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Structure of the Organic Semiconducting Radical Cation Salt Tris(2,3,6,7-tetramethoxynaphthalene) Bis(hexafluoroarsenate)

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Abstract

$(C_{14}H_{16}O_4)_3^{2+}.2AsF_6^-$, M_r = 1122·67, triclinic, $P\overline{1}$, a = 10·1564 (15), b = 11·0323 (13), c = 11·9157 (12) Å, α = 77·841 (10), β = 65·935 (9), γ = 76·633 (11)°, V = 1175·9 (2) Å^3, Z = 1, D_x = 1·585 g cm^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 15·2 cm^{-1}, $F(000)$ = 570, T = 298 K, final $R(F)$ = 0·049 for 3950 unique reflexions. Triads of planar 2,3,6,7-tetramethoxynaphthalene (TMN) molecules form stacks along the a direction. The average interplanar distances are 3·27 Å in the triad (0·5° dihedral angle) and 3·362 (6) Å between the triads. The centrosymmetric TMN molecule in the middle of the triad is rotated by 35° around the stacking direction with respect to the two outer asymmetric TMN molecules, in order to achieve short C—H···O contacts in the triad and make room for the AsF_6^- ion. Between the stacks the TMN molecules are connected into infinite chains *via* short C—H···O contacts. A rigid-body *TLS* analysis of the anisotropic displacement parameters reveals the significant effect of these C—H···O contacts on the thermal motion of the molecules.

Introduction

Cation radical salts of naphthalene have attracted considerable interest in recent years and have resulted in the renaissance of cation radical salts of aromatic hydrocarbons (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980; Fritz, Gebauer, Friedrich, Ecker, Artes & Schubert, 1978; Kröhnke, Enkelmann & Wegner, 1980). These salts exhibit high conductivity and the narrowest ESR line (2·5 mG) found so far (Müller, von Schütz & Wolf, 1983). One great problem with these compounds is their instability; they decompose within minutes at room temperature. Connecting methoxy groups to the naphthalene molecule has been shown to stabilize the cation radical salts (Hellberg, 1987). The present investigation is part of a series of studies of the structures and physical properties of electrochemically prepared cation radical salts of substituted aromatic donors. One of the problems encountered has been to obtain crystals of sufficiently good quality for a structure determination. In most cases partly amorphous or polycrystalline samples are obtained. Solvent molecules from the electrocrystallization process can also be easily incorporated into the structure and disorder of the molecules often occurs. Here, an ordered and solvent-free structure is reported. The structure of the corresponding perchlorate will be published in a subsequent paper.

Experimental

Good quality solvent-free brittle single crystals of $(TMN)_3(AsF_6)_2$ with a reddish-black metallic lustre were kindly provided by Dr Jonas Hellberg of KTH, Stockholm. They were prepared by the electrolytic oxidation of TMN in CH_2Cl_2 solution in the presence of $^nBu_4N.AsF_6$ at a constant current of 4–6 μA and a temperature of 277–281 K. Details of the synthesis, conductivity and magnetic properties are given by Krzystek, von Schütz, Ahlgren, Hellberg, Söderholm & Olovsson (1986). A polyhedral crystal of size 0·17 × 0·14 × 0·13 mm was used. Intensity

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data were collected on a PDP 8/a-controlled Enraf–Nonius CAD-4F four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation at room temperature. The ω-scan mode was used with scan width $\Delta\omega$ = 1·2, 1·1 and 1·3° for θ ranges 0–14, 14–28 and 28–30° respectively; the scan time was varied to maintain constant $\sigma(I)/I$ = 0·010; maximum scan time 150 s. The range of h, k, l was $0 \le h \le 14$, $-15 \le k \le 15$, $-15 \le l \le 16$ with $(\sin\theta/\lambda)_{max}$ = 0·7028 Å^{-1}. The unit-cell dimensions were determined from a least-squares refinement of the setting angles of 64 reflexions in the 2θ range 34–52°. Seven standard reflexions were measured every 200 min of X-ray exposure time; their intensities decreased by 10–15% during the data collection. A scaling function derived from the standard reflexions was used to correct the measured intensities. A contribution taking account of instability in the measurement and for uncertainty in the scaling function was added to the standard deviations estimated on the basis of counting statistics (McCandlish, Stout & Andrews, 1975). The raw intensities were corrected for background using the profile-analysis method of Lehmann & Larsen (1974). The intensities were corrected for Lorentz and polarization effects. An absorption correction was performed by the Gaussian integration method using a 12 × 10 × 12 grid. The crystal was described by ten faces. Transmission factors 0·79 to 0·85 for the 8132 collected intensities. Averaging equivalent reflexions (R_{int} = 0·0089) left 6829 unique intensities. All atoms (except hydrogens) were found with direct methods using the program system *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All hydrogens were located in a difference Fourier map. Neutral atomic and anomalous-scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–100, 102, 149). The spherical bonded hydrogen-atom scattering factor was used. The function minimized in the full-matrix least-squares program *DUPALS* (Lundgren, 1982) was $\sum w(|F_o|^2 - |F_c|^2)^2$ where $w^{-1} = \sigma^2_{count}(F^2_o) + (0{\cdot}040F^2_o)^2$. In the final cycle, 2878 reflexions with $F^2_o < \sigma(F^2_o)$ were excluded, leaving 3950 reflexions for the refinement of 404 parameters. These were: one scale factor, 174 positional parameters, 204 ansiotropic displacement parameters (non-hydrogen atoms), 24 isotropic displacement parameters (hydrogen atoms) and one isotropic extinction coefficient. The final agreement factors (3950 reflexions) are $R(F)$ = 0·049, $R(F^2)$ = 0·049, $wR(F^2)$ = 0·087, $S(F^2)$ = 1·29. $(\Delta/\sigma)_{max}$ < 0·1. Maximum and minimum peak heights in the final difference density map are 0·90 and −0·52 e Å^{-3} at 0·01 and 0·71 Å from the As atom, respectively. The secondary isotropic type-I extinction coefficient was refined to the value 970(460) (Becker & Coppens, 1974, 1975) (Lorentzian mosaic-spread distribution). The refined hydrogen positions give C—H distances ranging from 0·84 to 1·01 Å. As the true nuclear positions for hydrogen are desirable when calculating intermolecular distances *etc.*, the hydrogen positions given in the tables and figures were calculated by the program *SHELX*76 (Sheldrick, 1976); normal geometry of the C—H bonds relative to the carbon skeleton and a C—H distance of 1·08 Å was then assumed. The estimated standard deviations for the hydrogen positions were taken from the refinement. The *TLS* analysis of the thermal displacement parameters was performed using the program *THMV*9 (Trueblood, 1977) and the molecular plots were made using *ORTEP*II (Johnson, 1976). Other computations were performed using programs described by Lundgren (1982).

