	N3	C4	119·3 (3)	C1	C3	C2*d*	90·0 (2)
O3	N3	C4	118·1 (3)	C1	C3	C2*c*	90·0 (2)
N1	C1	C2	125·0 (2)	C2*d*	C3	C2*c*	89·7 (3)
N1	C1	C2*m*	125·0 (2)	N2	C4	N2*m*	126·6 (3)
N1	C1	C3	126·2 (2)	N2	C4	N3	116·2 (1)
C2	C1	C2*m*	90·2 (3)	N2*m*	C4	N3	116·2 (1)
C2	C1	C3	89·6 (2)				

	N—H (Å)	H···O (Å)	N···O (Å)	N—H···O (°)
N1—H3···O1*	0·86 (4)	2·20 (3)	2·906 (3)	139· (2)
N1—H4···O1	0·86 (3)	2·22 (3)	2·986 (2)	148· (2)
N1—H4···O2	0·86 (3)	2·37 (3)	3·163 (3)	154· (2)

* Atoms produced by the $\frac{3}{2} - x$, $-\frac{1}{2} + y$, $-z$ symmetry operation.

Table 3. *Mean* C—C *bond lengths and r.m.s. deviations* (Å) *from the mean in cubane and derivatives*

Compound	Symmetry	Mean C—C	R.m.s.d.	Reference
(I)	2/*m*	1·520	0·005	This work
(I), libration correction		1·568	0·005	This work
Cubane	$\bar{3}$	1·551	0·002	Fleischer (1964)
1,4-Dinitrocubane	$\bar{1}$	1·558	0·09	Eaton *et al.* (1984)
1,3-Dinitrocubane	1	1·554	0·007	Umrigar *et al.* (1988)
1,4-Diiodocubane	$\bar{1}$	1·553	0·016	Ammon, Choi & Reddy (1988)
(II)*	$\bar{1}$	1·568	0·018	Bashir-Hashemi, Ammon & Choi (1988)
(III),† molecule (1)	$\bar{1}$	1·567	0·008	Ermer & Lex (1987)
molecule (2)	$\bar{1}$	1·566	0·009	Ermer & Lex (1987)
Cubylcubane (IV)	1	1·553	0·008	Gilardi, Maggini & Eaton (1988)
2-*tert*-Butyl-(IV)	1	1·556	0·006	Gilardi *et al.* (1988)

* 2,5-Bis(*N*,*N*-Diisopropylaminomethyl)-1,4-diphenylcubane.
† 1,4-Cubanedicarboxylic acid.

centrosymmetry). However, the agreement between the observed temperature factors and the corresponding parameters from the rigid-body motions were rather poor. The r.m.s. deviation of 0·0096 Å^2, which was about four times larger than that of the cation, indicates that the anionic thermal parameters cannot be fitted realistically by a rigid-body model. Therefore, no bond-length corrections were applied to the anion.

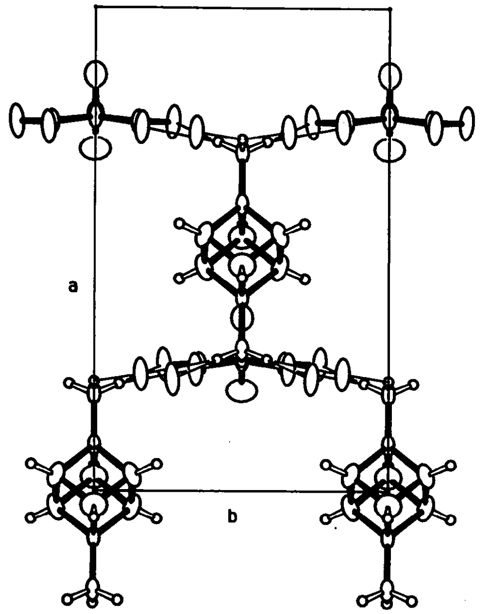

Fig. 2. An *ORTEP* drawing to illustrate how the cubanediyldiammonium cation is suspended between trinitromethanide anions. 50% probability ellipsoids are used for C, N and O.

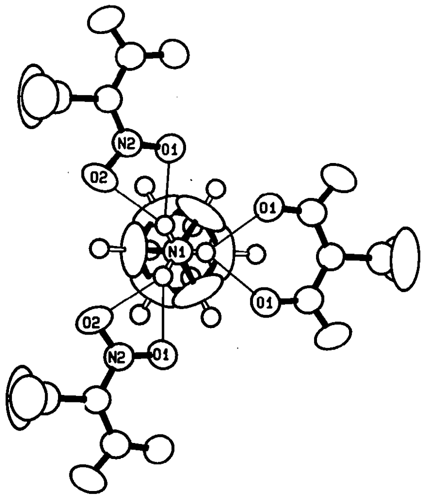

Fig. 3. An *ORTEP* drawing of the cubanediyldiammonium cation viewed along the N···N direction. 50% probability ellipsoids are used for C, N and O. The three trinitromethanide anions hydrogen-bonded to the top end of the cube are shown.

In the trinitromethanide anion, the O3—N3—O4 nitro group on the mirror plane is structurally and functionally distinct from the two out-of-plane O1—N2—O2 nitro groups. The in-plane and out-of-plane distances [C4—N3 = 1·458 (4), N3—O3 = 1·195(3), N3—O4 = 1·187, and C4—N2 = 1·361, N2—O1 = 1·242 (2), N2—O2 = 1·242 (2) Å] form a pattern which suggests that the majority of the negative charge is delocalized over the $O_2N—C—NO_2$ fragment that is perpendicular to the mirror plane. This bond-length pattern accords with the intermolecular hydrogen-bonding pattern in which all of the close $NH_3^+\cdots O$ contacts involve the out-of-plane nitro groups. An exactly analogous situation was observed in 1-adamantylammonium trinitromethanide (Ammon *et al.*, 1989).

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