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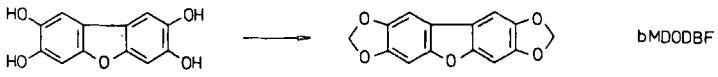
ABSTRACT: The AsF_6^- cation radical salt of 2,3,6,7-bis-methylenedioxydibenzofuran has been synthesized. Its structural, electrical and ESR properties are presented.

INTRODUCTION AND SYNTHESIS

In our recent investigation of cation radical salts with alkoxylated dibenzofurans as donors, we have now prepared the $(bMDODBF)_2AsF_6$ salt. The donor bMDODBF was prepared from 2,3,6,7-tetrahydroxydibenzofuran[1] by alkylation with $CH_2I_2/(nBu)_4NF/Na_2CO_3$ in 29% yield.[2]



Constant current electrolysis (4-5 $\mu A/cm^2$) of the donor in 0.05 M $(nBu)_4NAsF_6$ in dichloromethane gave the radical salt as black glimmering crystals in a blue solution. This is a true solvent free 2:1 salt, whereas electrolysis of 2,3,6,7-tetramethoxydibenzofuran gave a salt with dichloromethane incorporated[3].

Cyclovoltammetry of bMDODBF showed a quasireversible peak with $E_{\frac{1}{2}}$=1.24 V (vs SCE). Sample concentration was 2 mM in 0.15 M $(nBu)_4NBF_4$ in dichloromethane. Scan rate was 100 mV/s.

Visible absorption spectra of the mother liquor from electrolysis showed a maximum at 650 nm and a shoulder at 610 nm.

X-RAY STRUCTURE OF $(bMDODBF)_2\ AsF_6$

Crystal Data

Monoclinic, C2/c, a=9.564(1), b=13.899(2), c=19.364(3) Å, β=92.63(1)°, Z=8, T=298 K, λ(MoKα)=0.71069 Å. A refinement with 2047 independent reflexions ($\sin\theta/\lambda$<=0.710 $Å^{-1}$) gave R(F)=0.035.

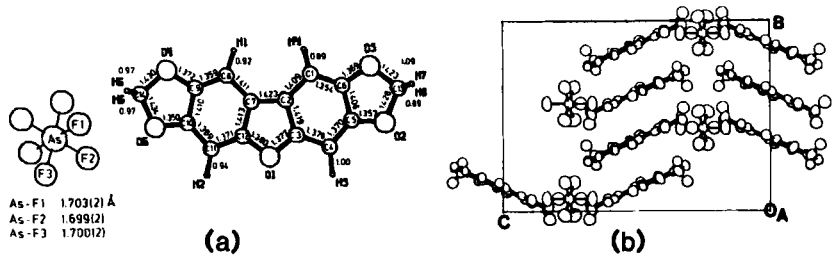


FIGURE 1 (a) Bondlengths in the molecules. σ(C-O,C-C)= 0.004 Å, σ(C-H)=0.03 Å. (b) Crystal packing.

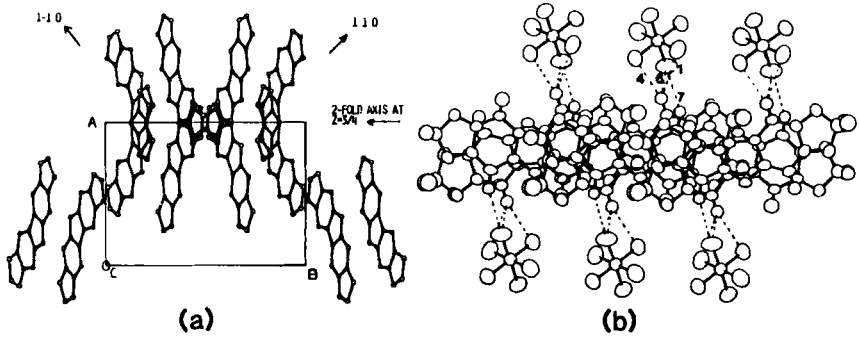


FIGURE 2 (a) 2 stacking directions (110) and (1-10) related by a 2-fold axis. (b) Molecular overlap in stacking direction (view pependicular to the molecule).