Discussion

Final atomic parameters are given in Table 1.* A stereoview of the crystal packing is shown in Fig. 1, bond distances and thermal displacement ellipsoids in Fig. 2 and bond angles in Fig. 3 (bond angles in the AsF_6^- ion are 89·3–90·4° with standard deviations 0·1°). The structure consists of stacks of TMN molecules along the a axis with AsF_6^- ions between the stacks in the c direction. The asymmetric unit consists of one TMN(2) molecule (in a general posi-

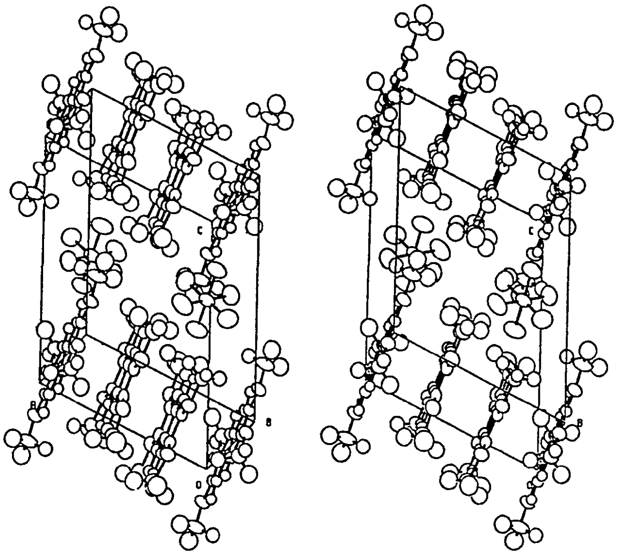

Fig. 1. A stereoscopic view of the molecular packing.

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* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53816 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and displacement parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for non-hydrogen atoms. U_{iso} is the mean-square amplitude of vibration for the hydrogen atoms.

