relevant angles from 90 or 180°: N(1)–Pt–N(2) and I–Pt–C(1) being 163·4 (2) and 179·6 (2)° respectively with a range of 81·6 (2)–98·4 (2)° for the four remaining angles. The angle between the coordination plane and the phenyl ring is 9·5 (3)°. The molecule shows approximate twofold symmetry along the line through Pt and C(1); this is illustrated by the ΔC_2[Pt–C(1)] asymmetry parameter for the eight-membered ring C(1)–C(2)–C(10)–N(2)–Pt–N(1)–C(7)–C(6) that amounts to 4·2 (6)° (Duax, Weeks & Rohrer, 1976). The molecular twofold axis is also present in the octahedral $PtCl_3$(NCN) complex (Terheijden, van Koten, de Booys, Ubbels & Stam, 1983) in which the angle between the coordination plane and the phenyl ring is 16·3 (5)° and the ΔC_2[Pt–C(1)] parameter is 4·9 (7)°. Some structural features of PtI(NCN) are comparable with those of the PtI(NCN)(η^1-I_2) complex (van Beek, van Koten, Smeets & Spek, 1986) which has a distorted square-pyramidal coordination with an I_2 molecule occupying the apical position, whereas the other coordinating atoms are the same as in the present structure. The geometry of the NCN ligand compares favourably with the geometries found in the studies of $PtCl_3$(NCN) and PtI(NCN)-(η^1-I_2). The Pt–C(1) distances are nearly equal: 1·933 (6) Å in the present PtI complex and 1·937 (9) Å in the PtI(η^1-I_2) structure. The Pt–I distance and the averages of the Pt–N distances are slightly different; 2·716 (2) and 2·093 (6) Å respectively in PtI(NCN) and 2·727 (1), 2·111 (8) Å in PtI(NCN)(η^1-I_2).

Characteristic differences between the PtI and PtI(η^2-I_2) complexes include the position of the Pt atom with respect to the coordination plane [I(1), N(1), N(2), C(1)] which is included in the plane in the present PtI compound and lifted 0·18 (2) Å out of this plane in the

square-pyramidal PtI(η^1-I_2) complex. The molecular symmetry of PtI(η^1-I_2) is also different, the molecule having an approximate mirror plane through the Pt–I–C(1) atoms, perpendicular to the phenyl ring. The different molecular symmetry can also be seen from the signs of the C–C–C–N torsion angles with values of –23·0 (7) and –20·5 (8)° for N(1) and N(2) in PtI(NCN) and –26 (1), 25 (1)° for the corresponding angles in the PtI(η^1-I_2) complex, indicating the different conformations of the side chains.

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Structure of the Organic Semiconducting Radical Cation Salt Bis[2,3:6,7-bis(methylenedioxydibenzofuran)]* Hexafluoroarsenate

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Abstract. $(C_{14}H_8O_5)_2^+.AsF_6^-$, $M_r = 701·33$, monoclinic, $C2/c$, $a = 9·564$ (1), $b = 13·899$ (2), $c = 19·364$ (3) Å, $\beta = 92·63$ (1)°, $V = 2571·4$ (6) Å^3, $Z = 4$, $D_x = 1·81$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 15·1$ cm^{-1}, $F(000) = 1404$, $T = 298$ K. Final $R = 0·035$ for 2047 unique reflexions. Dimers consisting of (bMDODBF)$_2^+$ molecules ($C_{14}H_8O_5$ = bMDODBF) form stacks along the [110] and [1$\bar{1}$0] directions and are surrounded by AsF_6^- ions. Interplanar distances are 3·19 (2) Å within the dimers and 3·25 (2) Å between the dimers in the stacks. Adjacent dimers have poor molecular overlap, giving rise to semiconducting electronic properties.

* 1',3'-Benzodioxolo[5',6':3,2]benzofuro[6,5-d][1,3]dioxole.

There are short C—H···O contacts [$\geq 2\cdot33$ (3) Å] between different stacks of bMDODBF molecules. The $+\frac{1}{2}$ formal charge of the bMDODBF molecule has the effect of shortening or lengthening some C—C bonds by up to 0·030 Å.

