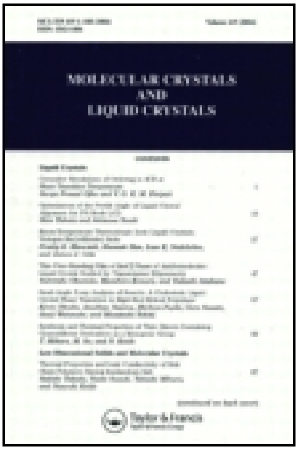

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Synthesis, Structure, Raman, and ESR Characterization of a New Organic Charge Transfer Salt, $(BEDT-TTF)_2[N(SO_2CF_3)_2]$

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SYNTHESIS, STRUCTURE, RAMAN, AND ESR CHARACTERIZATION OF A NEW ORGANIC CHARGE TRANSFER SALT, $(BEDT\text{-}TTF)_2[N(SO_2CF_3)_2]$

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Abstract The new charge transfer salt $(BEDT\text{-}TTF)_2[N(SO_2CF_3)_2]$ was synthesized and structually characterized. Its unit cell parameters at 295 K are: a = 6.6394(13) Å, b = 8.658(2) Å, c = 17.349(4) Å, α = 94.70(2)°, β = 97.21(2)°, γ = 68.95(2)°, V = 922.7(4) Å^3, space group $P\bar{1}$, and Z = 1. The anion, $N(SO_2CF_3)_2^-$, was found to be disordered, which may relate to the absence of the ν_4 and ν_5 A_g modes of the BEDT-TTF molecule in the Raman spectrum. ESR measurements reveal its semiconductive behavior with a small energy gap of 18.7 meV.

INTRODUCTION

Recently discovered charge transfer salts based on BEDT-TTF [bis(ethylenedithia)-tetrathiofulvalene] or ET, and containing the dicyanamide anion, $[N(CN)_2]^-$, or the tetrakis(trifluoromethyl)metallate anion, $[M(CF_3)_4]^-$, have stimulated renewed interest in the research area of organic superconductors. The complexation reaction of cuprous halides (CuBr or CuCl) with the $[N(CN)_2]^-$ anions leads to the two radical cation based organic superconductors, κ-$(ET)_2Cu[N(CN)_2]Br$ (T_c = 11.6 K) and κ-$(ET)_2Cu[N(CN)_2]Cl$ (T_c = 12.8 K 0.3 kbar pressure), with the highest T_c to date.[1, 2] More recently, the variation of the metal center (M = Cu, Ag, and Au) and of the crystallizing 1,1,2-trihaloethane solvents in the $[M(CF_3)_4]^-$ anion has yielded twenty-one organic superconductors in a single family, κ-$(ET)_2[M(CF_3)_4](Solv)$ with T_c = 2.4 to 11 K.[3] The anion of the title compound, bis(trifluoromethanesulfon)imide $N(SO_2CF_3)_2^-$, possesses characteristic features of both of the aforementioned superconductor families, i.e., an NR_2^- functional group which bears the same geometry as that of the $N(CN)_2^-$ anion, with terminal trifluoromethyl groups. We have explored the crystal growth of ET with this new $[N(SO_2CF_3)_2]^-$ anion and the possibility of complexing this anion with transition metal cations. Herein, we report the synthesis and characterization of a new ET salt, $(ET)_2[N(SO_2CF_3)_2]$.

SYNTHESIS

Typical experimental conditions for electrocrystallization of $(ET)_2[N(SO_2CF_3)_2]$ are as follows: ET (10 mg) and a large excess (more than 25 fold) of $LiN(SO_2CF_3)_2$ (3M Co.) and 12-crown-4 (Aldrich) were suspended in an H-cell filled with 15 mL of solvent (1,1,2-trichloroethane, TCE, or tetrahydrofuran, THF). Crystal growth was observed after one day at a low current density of 0.2 $\mu A/cm^2$ in TCE, while a higher current density of 0.8 $\mu A/cm^2$ was required in THF. Crystals were harvested after two to three weeks. Crystals grown from TCE or THF exhibited plate and rod-like morphologies but revealed the same ESR peak-to-peak line width of 28 to 38 G.