	x	y	z	U_{eq}/U_{iso}
C(1)	0·5893 (3)	0·4743 (2)	1·1828 (2)	0·0360 (14)
C(2)	0·6013 (3)	0·3580 (2)	1·1543 (2)	0·0343 (14)
C(3)	0·6604 (3)	0·3362 (2)	1·0269 (2)	0·0325 (13)
C(4)	0·7012 (3)	0·4339 (2)	0·9325 (2)	0·0340 (14)
C(5)	0·7259 (3)	0·6580 (2)	0·8641 (3)	0·0360 (14)
C(6)	0·7124 (3)	0·7739 (2)	0·8942 (2)	0·0380 (14)
C(7)	0·6588 (3)	0·7932 (2)	1·0218 (3)	0·0391 (15)
C(8)	0·6211 (3)	0·6952 (2)	1·1149 (3)	0·0375 (15)
C(9)	0·6328 (3)	0·5749 (2)	1·0867 (2)	0·0322 (13)
C(10)	0·6881 (3)	0·5547 (2)	0·9595 (2)	0·0317 (13)
C(11)	0·4959 (5)	0·2732 (4)	1·3652 (3)	0·062 (2)
C(12)	0·7321 (4)	0·1861 (3)	0·8858 (3)	0·044 (2)
C(13)	0·7899 (6)	0·8731 (4)	0·6851 (3)	0·065 (3)
C(14)	0·5920 (4)	0·9397 (3)	1·1651 (3)	0·056 (2)
O(1)	0·5620 (2)	0·2549 (2)	1·2376 (2)	0·0452 (11)
O(2)	0·6687 (2)	0·21811 (15)	1·0105 (2)	0·0422 (10)
O(3)	0·7436 (2)	0·8801 (2)	0·8132 (2)	0·0508 (12)
O(4)	0·6490 (2)	0·9119 (2)	1·0397 (2)	0·0512 (12)
C′(1)	0·9605 (3)	0·3459 (2)	1·0918 (2)	0·0316 (13)
C′(2)	1·0000 (3)	0·2725 (2)	0·9985 (2)	0·0330 (13)
C′(3)	1·0552 (3)	0·3273 (2)	0·8702 (2)	0·0330 (13)
C′(4)	1·0669 (3)	0·4509 (2)	0·8414 (2)	0·0326 (14)
C′(5)	1·0279 (2)	0·5274 (2)	0·9358 (2)	0·0286 (12)
C′(6)	0·9365 (4)	0·0893 (3)	1·1426 (3)	0·048 (2)
C′(7)	1·1403 (6)	0·2931 (4)	0·6601 (3)	0·066 (3)
O′(1)	0·9923 (2)	0·15039 (15)	1·0165 (2)	0·0412 (10)
O′(2)	1·0900 (2)	0·2447 (2)	0·7885 (2)	0·0445 (11)
As	0·79103 (4)	0·31898 (3)	0·52114 (3)	0·0581 (2)
F(1)	0·8233 (2)	0·2343 (2)	0·4062 (2)	0·092 (2)
F(2)	0·6981 (2)	0·4409 (2)	0·4536 (2)	0·094 (2)
F(3)	0·6329 (2)	0·2604 (2)	0·6063 (2)	0·104 (2)
F(4)	0·8846 (3)	0·1974 (2)	0·5870 (2)	0·094 (2)
F(5)	0·9492 (2)	0·3779 (2)	0·4337 (2)	0·0841 (14)
F(6)	0·7582 (3)	0·4051 (2)	0·6354 (2)	0·096 (2)
H(1)	0·547 (3)	0·490 (2)	1·279 (2)	0·033 (6)
H(2)	0·744 (2)	0·417 (2)	0·837 (2)	0·022 (6)
H(3)	0·765 (3)	0·644 (2)	0·768 (2)	0·041 (7)
H(4)	0·582 (3)	0·711 (2)	1·211 (2)	0·034 (7)
H(5)	0·483 (4)	0·178 (4)	1·409 (3)	0·091 (14)
H(6)	0·390 (4)	0·332 (3)	1·391 (3)	0·080 (12)
H(7)	0·566 (3)	0·307 (3)	1·396 (3)	0·070 (10)
H(8)	0·731 (3)	0·088 (3)	0·890 (2)	0·038 (8)
H(9)	0·844 (3)	0·204 (3)	0·842 (3)	0·051 (8)
H(10)	0·669 (3)	0·242 (2)	0·833 (2)	0·044 (8)
H(11)	0·803 (4)	0·968 (4)	0·641 (4)	0·10 (2)
H(12)	0·713 (4)	0·841 (3)	0·661 (3)	0·064 (11)
H(13)	0·894 (3)	0·812 (3)	0·654 (3)	0·073 (10)
H(14)	0·584 (3)	1·039 (3)	1·165 (3)	0·058 (9)
H(15)	0·664 (4)	0·888 (4)	1·211 (3)	0·088 (12)
H(16)	0·485 (3)	0·913 (3)	1·214 (3)	0·068 (11)
H′(1)	0·920 (2)	0·304 (2)	1·188 (2)	0·027 (6)
H′(2)	1·107 (2)	0·492 (2)	0·745 (2)	0·028 (6)
H′(3)	0·945 (3)	−0·008 (3)	1·135 (3)	0·048 (8)
H′(4)	0·824 (3)	0·127 (3)	1·191 (3)	0·059 (9)
H′(5)	1·001 (3)	0·097 (3)	1·193 (3)	0·074 (11)
H′(6)	1·157 (4)	0·215 (3)	0·612 (3)	0·083 (14)
H′(7)	1·242 (3)	0·329 (3)	0·628 (3)	0·074 (10)
H′(8)	1·058 (3)	0·366 (3)	0·642 (3)	0·049 (11)

tion), half a TMN(1) molecule (centrosymmetric) and one AsF_6^- ion (in a general position). The TMN(2) molecule is slightly puckered with a dihedral angle of 1·5(3)° between the least-squares planes defined by the two carbon rings; the corresponding dihedral angle in the TMN(1) molecule is 0° as the molecule is centrosymmetric. The largest deviations of the individual carbon and oxygen atoms from the least-squares plane defined by the ten ring carbons are 0·040 (6) Å for C′(7) in TMN(1) and 0·168 (5) Å for C(11) in TMN(2). The dihedral angle between these planes and the *bc* plane is 21·2 and 21·6° respectively.

In this system we have a 3:2 ratio between the number of cations and anions, which means that two charges have to be attributed to three TMN molecules, $(TMN)_3^{2+}.2AsF_6^-$. The fine structure of the ESR signal shows that the spins are localized (Krzystek *et al.*, 1986). Assuming integer charges on the cations, it is tempting to assume a zero charge on the centrosymmetric TMN(1) molecule and accordingly one positive charge on each of the non-centrosymmetric TMN(2) and TMN(2^i) molecules (2^i is related to 2 by a centre of symmetry). It might be worth noting that crystalline neutral naphthalene is centrosymmetric. Considering the interplanar spacings in the stack, we may thus describe the stack as