Introduction. The present investigation is part of a series of studies of the structure and physical properties of electrochemically prepared radical cation salts of substituted aromatic hydrocarbons. These types of compound have been the subject of increasing interest in recent years, since they often exhibit unique electronic and magnetic properties, and are also in most cases simple to prepare (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980). The main problem has been to obtain single crystals of sufficiently good quality for a structure determination. In most cases partly amorphous or polycrystalline samples were obtained. Solvent molecules can also be incorporated along with the anions in the relatively spacious channels surrounding the stacks of donor molecules. This can occur in an ordered or disordered way depending on the narrowness of the channels. A solvent-free ordered structure is reported here.

Experimental. Good-quality solvent-free brittle crystals of (bMDODBF)$_2$AsF$_6$ with a silver-black metallic lustre were prepared by electrolytic oxidation of bMDODBF in CH$_2$Cl$_2$ solution in the presence of (nBu$_4$N)AsF$_6$ at a constant current density of 4–5 μA cm^{-2} and a temperature of 279 (2) K. Details of the synthesis, conductivity and ESR properties are given by Hellberg, Ahlgren, Söderholm, Olovsson & von Schütz (1985). Crystal: polyhedron 0·23 × 0·18 × 0·14 mm; PDP8/a-controlled Enraf–Nonius CAD-4F diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; $\omega/2\theta$ scan mode: scan width = $(0\cdot9 + 0\cdot35\tan\theta)°$; scan speed varied to maintain constant $\sigma(I)/I = 0\cdot02$; maximum scan time 200 s. Range of h, k, l: $-6 \leq h \leq 13$, $0 \leq k \leq 19$, $-27 \leq l \leq 27$ with $(\sin\theta/\lambda)_{max} = 0\cdot7095$ Å^{-1}. The unit-cell dimensions were determined from a least-squares refinement of the setting angles of 31 reflexions in the 2θ range 34–52°. Five standard reflexions were measured every 200 minutes of X-ray exposure time; their intensities decreased by less than 5% during the data collection. A scaling function derived from the five standard reflexions was used to correct the measured intensities; a contribution taking account of instability in the measurement and of 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. Absorption correction was performed by the Gaussian integration method using an

8 × 12 × 16 grid. The crystal was described by 12 faces. Transmission factors fell in the range 0·82 to 0·86 for the 4977 collected intensities. Averaging symmetry-equivalent reflexions ($R_{int} = 0\cdot013$) and deleting space-group extinctions left 3841 unique intensities. The complete initial structure (except for hydrogens) was solved with the program system *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); reflexions with $F_o^2 \leq 0$ were excluded at this stage. Information about the geometry of the bMDODBF and AsF$_6^-$ molecules was provided in the calculation of E_0^2 values using spherically averaged molecular scattering factors. All hydrogens were located in a $\Delta\rho$ map. Neutral atomic and anomalous scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The spherical bonded H-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 $w^{-1} = \sigma_{count}^2(F_o^2) + (0\cdot040F_o^2)^2$. In the final cycle, 1794 reflexions with $F_o^2 < 2\sigma(F_o^2)$ were excluded, leaving 2047 reflexions for the refinement of 236 parameters. These were one scale factor, 91 positional parameters, 136 anisotropic temperature factors (non-hydrogens) and eight isotropic temperature factors (hydrogens). Final agreement factors: $R(F) = 0\cdot035$, $R(F^2) = 0\cdot046$, $wR(F^2) = 0\cdot085$, $S(F^2) = 1\cdot50$. $(\Delta/\sigma)_{max} = 0\cdot13$ in the final cycle. A final $\Delta\rho$ map revealed a maximum peak height of 0·51 and a minimum of $-0\cdot35$ e Å^{-3}; both values close to the As atom. No secondary-extinction correction was necessary. Computations were performed with 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 ellipsoids are in Fig. 2(a) and bond angles in Fig. 2(b). The asymmetric unit consists of one bMDODBF molecule and half an AsF$_6^-$ ion; the bMDODBF molecule thus carries an effective charge of $+\frac{1}{2}$. Comparing with bond lengths in neutral dibenzofurans (Table 2), we see that the effect of the charge is mainly to lengthen and shorten some of the C—C bonds, leaving the mean bond length essentially unchanged. The largest differences in bond length are about 0·030 Å. This effect is also seen in a comparison of (naphthalene)$_2$PF$_6$ (Fritz, Gebauer, Friedrich, Ecker, Artes & Schubert, 1978) with neutral naphthalene (Cruickshank, 1957), and in a comparison of TTT$_2$I$_3$ with neutral TTT (TTT = tetrathiatetracene) (Smith & Luss, 1977). The largest differences in C—C bond