Complexation of the $N(SO_2CF_3)_2^-$ anion with transition metal cations was also attempted. However, the reaction between two equivalents of $LiN(SO_2CF_3)_2$ and one equivalent each of $AgNO_3$ and PPNCl [PPN^+ = bis(triphenylphosponium)imminium cation] in water led only to $PPN[N(SO_2CF_3)_2]$, not to the desired metal complex salt $PPNAg[N(SO_2CF_3)_2]_2$. Elem. anal. for $C_{38}H_{30}F_6O_4S_2N_2P_2$, Found (Calcd)%, C: 55.44 (55.75); H: 3.63 (3.69); N: 3.36 (3.42); Ag: 0.081 %. mp. = 152–153°C. Electrocrystallization of ET with $PPN[N(SO_2CF_3)_2]$ in TCE with a current density of 0.2 $\mu A/cm^2$ gave a second phase with ESR line width near 7 G in addition to the aforementioned plate and rod phases. The 7 G phase will be the subject of future studies.

STRUCTURE

A crystal of $(ET)_2[N(SO_2CF_3)_2]$ grown from THF was mounted on a modified Nicolet *P*3/F four-circle X-ray diffractometer (MoKα radiation, λ = 0.7107 Å, graphite monochromator). At 295 K, triclinic lattice parameters a = 6.6394(13) Å, b = 8.658(2) Å, c = 17.349(4) Å, α = 94.70(2)°, β = 97.21(2)°, γ = 68.95(2)°, V = 922.7(4) $Å^3$ (corresponding to $Z = 1$) were obtained from the carefully centered setting angles of 72 reflections with $20.1° < 2\theta < 35.6°$. 5569 intensity data were collected (ω-scans, 1.35° wide, $1.5°min^{-1}$, $4° < 2\theta < 55°$, $-1 < h < +8$, $-10 < k < +11$, $-22 < l < +22$), corrected for Lorentz, polarization, and absorption (μ = 10.7 cm^{-1}, T_{min} = 0.867, T_{max} = 0.948, based on measured crystal shape), and averaged (R_{int} = 0.040) to 4248 unique, allowed reflections. The structure was solved by direct methods in the centrosymmetric space group $P\bar{1}$, resulting in atomic coordinates for the entire crystallographically unique ET molecule. The anion was located with the use of a subsequent difference Fourier map. A disordered model with two superimposed orientations, related by an inversion center, of the intrinsically non-centrosymmetric anion was adopted (see Figure 1). Two atoms, S9 and C11, coincide in both orientations, whereas all the other anion atoms were refined with 50% occupancy parameters. Anisotropic refinement of all non-hydrogen atoms [2852 reflections with $F_o > 4\sigma(F_o)$, 280 variables] and fixed hydrogen atoms at calculated positions ($d_{C-H} = 0.95$ Å, $U_{iso} = 0.063$ Å^2) resulted in the following agreement factors: $R(F_o) = 0.057$, $R_w(F_o) = 0.050$, $S = 2.06$. The largest excursions on the final difference map were −0.92 and +0.96 e Å^{-3}, both near the center of the anion. A model with two independent ET molecules and an ordered anion in the space group $P1$ did not result in a significant reduction of the agreement factors, but instead led to strong correlations among the positional and thermal parameters.

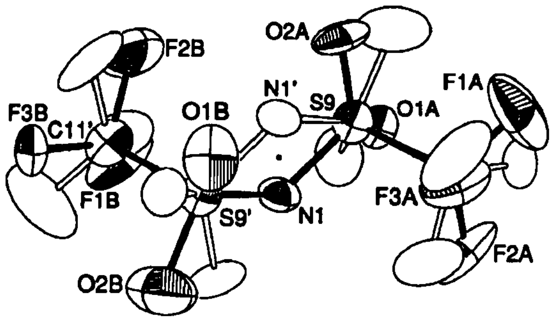

FIGURE 1 The disordered anion in $(ET)_2[N(SO_2CF_3)_2]$ showing the two possible orientations (one drawn with dark bonds and decorated atoms, the other with outlined bonds and atoms). The ellipsoids are drawn at the 25% probability level, and the inversion center is indicated by a dot.