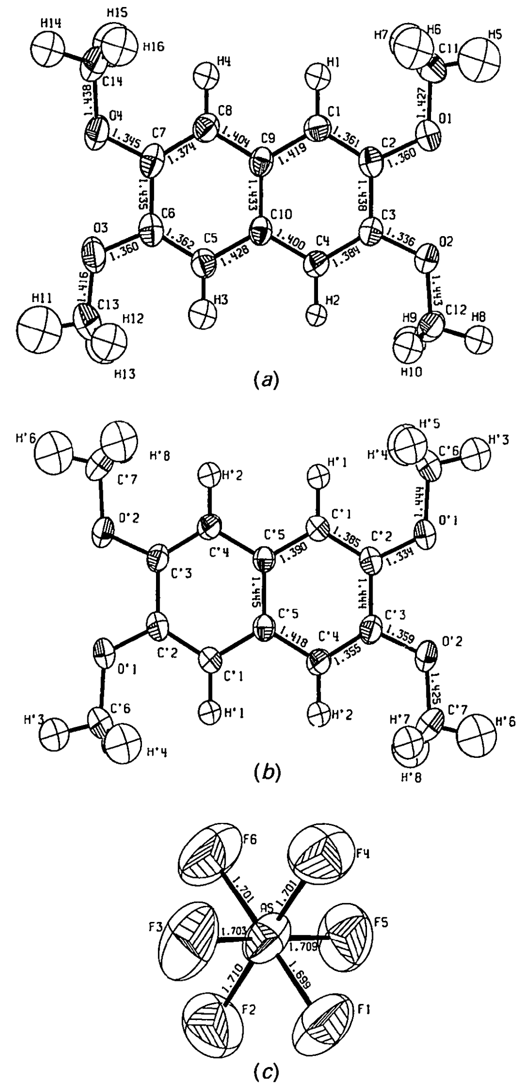

Fig. 2. Bond distances (Å), atomic notations and thermal ellipsoids (50% probability): (*a*) TMN(2) molecule (non-centrosymmetric), (*b*) TMN(1) molecule (centrosymmetric) and (*c*) AsF_6^- ion. Standard deviations for As—F distances are 0·002 Å, for C—C and C—O distances 0·003–0·004 Å.

consisting of triads of $TMN^+(2)$–$TMN^0(1)$–$TMN^+(2^i)$ (Fig. 4). This is analogous to the distribution of charges suggested in tetraselenatetracene $(TSeT)_3^{2+}.Hg_2Br_6^{2-}$ (Kaminskii, Kostuchenko, Shibaeva, Yagubskii & Zvarykina, 1983), a compound which closely resembles the title compound. A comparison of the intramolecular distances was made with neutral naphthalene (Cruickshank, 1957) to investigate if any systematic lengthening and shortening could be found which might be related to the charges of the molecules, as we found in the $bMDODBF^{1/2+}$ molecule of bis[2,3:7,8-bis(methylenedioxy)dibenzofuran] hexafluoroarsenate (Olovsson, 1987). However, no clear trends could be found in the present case. Bond distances in TMN(1) and TMN(2) are quite similar; the maximum difference in the corresponding bond lengths is 0·014 Å, corresponding to $\sim 3{\cdot}5\sigma$. This may be an indication that the distribution of charges on TMN(1) and TMN(2) is more equal than was assumed above.

Intrastack arrangement

The TMN molecules are stacked like poker chips along the *a* axis with AsF_6^- between the stacks in the *c* direction (Figs. 1 and 4). The TMN(2) and TMN(2^i) molecules within the triad are related by the centre of symmetry in the middle of TMN(1) and are thus mutually parallel. There is a slight tilt of 0·5° between the least-squares plane of TMN(1) and the least-squares planes of TMN(2) and TMN(2^i). The average distance between these planes is 3·27 Å (Fig. 4). TMN(1) is rotated by 35° around the stacking direction with respect to TMN(2) and TMN(2^i) (see Fig. 6). The corresponding interplanar distance between the triads [TMN(2) and TMN(2^i)] is significantly longer, 3·362 (6) Å, in agreement with the greater distances expected between molecules of the same charge. These two molecules are displaced

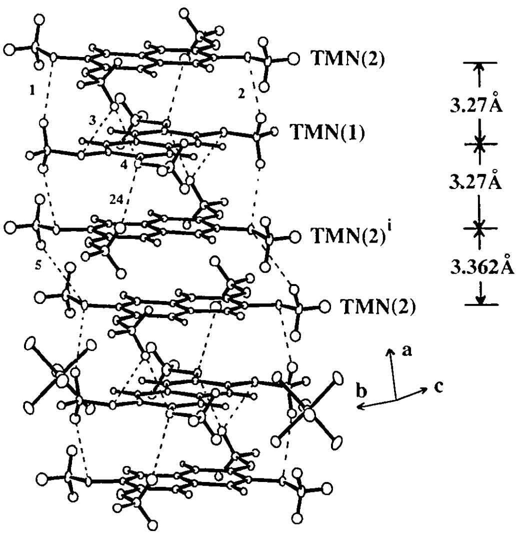

Fig. 4. Stacking of the TMN molecules along the *a* axis. The intermolecular distances in the stack ≤3·0 Å are indicated as dotted lines (*cf.* Table 2). The interplanar distances are between the least-squares planes of the TMN molecules (defined by the ten ring carbon atoms). For clarity the AsF_6^- ions in the upper triad are omitted.

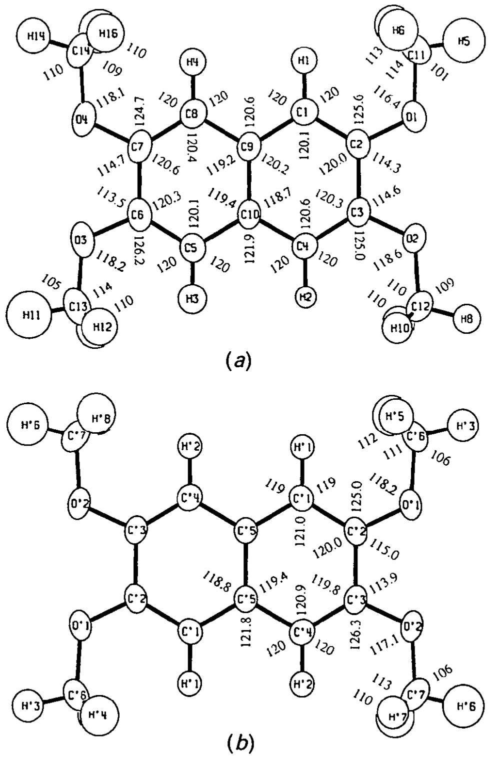

Fig. 3. Bond angles (°) in (*a*) TMN(2) and (*b*) TMN(1). Standard deviations for angles involving non-hydrogen atoms are 0·2–0·3°.