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43505 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic fractional coordinates and thermal parameters* ($Å^2 \times 10^4$)

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ for nonhydrogen atoms. U_{iso} is the mean square amplitude of vibration for the hydrogen atoms.

	x	y	z	$U_{eq}(U_{iso})$
C(1)	−0·00574 (26)	0·12765 (19)	0·47563 (13)	403 (14)
C(2)	0·14077 (24)	0·13536 (16)	0·47234 (11)	360 (12)
C(3)	0·19807 (25)	0·17871 (17)	0·41378 (11)	379 (13)
C(4)	0·12173 (28)	0·21482 (18)	0·35727 (12)	419 (14)
C(5)	−0·01956 (27)	0·20536 (18)	0·36305 (12)	409 (13)
C(6)	−0·08088 (25)	0·16391 (17)	0·42068 (13)	404 (14)
C(7)	0·25712 (24)	0·10963 (17)	0·51697 (11)	357 (12)
C(8)	0·27174 (26)	0·06425 (18)	0·58205 (12)	394 (13)
C(9)	0·40582 (28)	0·05276 (17)	0·60698 (12)	412 (13)
C(10)	0·52301 (25)	0·08291 (17)	0·57115 (13)	417 (14)
C(11)	0·51311 (28)	0·12716 (19)	0·50784 (13)	436 (15)
C(12)	0·37775 (26)	0·13900 (17)	0·48297 (12)	388 (13)
C(13)	−0·25202 (33)	0·20850 (27)	0·34412 (17)	578 (19)
C(14)	0·60101 (32)	0·02112 (28)	0·67214 (16)	560 (19)
O(1)	0·34199 (17)	0·18038 (12)	0·41978 (8)	416 (9)
O(2)	−0·12159 (18)	0·23725 (13)	0·31751 (9)	506 (11)
O(3)	−0·22327 (17)	0·16958 (14)	0·41122 (10)	554 (12)
O(4)	0·45236 (18)	0·00987 (15)	0·66767 (10)	570 (12)
O(5)	0·64209 (18)	0·06074 (14)	0·60784 (10)	549 (11)
H(1)	0·1943 (27)	0·0470 (17)	0·6059 (13)	463 (73)
H(2)	0·5915 (26)	0·1505 (18)	0·4844 (13)	492 (73)
H(3)	0·1706 (25)	0·2408 (17)	0·3169 (12)	389 (64)
H(4)	−0·0451 (29)	0·1051 (21)	0·5134 (15)	619 (88)
H(5)	0·6420 (35)	−0·0416 (25)	0·6758 (17)	790 (109)
H(6)	0·6305 (37)	0·0648 (23)	0·7087 (18)	864 (121)
H(7)	−0·3034 (29)	0·1557 (21)	0·3104 (15)	667 (92)
H(8)	−0·3051 (29)	0·2592 (21)	0·3481 (14)	524 (89)
As	0·00000	0·06488 (3)	0·75000	490 (2)
F(1)	0·11962 (19)	−0·02185 (15)	0·73294 (10)	866 (14)
F(2)	0·94533 (20)	0·06510 (15)	0·66533 (9)	818 (13)
F(3)	0·12248 (22)	0·14960 (15)	0·73385 (10)	957 (15)