The crystal structure (coordinates given in Table I) contains layers of ET electron donor molecules alternating with layers of anions, as is the case in most representatives of this class of materials. The ET molecule layers are shown in Figure 2. Two ET molecules, related to each other by inversion symmetry, comprise one unit cell. Loose stacks of electron donor molecules, with alternating interplanar distances of 3.73 and 3.77 Å, run along the (a–b)-diagonal direction. However, all intermolecular S···S contacts shorter than the sum of the van der Waals radii (3.60 Å) are located in ribbons along the *a*-direction. The shortest contacts to the other four surrounding ET molecules are considerably longer at 3.81 and 3.88 Å (intrastack), 3.72 and 3.84 Å (interstack), respectively. The ribbon-like topology of the short intermolecular contacts (believed to be indicative of good electronic conduction pathways) is expected to lead to largely one-dimensional electronic behavior, in contrast to the structurally similar β-phase family of ET salts, i.e., β-$(ET)_2I_3$ and related compounds.[2] In those salts, the two-dimensional topology of short intermolecular S···S contacts is related to the two-dimensional band electronic structure which favors metallic conduction and even superconductivity at sufficiently low temperatures [i.e., 1.5 K in the absence of external pressure in the case of β-$(ET)_2I_3$]. However, in quasi-one-dimensional systems, such as the title compound, on-site Coulombic repulsion usually favors charge localization, even if the band electronic structure indicates metallic behavior in one direction.

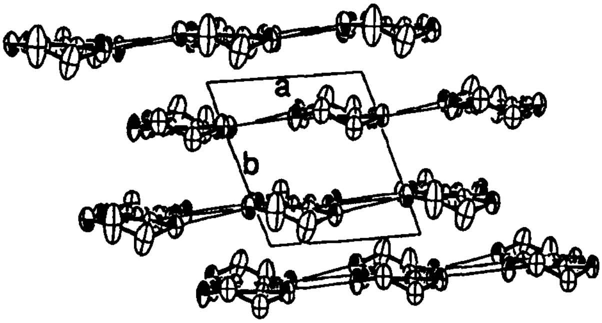

FIGURE 2 Perspective view of the ET molecule layer in $(ET)_2[N(SO_2CF_3)_2]$ projected approximately along the central C=C bond direction. Intermolecular S···S contacts shorter than 3.60 Å are drawn as thin lines.

TABLE I Fractional atomic coordinates and equivalent isotropic displacement parameters in (ET)$_2$[N(SO$_2$CF$_3$)$_2$]. Atom N1 as well as those with label suffix "A" or "B" were refined with an occupancy factor of 0.5 in order to account for the disordered model (see text).

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
S1	0.0637(2)	0.8138(2)	0.56563(6)	0.0508(4)
S2	0.4877(2)	0.7903(2)	0.52321(6)	0.0486(5)
S3	−0.0086(2)	0.6040(2)	0.40823(6)	0.0484(4)
S4	0.4071(2)	0.5935(2)	0.36285(6)	0.0482(4)
S5	0.0898(2)	1.0071(2)	0.71300(7)	0.0567(5)
S6	0.6022(2)	0.9677(2)	0.66201(7)	0.0694(6)
S7	−0.1324(2)	0.4429(2)	0.26432(7)	0.0606(5)
S8	0.3551(2)	0.4413(2)	0.20633(7)	0.0595(5)
C1	0.2532(6)	0.7439(5)	0.4988(2)	0.0391(15)
C2	0.2212(6)	0.6573(5)	0.4311(2)	0.0367(15)
C3	0.2125(6)	0.9082(5)	0.6304(2)	0.0402(15)
C4	0.4082(6)	0.8962(5)	0.6107(2)	0.0398(15)
C5	0.0605(6)	0.5144(5)	0.3163(2)	0.0390(15)
C6	0.2485(6)	0.5128(5)	0.2950(2)	0.0387(15)
C7	0.3191(8)	1.0242(7)	0.7746(3)	0.068(2)
C8	0.4614(8)	1.0906(7)	0.7389(3)	0.069(2)
C9	−0.0153(11)	0.3645(11)	0.1784(3)	0.140(4)
C10	0.1254(11)	0.4217(10)	0.1477(3)	0.116(4)
N1	0.024(2)	0.0560(12)	0.0354(6)	0.082(5)
S9	0.0970(3)	−0.1353(2)	0.04737(9)	0.0802(7)
O1A	0.117(2)	−0.1485(15)	0.1327(7)	0.078(5)
O2A	−0.008(2)	−0.230(2)	0.0040(7)	0.117(6)
C11	0.3788(12)	−0.2147(11)	0.0283(4)	0.090(4)
F1A	0.448(4)	−0.375(2)	0.0407(14)	0.231(13)
F2A	0.490(2)	−0.130(3)	0.0625(7)	0.151(10)
F3A	0.419(6)	−0.217(5)	−0.040(2)	0.156(12)
O1B	−0.073(2)	0.057(2)	−0.1118(7)	0.117(7)
O2B	−0.081(4)	0.307(2)	−0.0358(11)	0.227(13)
F1B	−0.396(6)	0.249(5)	0.044(2)	0.165(15)
F2B	−0.426(3)	0.071(3)	−0.0426(15)	0.257(13)
F3B	−0.499(2)	0.310(2)	−0.0790(7)	0.097(5)