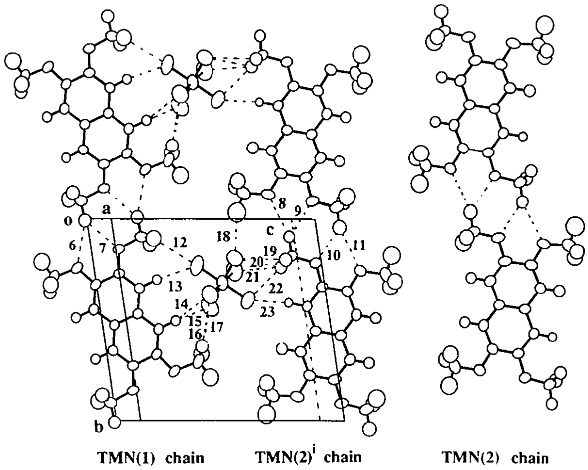

Fig. 5. Intermolecular distances ≤3·0 Å between the stacks, in the plane defined by the $-\boldsymbol{a} + 3\boldsymbol{c}$ and the $\boldsymbol{b}$ vectors (*cf.* Table 2).

in a parallel fashion relative to one another, in order to avoid methyl H···H collisions (Fig. 7).

The shortest intermolecular distances are shown in Table 2 (*cf.* Figs. 4 and 5). All the intermolecular distances within the stack ≤ 3·0 Å are of the type methyl C—H···O with H···O distances ranging from 2·45 (3) to 2·94 (3) Å. The shorter contacts are thus approximately equal to the van der Waals distance 2·40 Å [for oxygen the Pauling (1960) radius 1·40 Å has then been used, whereas for hydrogen the value 1·00 Å has been chosen, in accordance with later neutron diffraction measurements of H—H distances (Baur, 1972)]. Within the triad the intermolecular contact C(3)···C′(2) is 3·245 (3) Å and thus shorter than the van der Waals C···C contact distance 3·54 Å proposed by Bondi (1964) as well as the distance 3·4 Å proposed by Pauling (1960). By rotation of the middle TMN(1) molecule in the triad by 35°, less repulsion is obtained between the bulky CH$_3$ groups of the three TMN molecules, and thus the molecules can pack closer together. Also by this rotation, the methyl C—H···O interactions become much more favoured within the triads. The C—H···F—As contacts for the two outer TMN(2) molecules in the triad are also favoured in this way (see Fig. 4). The rigid-body analysis of the anisotropic displacement

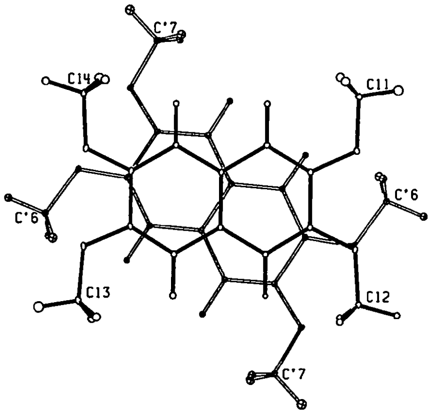

Fig. 6. Overlap within half the triad. The view is perpendicular to the molecular plane. The TMN(2) molecule has filled bonds. There is a centre of symmetry in the middle of TMN(1).

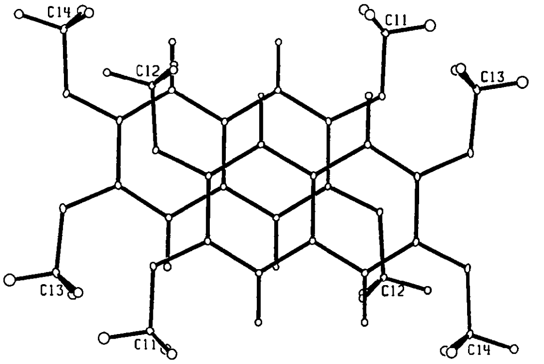

Fig. 7. Overlap between adjacent triads [between TMN(2) and TMN(2′), related by a centre of symmetry].

Table 2. *Shortest intermolecular distances* (Å) *and corresponding angles* (°)