Fig. 2. (*a*) Bond distances (Å) and atomic notations for the bMDODBF molecule. (*b*) Bond distances (Å) and angles (°) for the AsF$_6^-$ ion and bond angles (°) for the bMDODBF molecule. The thermal ellipsoids are plotted at 50% probability. In both (*a*) and (*b*) the upper distances are uncorrected while the bottom distances (in italics) are corrected for rigid-body thermal motion (*cf.* the text). Standard deviations for As—F distances are 0·002 Å and for angles 0·1°. Standard deviations for C—C and C—O distances are 0·003–0·004 Å and for angles 0·1–0·2°, and for C—H distances 0·03 Å and 2°, respectively.
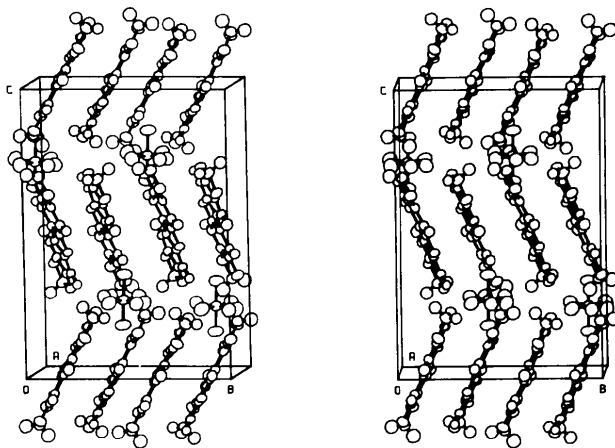

Fig. 1. A stereoscopic view of the molecular packing.

lengths in these cases are ∼0·030 and ∼0·040 Å respectively, while the mean bond lengths in these cases also remain about the same. Quantum-chemical calculations performed for TTT and TTT⁺ are in agreement with this character of lengthening and shortening of the bonds (Kiss, Kertész, Cársky & Wedel, 1979). Semi-empirical SCF-MO calculations performed by Appling, Burdick, Hayward, Abbey & Moran (1985) on benzene and benzene⁺ give further
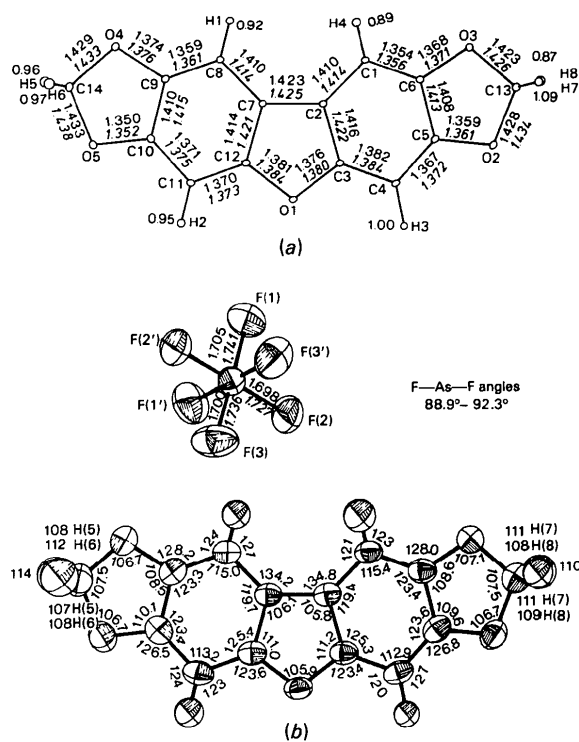
evidence for this. The differences (C₆H₆⁺–C₆H₆) in C—C bond lengths are here 0·043 (two bonds), 0·024 (two bonds), −0·026 and −0·018 Å. The bMDODBF molecule is close to planar, with C(13) and C(14) deviating most from the least-squares plane defined by all carbon and oxygen atoms [+0·044 (4) and −0·086 (4) Å respectively]. The dioxole rings are slightly bent around O(2)—O(3) and O(4)—O(5) (dihedral angles 7·4 and −7·5° respectively) giving rise to a slight chair conformation for the bMDODBF molecule. Atom C(13) deviates by 0·109 (4) Å from the plane defined by C(5), C(6), O(2) and O(3) [coplanar within 0·0008 (25) Å], and C(14) deviates by −0·110 (4) Å from the plane defined by C(9), C(10), O(4) and O(5) [coplanar within 0·0023 (25) Å]. This is in good agreement with the findings of Huber (1970), where the two end methylene carbons of the dioxole rings in the *N*-methylrhoeagenine molecule (which has two benzene rings with dioxole groups) deviate by 0·16 and 0·30 Å respectively from the planes defined as above (coplanar within 0·012 and 0·044 Å respectively).