RAMAN STUDIES

Single crystals of $(ET)_2[N(SO_2CF_3)_2]$ were subjected to Raman reflectance studies at room temperature with use of a laser Raman microscope spectrometer (Renishaw, Ltd.) equipped with a He-Ne laser (λ_0 = 6328 Å). Low incident laser power of 0.06 mW was applied to avoid any sample damage. Raman shifts between 50 and 2500 cm^{-1} were recorded and calibrated against the standard Si peak at 520 cm^{-1}. The crystals prepared from TCE and THF gave identical spectra. The absorption peaks as well as their assignments based on calculated values for the neutral ET molecule by Eldridge et al. are listed in Table II.[4, 5]

TABLE II Raman spectra of $(ET)_2[N(SO_2CF_3)_2]$ compared with neutral ET.

$(ET)_2N(SO_2CF_3)_2$ cm^{-1}	Assignments	ET (calcd) cm^{-1}
1490 br sh	ν_2 A_g	1554.2
1469.1 vs	ν_3 A_g	1487.5
	ν_4 A_g	1412.6
	ν_5 A_g	1283.1
1008.8 w	ν_{58} B_{3g}	1022
970.6 m	ν_6 A_g	982.5
~920 br	ν_7 A_g	917.7
889.7 m	ν_{60} B_{3g}	885
827.9 w		
775.0 w	B_{1g}	790
738.2 w		
682.4 w	ν_{61} B_{3g}	688
648.5 m	ν_8 A_g	629.6
507.0 br		
484.1 m	ν_9 A_g	490.1
446.3 w	ν_{10} A_g	433.9
315.6 w	ν_{11} A_g	306.1
267.6 br	anion	
182.1 m		
159.2 s	ν_{12} A_g	141.7
132.2 m	anion	
77.0 s		

The most prominent absorption is the ν_3 A_g mode (previously ν_4 peak in ref. 6) at 1469 cm^{-1}. The Raman shift agrees well with other 2:1 ET salts and is consistent with ET molecules in the +0.5 oxidation state.[6] As shown in Table II, most of the Raman active A_g modes can be identified except for ν_4 and ν_5 which involve out-of-plane C–H bending. The reason for their absence might be associated with the H···F (from the $-CF_3$ groups) interactions and the disordered $N(SO_2CF_3)_2^-$ anions (see Structure section). Support of this argument comes from the significantly broadened, yet identifiable, ν_7 A_g mode (~920 cm^{-1}) which also involves C–H bonds.

ESR STUDIES

A platelet crystal of $(ET)_2[N(SO_2CF_3)_2]$ was oriented with the *ab* -plane vertical and the c^* axis horizontal in the ESR cavity (IBM ER 200D spectrometer with TE_{102} rectangular cavity). At room temperature, orientation studies were carried out with $\theta = 0°$ and 90° indicating the static field direction parallel and perpendicular to the *ab*-plane, respectively. The results are shown in Figure 3.

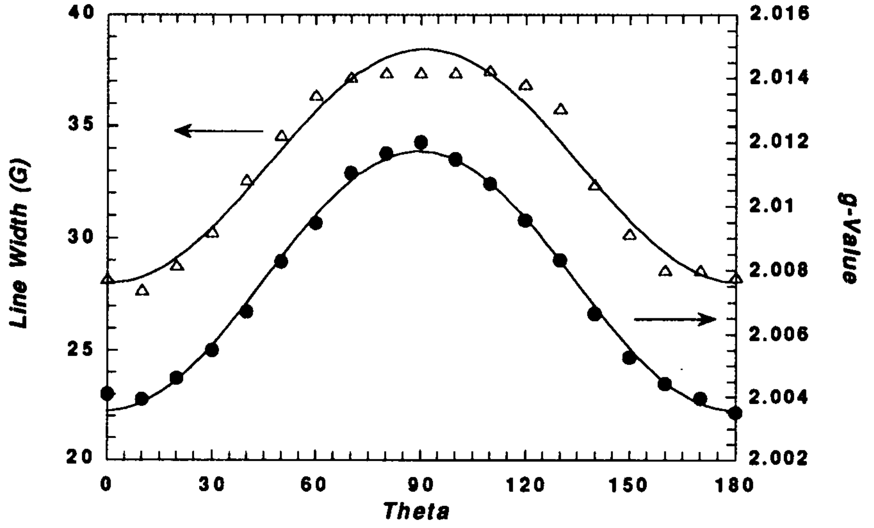

FIGURE 3 Angular-dependent peak-to-peak line widths (triangles) and *g*-values (circles) in the $(ET)_2[N(SO_2CF_3)_2]$ salt. The lines are the least-squares fitted curves.