	H···*A*	Angle	Comment	No. in Figs. 4 and 5
(*a*) Contacts to TMN(2) ≤ 3·0 Å				
C(11)—H(7)···F(2)	2·56 (3)	166 (3)		—
C(11)—H(7)···F(1)	2·60 (3)	137 (2)		—
C(11)—H(7)···F(3)	2·78 (3)	136 (2)		—
C(11)—H(6)···F(6)	2·96 (3)	143 (2)		—
C(12)—H(8)···O(4)	2·39 (3)	140 (2)	Interstack	9
C(12)—H(9)···O′(2)	2·45 (3)	167 (2)	Intrastack	4
C(12)—H(8)···O(3)	2·60 (3)	158 (2)	Interstack	8
C(12)—H(9)···O′(1)	2·94 (3)	112 (2)	Intrastack	3
C(12)—H(10)···F(6)	2·62 (3)	127 (2)		22
C(12)—H(10)···F(3)	2·83 (3)	142 (2)		21
C(12)—H(9)···F(4)	2·90 (3)	98 (2)		19
C(12)—H(10)···F(4)	2·92 (3)	98 (2)		20
C(13)—H(12)···O(1)	2·91 (3)	144 (2)	Intrastack	5
C(13)—H(13)···F(5)	2·46 (4)	152 (3)		—
C(13)—H(13)···F(1)	2·61 (3)	152 (3)		—
C(13)—H(11)···F(4)	2·71 (4)	159 (3)		18
C(13)—H(13)···F(4)	2·84 (3)	130 (2)		—
C(14)—H(14)···O(2)	2·45 (3)	137 (2)	Interstack	10
C(14)—H(15)···O′(2)	2·59 (3)	152 (3)	Intrastack	24
C(14)—H(14)···O(1)	2·64 (3)	161 (2)	Interstack	11
C(14)—H(16)···O(3)	2·93 (3)	111 (2)	Interstack	—
C(14)—H(16)···F(3)	2·63 (3)	137 (2)		—
C(4)—H(2)···F(6)	2·38 (2)	162 (2)		23
C(8)—H(4)···F(3)	2·39 (2)	143 (2)		—
C(1)—H(1)···F(6)	2·87 (2)	112 (1)		—
C(5)—H(3)···F(5)	2·91 (3)	135 (2)		—
C(1)—H(1)···F(2)	2·96 (2)	129 (2)		—
O(1)···H′(4)—C′(6)	2·60 (3)	161 (2)	Intrastack	1
O(1)···H(14)—C(14)	2·64 (3)	161 (2)	Interstack	11
O(1)···H(12)—C(13)	2·91 (3)	144 (2)	Intrastack	5
O(2)···H(14)—C(14)	2·45 (3)	137 (2)	Interstack	10
O(3)···H(8)—C(12)	2·60 (3)	158 (2)	Interstack	8
O(3)···H′(5)—C′(6)	2·63 (3)	148 (2)	Intrastack	2
O(3)···H(16)—C(14)	2·93 (3)	111 (2)	Interstack	—
O(4)···H(8)—C(12)	2·39 (3)	140 (2)	Interstack	9
(*b*) Contacts to TMN(1) ≤ 3·0 Å (each contact occurs twice)				
C′(6)—H′(3)···O′(1)	2·43 (3)	142 (2)	Interstack	7
C′(6)—H′(4)···O(1)	2·60 (3)	161 (2)	Intrastack	1
C′(6)—H′(5)···O(3)	2·63 (3)	148 (2)	Intrastack	2
C′(6)—H′(3)···O′(2)	2·63 (3)	157 (2)	Interstack	6
C′(6)—H′(5)···F(1)	2·94 (3)	111 (2)		12
C′(7)—H′(7)···F(2)	2·64 (3)	131 (2)		17
C′(7)—H′(8)···F(5)	2·77 (3)	132 (2)		16
C′(7)—H′(6)···F(4)	2·95 (4)	111 (2)		—
C′(1)—H′(1)···F(1)	2·40 (2)	174 (2)		13
C′(4)—H′(2)···F(2)	2·49 (2)	154 (2)		15
C′(4)—H′(2)···F(5)	2·50 (2)	148 (2)		14
O′(1)···H′(3)—C′(6)	2·43 (3)	142 (2)	Interstack	7
O′(1)···H(9)—C(12)	2·94 (3)	112 (2)	Intrastack	3
O′(2)···H(9)—C(12)	2·45 (3)	167 (2)	Intrastack	4
O′(2)···H(15)—C(14)	2·59 (3)	152 (3)	Intrastack	24
O′(2)···H′(3)—C′(6)	2·63 (3)	157 (2)	Interstack	6

(*c*) Shortest C···C, C···O and O···O distances between the TMN molecules within the stack

	X···*Y*	Comment
C(3)···C′(2)	3.245 (3)	In the triad
C(3)···C(10)	3·413 (3)	Between the triads
C(5)···O(1)	3·470 (3)	Between the triads
C(3)···O′(1)	3·486 (3)	In the triad
O(2)···O′(1)	3·225 (3)	In the triad
O(1)···O(3)	4·033 (3)	Between the triads

Table 3. *TLS analysis of the anisotropic displacement parameters of* $(TMN)_3(AsF_6)_2$

	Librational components (°)			Translational components (Å)			
	L_1	L_2	L_3	T_1	T_2	T_3	
Rigid model (*a*) for TMN(1)	4·0	2·6	1·8	0·17	0·16	0·15	R.m.s. difference of U_{obs} and U_{calc}: 0·0018 (14) Å^2
Angles to the principal inertial axes I	17 (I_1)	20 (I_2)	14 (I_3)	175 (I_2)	6 (I_1)	2 (I_3)	Weighted *R* for the *U*'s: 0·074
Non-rigid model (*b*) for TMN(1)	4·4	2·7	1·8	0·17	0·16	0·15	R.m.s. difference of U_{obs} and U_{calc}: 0·0015 (14) Å^2
Angles to the principal inertial axes I	7 (I_1)	15 (I_2)	15 (I_3)	175 (I_2)	6 (I_1)	2 (I_3)	Weighted *R* for the *U*'s: 0·059 Non-rigid librational axes: $L_{C(2)—O(1)} = -49\ (25)$ deg^2, $L_{C(3)—O(2)} = 5\ (3)$°
Rigid model (*a*) for TMN(2)	3·2	2·7	2·0	0·19	0·17	0·16	R.m.s. difference of U_{obs} and U_{calc}: 0·0024 (14) Å^2
Angles to the principal inertial axes I	22 (I_1)	22 (I_2)	5 (I_3)	160 (I_2)	9 (I_1)	18 (I_3)	Weighted *R* for the *U*'s: 0·091
Non-rigid model (*b*) for TMN(2)	5·1	2·7	2·0	0·19	0·17	0·14	R.m.s. difference of U_{obs} and U_{calc}: 0·0019 (14) Å^2
Angles to the principal inertial axes I	2 (I_1)	2 (I_2)	2 (I_3)	165 (I_2)	9 (I_1)	12 (I_3)	Weighted *R* for the *U*'s: 0·073 Non-rigid librational axes: $L_{C(2)—O(1)} = -29\ (19)$ deg^2, $L_{C(3)—O(2)} = -108\ (17)$ deg^2, $L_{C(6)—O(3)} = -24\ (20)$ deg^2, $L_{C(7)—O(4)} = -95\ (18)$ deg^2

parameters (see below) shows that the TMN(2) molecule librates approximately about the diagonal O(4)—O(2) vector. This is to be expected as C(12) and C(14) are held tighter not only by the above mentioned C—H···O interactions in the stack but also between the stacks in the *b* direction (see Figs. 4 and 5). This libration about the body diagonal is also seen for molecule TMN(1) for the same reasons.