Table 2. *A comparison between bond lengths (Å) of the* bMDODBF$^{0.5+}$ *molecule and some dibenzofuran derivatives (for notation see Fig. 2)*

No distances are corrected for thermal motion.

Bond	This work	(1)	(2)	(3)	(4)
C(1)–C(2)	1·410 (3)	1·398 (2)	1·395 (5)	1·405 (3)	1·403 (5)
C(1)–C(6)	1·354 (4)	1·388 (2)	1·380 (5)	1·388 (3)	1·380 (5)
C(2)–C(3)	1·416 (3)	1·399 (2)	1·387 (5)	1·380 (3)	1·390 (5)
C(2)–C(7)	1·423 (3)	1·438 (2)	1·457 (5)	1·455 (3)	1·452 (5)
C(3)–C(4)	1·382 (3)	1·380 (2)	1·373 (5)	1·386 (3)	1·384 (5)
C(3)–O(1)	1·376 (3)	1·384 (2)	1·386 (5)	1·400 (3)	1·390 (5)
C(4)–C(5)	1·367 (4)	1·388 (2)	1·374 (5)	1·391 (3)	1·391 (5)
C(5)–C(6)	1·408 (4)	1·400 (2)	1·403 (5)	1·390 (3)	1·388 (5)
C(7)–C(8)	1·410 (3)	1·398 (2)m	1·406 (5)	1·383 (3)	1·389 (5)
C(7)–C(12)	1·414 (3)	1·399 (2)m	1·391 (5)	1·408 (3)	1·382 (5)
C(8)–C(9)	1·359 (4)	1·388 (2)m	1·382 (5)	1·403 (3)	1·374 (5)
C(9)–C(10)	1·410 (4)	1·400 (2)m	1·404 (5)	1·423 (3)	1·392 (5)
C(10)–C(11)	1·371 (4)	1·388 (2)m	1·368 (5)	1·388 (3)	1·377 (5)
C(11)–C(12)	1·370 (4)	1·380 (2)m	1·381 (5)	1·371 (3)	1·383 (5)
C(12)–O(1)	1·381 (3)	1·384 (2)m	1·375 (5)	1·376 (3)	1·389 (5)
mean value	1·390 (3)	1·394 (2)	1·391 (5)	1·396 (3)	1·391 (5)

Dihedral angles (°)

6-ring–	0·6	1·5		0·3	0·3 (2)
5-ring	0·5	1·5		0·5	1·5 (6)
6-ring–					
6-ring–	0·6		4 (2)		1·7 (9)
6-ring					

Compounds and references:
(1) Dibenzofuran; Reppart, Gallucci, Lundstedt & Gerkin (1984).
(2) 2,8-Dimethoxydibenzofuran; Berg, Karlsson, Pilotti & Söderholm (1978).
(3) Ruscodibenzofuran; El Sohly, Slatkin, Knapp, Doorenbos, Quimby & Shiff (1977).
(4) 2-(4-Dibenzofuranyloxy)-2-methylpropionic acid; Wägner & Malmros (1979).
m Related by mirror symmetry.

