

Scheme I

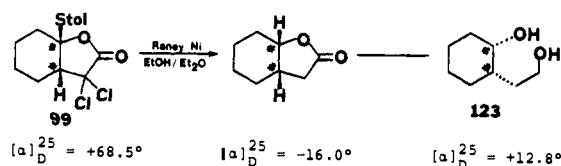


Table I

Sulfoxide	$[\alpha]_D^{25}$	Lactone ^{1,2}	Yield ^b	$[\alpha]_D^{25}$
	+5.9°		70	+68.5°
	-6.2°		68	-68.3°
	+166.5°		60	-91.1°
	+24.3°		25	+13.9°
	+5.9°		60	+50.7°

presence of a chiral shift reagent [Eu(tfc)₃] did not lead to satisfactory resolution of the enantiomers. Therefore, we converted the lactones to the corresponding enantiomeric diols⁸ **5** (Scheme I), which were then esterified with Mosher's acid⁹ to the diastereomeric diesters **6**. The 360-MHz ¹H NMR spectra of the diesters **6** clearly indicated that each was pure within the limits of detection.¹⁰

In order to extend the generality of this reaction and test the asymmetric induction in more highly functionalized cyclohexenes, we examined the reactions of the *S* enantiomers of the known cyclohexenone derivative **3** (R,R = O) and its ketal (**3**, R,R = OCH₂CH₂O).¹¹ The results are summarized in Table I.

A particularly intriguing possibility arises when an unsymmetrical ketene is employed in the reaction, since an additional chiral center is generated. We found that addition of monochloroketene to 1-cyclohexenyl tolyl sulfoxide led to a single stereoisomer of the lactone **3d**. It would appear that the approach of the incipient carbanion to the double bond is such as to orient the larger chlorine atom away from the cyclohexane ring. Thus, steric factors have controlled the stereocenter α to the lactone

(8) The optically active lactones **3a** were treated with excess Raney nickel at room temperature overnight. The 360-MHz ¹H NMR spectrum of **4** clearly indicated the *cis*-lactone. Further treatment of **4** with LiAlH₄ in ether yielded the optically active diols **5**.

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(10) In the 360-MHz ¹H NMR spectra of the diastereomeric diesters **6**, the methoxyl hydrogens resonate at δ 3.41 and 3.53 with base-line separation. Thus, it was easily discernible that the product diesters were pure diastereomers.

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(12) All new compounds gave correct elemental analyses for C, H, and Cl and possessed IR, ¹H NMR, ¹³C NMR, and MS spectral data consistent with the assigned structures.

carbonyl, and a third chiral center is set.

The ability to use either enantiomeric sulfoxide provides access to highly functionalized γ -butyrolactones of both configurations. The high enantiospecificity of this cyclization renders this process one of the best for chirality transfer from sulfur to carbon. Further studies are in progress to extend this enantiospecific lactonization to other types of ketenes and ketene equivalents.

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Registry No. (R)-(+)-**1a**, 93062-20-5; (S)-(-)-**1a**, 93062-21-6; (S)-(+)-**1b**, 86505-46-6; (S)-(+)-**1c**, 93062-22-7; **2** (R = Cl), 76-02-8; **2** (R = H), 79-36-7; (R,R)-**3a**, 93062-23-8; (S,S)-**3a**, 93062-24-9; **3b**, 93062-25-0; **3c**, 93062-26-1; **3d**, 93062-27-2; Cl₂C=C=O, 4591-28-0; ClHC=C=O, 29804-89-5.

Novel Structural Modulation in the First Ambient-Pressure Sulfur-Based Organic Superconductor (BEDT-TTF)₂I₃

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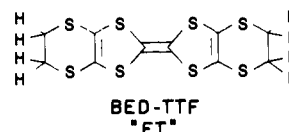
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The title compound [BEDT-TTF or "ET" herein bis(ethyl-



enedithio)tetrathiofulvalene, C₁₀S₈H₈] is the first ambient-pressure sulfur-containing organic superconductor (*T_c* = 1.4-1.5 K).^{1,2} This compound is further unique in having a displacively modulated structure below ~200 K, the first to be observed in an organic superconductor, which persists to a temperature of at least 11 K.³ Important features of the room-temperature structure are the existence of ribbons of I₃⁻ anions and loose columnar stacks of ET molecules having *intrastack* S...S distances >3.60 Å, the sum of the van der Waals radii. The ET molecules are linked into infinite "corrugated" sheets by short *interstack* S...S distances less than 3.6 Å and which lay approximately perpendicular to the ET molecule column-packing axis.² These short interstack distances appear especially pertinent to the anisotropic (two-dimensional) electrical properties, which includes a relatively high conductivity in directions parallel to the sheets. Similarly short interstack, but long intrastack, S...S distances and anisotropic electrical conductivity were first observed in prototypical