Interstack arrangement

The interstack arrangement is shown in Figs. 1 and 5; the contacts ≤ 3·0 Å are tabulated in Table 2. It is natural to look at the plane defined by the $-\mathbf{a} + 3\mathbf{c}$ and **b** vectors, as all molecules lie approximately in that plane. Here it is clearly seen how both the TMN(1) and the TMN(2) molecules make individual chains in the *b* direction, *via* short methyl C—H···O contacts ranging from 2·39 (3) to 2·93 (3) Å. The lower limit is thus close to the van der Waals distance 2·40 Å (*cf.* above). These contacts are made possible by the parallel displacement of the individual molecules, but in opposite directions for TMN(1) and TMN(2) (this also explains their relative rotation). In the $-\mathbf{a} + 3\mathbf{c}$ direction we have the sequence of molecules: TMN(1)–AsF_6^-–TMN(2^i)–TMN(2)–AsF_6^-–TMN(1)··· (*cf.* Fig. 5). The AsF_6^- ion is located in the hole created by the relative rotation of 35° between TMN(1) and TMN(2). The two neighbouring TMN(2) molecules are parallel but displaced in order to fit into each other better. The building block of the structure is the triad TMN(2)–TMN(1)–TMN(2^i) surrounded by AsF_6^- on two sides (in the *c* direction, at the middle of the triad). In order to avoid anion collisions, the triad is tilted by 21° relative to the *bc* plane, and in this way the AsF_6^- ion also fits in well in the opening created by the 35° rotation of TMN(1) relative to TMN(2). This tilt also makes the charges more evenly distributed, minimizing the potential energy of the crystal. The molecules TMN(2)–TMN(2^i) (between two triads) are now also tied together *via* C—H···F—As interactions, as the anion now lies approximately between them.

There are four H···F contacts shorter than the van der Waals contact distance 2·47 Å [assuming $r_F = 1·47$ Å (Bondi, 1964) but $r_H = 1·00$ Å, *cf.* above]; see Table 2 and Fig. 5. These short contacts are probably responsible for the AsF_6^- ions being ordered in this compound (Beno, Blackman, Leung & Williams, 1983). The AsF_6^- ions have no contacts with each other; the shortest distance [3·697 (4) Å] is between F(2)···F(2) [the sum of the van der Waals radii is 2·94 Å (Bondi, 1964)].

Rigid-body analysis

The rigid-body analysis of Schomaker & Trueblood (1968) was used to fit the **T**, **L** and **S** tensors to the observed anisotropic displacement parameters for the carbon and oxygen atoms of the TMN(1) and the TMN(2) molecules. The approximation of Dunitz & White (1973) was used for the libration of the non-rigid groups of the molecule. Analysis of the AsF_6^- ion was not attempted due to difficulties with nearly spherical molecules. Several models were tried: (*a*) the whole carbon and oxygen skeleton as a rigid group and (*b*) as in (*a*) but with the methoxy groups non-rigid and testing different librational axes.

For the non-centrosymmetric molecule TMN(2), the rigid and non-rigid model is described by non-intersecting libration axes. The translation tensor is the reduced **T**, after diagonalizing **S**. For this molecule the rigid model (*a*) (see Table 3) resulted in a principal librational motion around the molecular body diagonal approximately parallel to the vector O(4)—O(2) (*cf.* Fig. 2). This suggests that the C(12) and the C(14) methyl groups are held in place by some intermolecular interaction, whereas groups

C(11) and C(13) can move more freely. This is seen clearly by looking at the intermolecular contacts (≤ 3·0 Å) to the methyl hydrogens (see Table 2 and Figs. 4 and 5). Here we see that the hydrogens of C(12) make four contacts with oxygen and four contacts with fluorine. In this case we have the shortest interstack [2·39 (3) Å] as well as the shortest intrastack contact [2·45 (3) Å] in the structure. The hydrogens of C(14) make four contacts with oxygen and one contact with fluorine. For C(11) the hydrogens have four contacts with fluorine only, and for C(13) there is one long intrastack H···O contact [2·91 (3) Å] and four fluorine contacts. It is difficult to compare the strengths of these contacts, but taking the mean value of the four shortest gives some hints. C(12) has the shortest mean value (2·52 Å) followed by C(14) (2·58 Å), C(13) (2·66 Å) and C(11) (2·73 Å), which is in agreement with the rigid-body analysis of the anisotropic displacement parameters (the isotropic displacement parameters of the hydrogens also follow the same trend). The principal components of the translation tensor (**T**) are in agreement with what would be expected looking at the intermolecular interactions (Table 3). For TMN(2) the rigid model (*a*) gives an effective screw translation parallel to $\mathbf{L}_1$ of −0·007 Å, parallel to $\mathbf{L}_2$ of −0·002 Å and parallel to $\mathbf{L}_3$ of 0·014 Å. The non-rigid model (*b*) for this molecule gives effective screw translations parallel to $\mathbf{L}_1$ 0·002 Å, $\mathbf{L}_2$ −0·014 Å and $\mathbf{L}_3$ 0·015 Å.