The line widths (triangles) range from 27 to 38 G, and the *g*-values (circles) from 2.003 to 2.012. The maximum *g*-value is in-phase with the maximum line width, which is typical of a β-like structure. The maximum *g* value at 90° is common to all two-dimensional layered ET salts, due to the largest *g* value contribution along the central C=C bond in the ET molecules.[2]

The low temperature ESR measurements were carried out between 3 and 280 K with the $(ET)_2[N(SO_2CF_3)_2]$ crystal oriented at 90°. Data acquisition was accomplished with use of the LabVIEW® software (National Instruments Corporation) and a locally developed user interface program. Spectra were satisfactorily fitted with a one-line Lorentzian derivative curve[7] at all temperatures. The temperature-dependent peak-to-peak line widths (triangles) and the relative spin susceptibilities (circles) are shown in Figure 4. The line width and spin susceptibility both decrease monotonically with decreasing temperature. The spin susceptibility drops by 50% from room temperature to 150 K and indicates semiconductive behavior. This result is consistent with the observation that all intermolecular S···S contacts shorter than the sum of van der Waals radii are located along the *a*-direction, and thus we expect one-dimensional electronic behavior to occur.

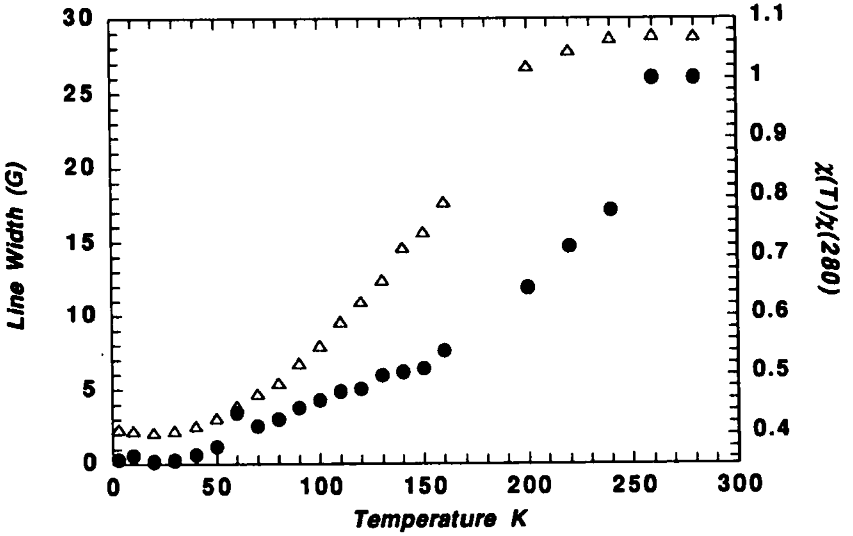

FIGURE 4 Temperature dependent peak-to-peak line width (triangles) and relative spin susceptibility (circles) of $(ET)_2[N(SO_2CF_3)_2]$ salt.

In order to extract the semiconductive energy gap, E_g, $\ln[\chi(T)/\chi(280)]$ was plotted against $1/T$ according to the following equation:

$$\frac{\chi(T)}{\chi(280)} = A \exp\left(\frac{-E_g}{k_B T}\right)$$

where k_B is Boltzmann constant.[8] The semiconductive energy gap, E_g, derived from the slope of the data between 280 and 150 K, is 18.7 meV or 151 cm^{-1}. This value is relatively small compared to typical band gaps near 100 meV in other organic semiconductors.[2]

AC susceptibility measurements (LakeShore 7000 Susceptometer) were performed on 6.2 mg crystals (prepared from TCE) and 3.5 mg crystals (prepared from THF) of the $(ET)_2[N(SO_2CF_3)_2]$ salt between 1.3 and 300 K. No signals of superconductivity were found. This result is in consistent with the semiconductive behavior revealed by use of ESR measurements.

CONCLUSIONS

A new charge transfer salt, $(ET)_2[N(SO_2CF_3)_2]$, was synthesized and studied with use of X-ray diffraction, Raman, and ESR techniques. It is a semiconductor with a small energy gap. Further studies to explore the possibility of incorporating this novel anion into metal complexes in order to grow new ET based superconductors are in progress.

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