Intrastack

The planar bMDODBF molecules are packed like a pile of pancakes above each other in stacks along the [110] and [1$\bar{1}$0] directions, with the AsF$_6^-$ ions surrounding the stacks (Figs. 1 and 3). The two stacking directions are related by a twofold axis in the **b** direction passing through the arsenic atoms. Adjacent bMDODBF molecules in the same stack are related by a centre of symmetry and are thus mutually parallel. Within a stack, the bMDODBF molecules also form dimers with their electric dipole moment vectors [passing approximately through O(1) and midway between C(2) and C(7)] oriented in opposite directions. Adjacent dimers are slightly displaced along **a**, giving rise to two modes of molecular overlap (Figs. 3 and 5). The distance between the least-squares planes (defined by the carbon and oxygen atoms) in the dimer is 3·19 (2) Å, and between the dimers 3·25 (2) Å; an unusually close spacing. The shortest intermolecular contacts are given in Table 3. The shortest C···C contact in the dimer [3·208 (4)] and between the dimers [3·307 (4) Å] is significantly shorter than the van der Waals contact distance for aromates of 3·54 Å proposed by Bondi (1964). [Pauling (1960) gives a van der Waals thickness for aromates of 3·4 Å.] The corresponding shortest C···C contact for dibenzofuran (Dideberg, Dupont & André, 1972) is 3·724 (3) Å.
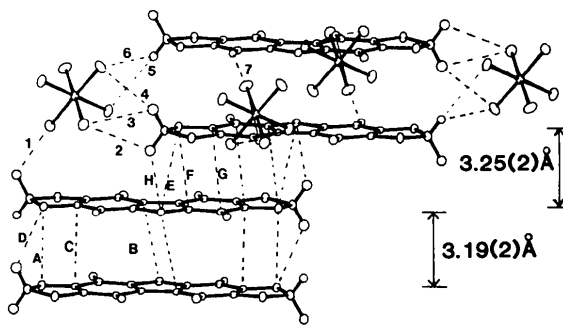

Fig. 3. Stacking along the [110] direction. The shortest intermolecular distances in the stack, and the H···F distances <3·0 Å are marked as dotted lines (*cf.* Table 3). The interplanar distances are between the least-squares planes (based on all C and O atoms) of the bMDODBF molecule. For clarity the AsF$_6^-$ ions surrounding the lower dimer in the figure are omitted.

Table 3. *Shortest intermolecular distances (Å) and angles (°) (all distances* <3·0 Å *are of the type* H···O *or* H···F)

Intrastack distances <3·0 Å, and shortest O···O, O···C, C···C distances (see Fig. 3)

O(2)···O(5)	3·168 (3)		A	
O(1)···C(2)	3·304 (3)		B	In
C(5)···C(10)	3·208 (4)		C	dimer
C(14)–H(6)···O(2)	2·80 (3)	119 (3)	D	
O(1)···O(5)	3·398 (3)		E	
O(5)···C(12)	3·287 (3)		F	Between
C(10)···C(11)	3·307 (4)		G	dimers
C(14)–H(5)···O(1)	2·68 (3)	130 (3)	H	

Interstack distances <3·0 Å (see Fig. 4)

C(4)–H(3)···O(2)	2·62 (3)	135 (2)	
C(11)–H(2)···O(3)	2·33 (3)	165 (2)	
C(13)–H(7)···O(4)	2·75 (3)	134 (2)	Not seen
C(14)–H(6)···O(4)	2·67 (4)	113 (2)	

Distances to F<3·0 Å (see Fig. 3)

C(13)–H(7)···F(1)	2·72 (3)	112 (2)	1
C(14)–H(5)···F(1)	2·83 (3)	106 (2)	2
C(14)–H(6)···F(1)	2·86 (4)	104 (2)	3
C(14)–H(6)···F(3)	2·82 (4)	140 (3)	4
C(13)–H(8)···F(2)	2·79 (3)	167 (2)	5
C(13)–H(8)···F(3)	2·62 (3)	117 (2)	6
C(4)–H(3)···F(3)	2·72 (2)	150 (2)	7
C(8)–H(1)···F(1)	2·76 (3)	142 (2)	Not seen
C(8)–H(1)···F(2)	2·70 (3)	159 (2)	Not seen
C(8)–H(1)···F(3)	2·97 (3)	121 (2)	Not seen

Here also the molecules are arranged in parallel pairs with their electric dipole moment vectors in opposite directions.