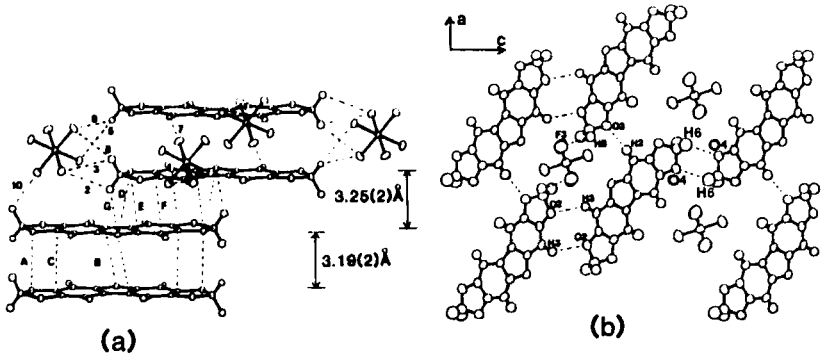


FIGURE 3 (a) Intrastack contacts. (b) Interstack contacts

Description of the Structure

There are 2 stacking directions (110) and (1-10) related by a 2-fold axis (fig 2a and 1b). The bMDODBF molecules form dimers in the stacks with interplanar distances of 3.19(2) and 3.25(2) Å. The shortest O•••O, O•••C, C•••C and O•••H contacts in the dimers: (A) O2•••O5 3.168(3), (B) O1•••C2 3.304(3), (C) C5•••C10 3.208(4) and between the dimers: (D) O1•••O5 3.398(3), (E) O5•••C12 3.287(3), (F) C10•••C11 3.307(4), (G) O1•••H5 2.68(3) Å (fig 3a). AsF_6 surrounds the dimers on 4 sides and the electronegative fluorines orient themselves towards the electropositive methyl hydrogens[4]. The As lie in the 2-fold axis. Distances to F<3.0 Å in the dimers: (1) F1•••H1 2.76(3), (2) F1•••H5 2.83(3), (3) F1•••H6 2.86(4), (5) F2•••H8 2.79(3), (6) F3•••H1 2.97(3) (7) F3•••H3 2.72(2), (8) F3•••H6 2.82(4), (9) F3•••H8 2.62(3), and between dimers: (10) F1•••H7 2.72(3) Å (fig 3a and 2b).

There are interstack hydrogen bondings (fig 3b) i.e O3•••H2 2.33(3) Å. Other short contacts are: O2•••H3 2.62(3), O4•••H6 2.67(4), F3•••H8 2.62(3) Å. Figures 1b,2b and 3b are drawn with 50% probability ellipsoids.

CONDUCTIVITY

$(bMDODBF)_2AsF_6$ showed semiconducting behaviour, with an activation energy of $\Delta \sim 370$ meV and $\sigma_{rt} \sim 2 \cdot 10^{-4} (\Omega cm)^{-1}$, measured in the (110) direction which corresponds to the stacking axis. Measurements along the a- and b-axis gave $\Delta_a \sim 390$ meV and $\Delta_b \sim 320$ meV with an anisotropy of $\sigma_b/\sigma_a \geq 2$. The room temperature conductivities are both $\sim 10^{-4} (\Omega cm)^{-1}$.

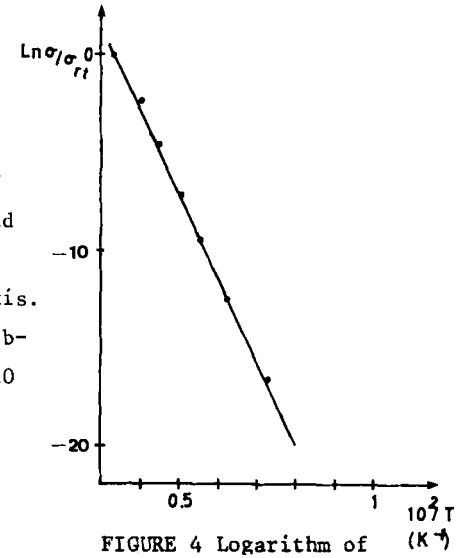
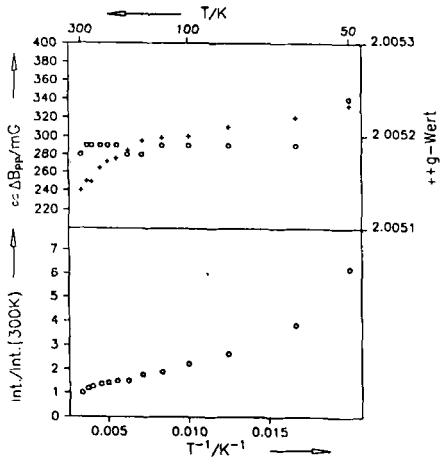


FIGURE 4 Logarithm of the conductivity in the (110) direction vs. 1/T.

ESR

The $(bMDODBF)_2AsF_6$ salt showed a temperature independent linewidth ($\simeq$290 mG) between 300 and 60 K. The intensity indicated metallic contributions above 180 K, although a well pronounced phase transition is not obvious. It may be obscured by still mobile paramagnetic centers which obey Curie's law.



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