The best fit and most reasonable description of the motion for TMN(2) was obtained using a non-rigid-body model (*b*) where all four methoxy groups were allowed to librate freely around the inner C—O bond. The motions around the non-rigid librational C—O axes were obtained as negative values (deg^2). These negative values were interpreted as a librational motion by 5(4), 10(4), 5(4) and 10(4)° less than the rigid naphthalene group, around the non-rigid axes C(2)—O(1), C(3)—O(2), C(6)—O(3) and C(7)—O(4) respectively (see Table 3). This result is in agreement with the lengths of the intermolecular contacts as discussed above. As would be expected, the **L** tensors in the non-rigid model become more parallel to the principal inertial axes **I** than for the totally rigid model (the **L** values also increase). The origin of the inertial axes **I** is the centre of mass, $\mathbf{I}_1$ is parallel to C(9)—C(2), $\mathbf{I}_2$ is parallel to C(9)—C(10) and $\mathbf{I}_3$ is normal to the molecular plane. A test calculation where C(14), O(4), C(7), C(3), O(2) and C(12) were regarded as rigid while the rest was regarded as a non-rigid group librating around the O(4)—O(2) vector, gave a value of 9 (6)° for this non-rigid librational motion, in agreement with the previous result.

The result for TMN(1) is quite similar (see Table 3). The rigid model (*a*) resulted in a main librational motion ($\mathbf{L}_1$) approximately around the body diagonal C′(2)—C′(2). This diagonal libration can, as before, be explained by looking at the intermolecular contacts ≤ 3·0 Å (Table 2, and Figs. 4 and 5). Here we see clearly that C′(6) is far more closely bound than C′(7) [atom C′(6) has five close contacts while C′(7) only has three], and C′(7) can thus librate much more freely. Also for TMN(1) a better fit was obtained using model (*b*) with non-rigid axes along the C—O bonds closest to the ring (Table 3). The motion of the methoxy group around the non-rigid librational axis $\mathbf{L}_{C'(2)—O'(1)}$ was interpreted as a librational motion by 7 (5)° less than the rigid naphthalene group (negative deg^2).

To summarize, model (*b*), with all methoxy groups free to librate around the inner C—O axes, gives a significantly better fit to the observed anisotropic displacement parameters, especially for the outer methyl carbons which librate less than the rigid naphthalene molecule [except for C′(7)]. The amount of this smaller motion can be directly correlated to the number and shortness of the methyl hydrogen contacts to oxygen or fluorine.

The rigid bond test of Hirshfeld (1976) was applied to the observed anisotropic displacement parameters (ADP's) of the non-hydrogen atoms in the TMN molecules. In this test a bond is regarded as rigid if the difference of the mean-square displacement amplitudes in the line of a bond is smaller than 0·001 Å^2. For TMN(1) $\Delta_{\rm max}$ = 0·0024 and $\Delta_{\rm mean}$ = 0·0011 Å^2 and for TMN(2) $\Delta_{\rm max}$ = 0·0040 and $\Delta_{\rm mean}$ = 0·0015 Å^2. As all these C—C and C—O bonds are expected to be rigid, the result above would indicate that the ADP's are fairly well determined. This can also be judged from the relatively good fit (Table 3) and sensible results of the *TLS* analysis.

Physical properties

The temperature dependence of the conductivity is characteristic for a semiconductor, and the room-temperature conductivity along the stacking direction (*a* axis) is ~0·05 S m^{-1} according to Krzystek *et. al.* (1986). In a later investigation a value of 0·06–0·9 S m^{-1} was reported (Söderholm, von Schütz & Hellberg, 1987). The salt has a diamagnetic ground state, with thermally accessible triplet spin excitons [activation energy 0·19 (1) e V]. These properties are due to the trimerization of the TMN donor molecules in the stack. For further details of the electronic and magnetic properties see the references just cited.

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Dipotassium and Sodium/Potassium Crystalline Picrate Complexes with the Crown Ether 6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b*,*n*]-[1,4,7,10,13,16,19,22]octaoxacyclotetracosin (Dibenzo-24-crown-8)

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Abstract

The crystal structures of the dipotassium and the mixed sodium/potassium picrate complexes with the crown ether dibenzo-24-crown-8 (DB24C8) were solved and found to be nearly identical. (I): NaKpic$_2$(DB24C8), $[NaK(C_6H_2N_3O_7)_2(C_{24}H_{32}O_8)]$, M_r = 966·8, triclinic, $P\bar{1}$, a = 8·164 (2), b = 9·960 (2), c = 13·368 (3) Å, α = 103·92 (3), β = 108·03 (2), γ = 93·23 (2)°, V = 993·0 (7) Å^3, Z = 1, D_m = 1·54 (T = 298 K), D_x = 1·62 (1) g cm^{-3}, λ = (Mo $K\alpha$) 0·71069 Å, μ = 2·37 cm^{-1}, F(000) = 500, T = 103 K, R = 0·086 for 2904 unique reflections. (II): K$_2$pic$_2$(DB24C8), $[K_2(C_6H_2N_3O_7)_2(C_{24}H_{32}O_8)]$, M_r = 982·9, triclinic, $P\bar{1}$, a = 8·231 (4), b = 9·850 (2), c = 13·346 (4) Å, α = 103·91 (2), β = 106·82 (3), γ = 93·37 (2)°, V = 995·7 (9) Å^3, Z = 1, D_m = 1·59 (T = 298 K), D_x = 1·638 (8) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 3·30 cm^{-1}, F(000) = 508, T = 163 K, R = 0·042 for 4835 unique reflections. Both structures feature eight-coordinated cations between alternating layers of relatively flat crown ligands and paired picrates. In the mixed-metal system the two cations are disordered between two $P\bar{1}$-related sites; these metal sites have a coordination environment only slightly different from that in the dipotassium

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