Dimer radical cations of fluoranthene would appear to have formed already in the solution during the electrocrystallization process according to the reaction $D^+ + D = D_2^+$ (Enkelmann, Morra, Kröhnke, Wegner & Heinze, 1982). Evidence for this is given in the non-reversible cyclic voltammogram of fluoranthene. Cyclovoltametry of bMDODBF (Hellberg *et al.*, 1985) showed a quasi-reversible peak indicating the possibility

of dimer radical cation formation in solution. More evidence for the formation of such dimers is given by Delcourt & Rossi (1982) where most dimer radical cations of unsaturated hydrocarbons seem to absorb light in the blue–green region 480–550 nm. The absorption spectra of the mother liquor from the electrolysis of the title compound showed a maximum at 650 nm and a shoulder at 610 nm (Hellberg et al., 1985), which is not in this blue–green region. However, there remains the possibility that $(bMDODBF)_2^+$ does not absorb around 500 nm and the two peaks could be ascribed to D^+ and D_2^+.

Short intermolecular spacings in columnar stacks seem to be characteristic of radical cation salts of aromates. For example, perylene radical salts have interplanar distances of about 3·40 Å (Endres, Keller & Müller, 1985), $(fluoranthene)_2PF_6$ (and AsF_6) have distances 3·28 and 3·33 Å (Enkelmann et al., 1982; Enkelmann, 1983) and $(naphthalene)_2PF_6$ (and AsF_6) (Fritz et al., 1978) have stacking distances of 3·20 Å. The question arises as to whether these short stacking distances are due to the electrostatic influence of the anions, the polarization interaction between the two molecules in the dimer, or to a combination of the two. To establish this, one would need to perform elaborate theoretical calculations. It would also be very interesting to know the distance between the molecules in the dimer radical cation D_2^+ in solution.

Interstack

The interstack contacts are shown in Fig. 4 and Table 3. The bMDODBF molecules seem to orient themselves relative to one another to achieve short C—H···O contacts between the stacks (Fig. 4). These are probably weak electrostatic interactions with
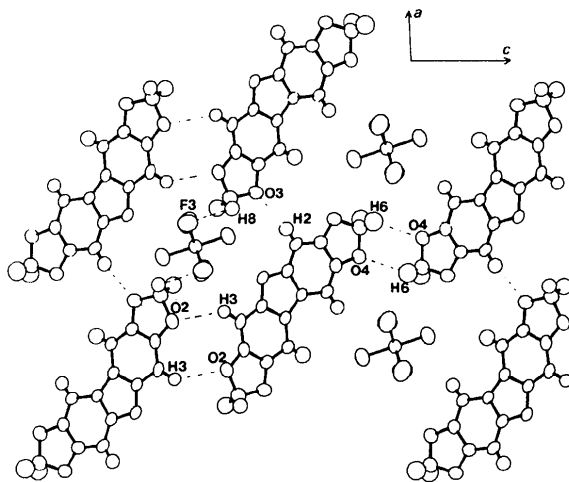

Fig. 4. Intermolecular distances <3·0 Å between the stacks of MDODBF molecules, viewed along the twofold axis (cf. Table 3).

distances greater than the corresponding van der Waals distances (2·40 Å), except for H2···O3 [2·33 (3) Å], which could thus be regarded as a weak hydrogen bond. This type of orientation is also seen in $(TMN)_3$-$(AsF_6)_2$ (TMN ≡ 2,3,6,7-tetramethoxynaphthalene) (Krzystek, von Schütz, Ahlgren, Hellberg, Söderholm & Olovsson, 1986).

The AsF_6^- ion

The dimers of bMDODBF molecules are surrounded on four sides by AsF_6^- ions (Fig. 3); the only close fluorine contacts are to hydrogen atoms (H···F < 3·0 Å, Table 3). These contacts are probably responsible for the AsF_6^- ion being ordered in this compound (Beno, Blackman, Leung & Williams, 1983). It is also interesting to note that nine of the ten short H···F contacts are within the dimer (only one between). It is difficult to assess what effect this arrangement has on the stacking of the bMDODBF molecules.

Electrical properties

The room-temperature electrical conductivity for perylene salts ranges from metallic [$\sim 10^3(\Omega\,cm)^{-1}$] to semiconducting or insulating. Important factors favouring high conductivity in this type of compound seem to be: good crystal quality, stoichiometry near $D_2^+X^-$, large and the same type of overlap between adjacent molecules and uniformity in the short stacking distances. The $(bMDODBF)_2AsF_6$ salt has a room-temperature conductivity of $\sim 2 \times 10^{-4}(\Omega\,cm)^{-1}$ with an activation energy of $\Delta \sim 370$ meV measured along [110]. The room-temperature conductivities along the a and b axes are both $\sim 10^{-4}(\Omega\,cm)^{-1}$. The temperature dependence of the conductivity and the ESR signal is typical of a semiconductor (Hellberg et al., 1985). Reasons for this semiconducting behaviour can probably be found in the relatively weak overlap between adjacent bMDODBF dimers (Figs. 3 and 5). A comparison can be made with $(fluoranthene)_2AsF_6$ (Enkelmann, 1983) where we have a metal-to-semiconductor phase transition near 200 K involving a very slight change in the geometry of the molecular overlap. The room-temperature stacking distances are 3·28 and 3·33 Å and this difference of 0·05 Å remains constant through the phase transition and down to 120 K (although the individual stacking distances become slightly shorter). It can thus be suspected that neither the difference (0·06 Å) in stacking distance for $(bMDODBF)_2AsF_6$ nor the length of the stacking distances in themselves necessarily oppose metallic conductivity, but that the detailed nature of the overlap is probably not ideal.

Rigid-body analysis

The rigid-body analysis of Schomaker & Trueblood (1968) was used to fit the T, L and S tensors to the observed thermal parameters for the C and O atoms of
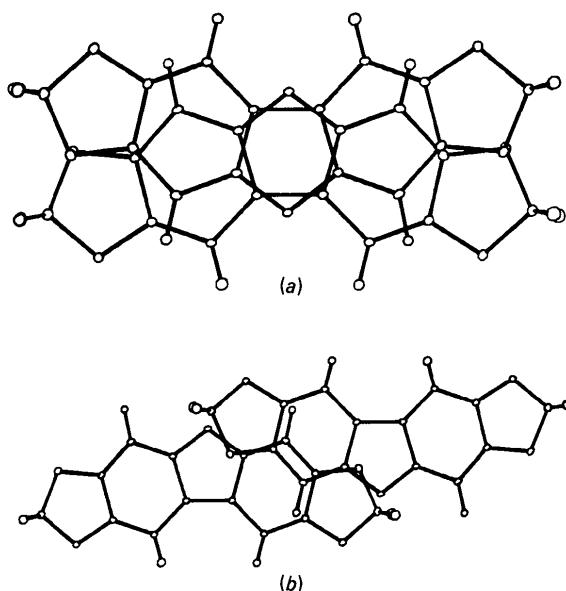
Fig. 5. Overlap between the two bMDODBF molecules (a) in the dimer and (b) between the dimers themselves. The view is perpendicular to the molecular plane.

the bMDODBF molecule and separately to the As and F atoms of the AsF_6^- ion (Fig. 2). The r.m.s. difference between the observed U_{ij}'s and those calculated from the rigid-body model was $0.0025 (13) Å^2$ for the bMDODBF molecule and $0.0006 (12) Å^2$ for the AsF_6^- ion. Agreement between corresponding covalent bond distances of the bMDODBF molecule showed no significant improvement after application of the rigid-body correction (indeed, in the AsF_6^- ion the As—F bond lengths differed more after the correction). Owing to the near-octahedral symmetry of the AsF_6^- ion, one must be careful in the interpretation of the T, L and S tensors as they may not be uniquely determined. With the origin at the centre of mass, I_1 approximately parallel to C(13)—C(14), I_2 approximately perpendicular to C(2)—C(7) and in the plane of the molecule and I_3 approximately perpendicular to the mean plane of the molecule, the principal components of the translation (T) tensor for the bMDODBF molecule are $T_1 = 0.214$, $T_2 = 0.171$ and $T_3 = 0.147$ Å with angles 9.4, 9.6 and 11.8° to the principal inertial axes. The principal components of the librational tensor (L) are $L_1 = 5.1$, $L_2 = 2.3$ and $L_3 = 1.9°$ with angles 2.9, 2.6 and 1.4° to the inertial axes. It is interesting to note that the smallest and the largest translations occur in directions of greatest and least intermolecular interaction respectively.

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