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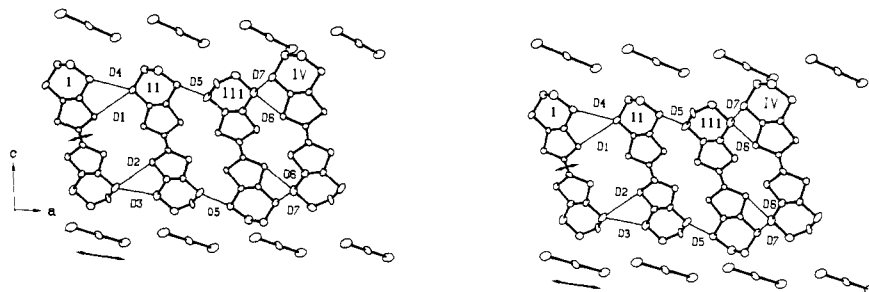


Figure 1. Stereoview of the molecular packing in $(\text{ET})_2\text{I}_3$ on the ac plane (90% probability ellipsoids). The allowed displacement vectors of an ET molecule and an I_3^- anion are indicated by a pair of arrows whose length is approximately 5 times the magnitude of the observed displacements. Symmetry operations which relate the ET molecules: (I) $x - 1, y, z$; (II) x, y, z ; (III) $1 - x, -1 - y, 1 - z$; (IV) $x + 1, y - 1, z$.

Table I. Interstack S...S and I...I Distances (\AA) in $(\text{BEDT-TTF})_2\text{I}_3^a$

		125 K		
		298 K	av ^c	range
D_1 ^b	S(3)...S(8) (a)	3.651 (2)	3.578 (2)	3.527–3.633
D_2	S(5)...S(2) (a)	3.574 (2)	3.556 (2)	3.503–3.613
D_3	S(5)...S(6) (a)	3.600 (2)	3.548 (2)	3.505–3.589
D_4	S(7)...S(8) (a)	3.598 (2)	3.532 (2)	3.493–3.575
D_5	S(5)...S(7) (b)	3.628 (2)	3.547 (2)	3.542–3.554
D_6	S(4)...S(6) (c)	3.691 (2)	3.625 (2)	3.553–3.698
D_7	S(8)...S(6) (c)	3.593 (2)	3.553 (2)	3.474–3.636
	I(2)...I(2) ^c (d)	4.211 (1)	4.204 (1)	4.189–4.275

^a Only the S...S interactions whose average distances at 125 K are less than the van der Waals sum of 3.6 \AA (except D_6) are shown. All such distances are of the interstack type. The symmetry operations of the second atom in each pair are as follows: (a) $1 + x, y, z$; (b) $1 - x, -1 - y, 1 - z$; (c) $-x, -y, 1 - z$; (d) $1 - x, 1 - y, -z$. ^b The S...S interactions labeled D_1 – D_7 are illustrated in Figure 1. ^c The average structure refers to the refined atomic parameters using both fundamental and satellite reflections. These atomic distances are affected by the sinusoidal modulation resulting in a range of distances, which are calculated by use of eq 1.

$(\text{ET})_2\text{ClO}_4(1,1,2\text{-C}_2\text{H}_3\text{Cl}_3)_{0.5}$ which exhibited metallic behavior to 1.4 K.⁴

The existence of both superconductivity and an incommensurate structural modulation in one material has not been reported in any organic superconductor. Incommensurate and commensurate structural transitions in TTF-TCNQ,⁵ and in the $(\text{TMTSF})_2\text{X}$ salts ($\text{X} = \text{ReO}_4^-, \text{BF}_4^-, \text{etc.}$),⁶ are associated with metal-insulator transitions, based on structural and electrical conductivity data. As the displacive modulations of the "average structure", determined using normal crystallographic techniques, can lead to significant local variations in interatomic distances and intermolecular overlaps, its complete analysis is of prime importance for the eventual understanding of the unusual transport properties of $(\text{ET})_2\text{I}_3$.

Crystals were grown by electrochemical oxidation of ET, in the presence of $(n\text{-Bu}_4\text{N})\text{I}_3$ as described previously,² and low-temperature X-ray data were collected at 125 (2) K.⁷ The analysis

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(7) Low-temperature data were collected well below the structural transition temperature of ~ 200 K,³ by using graphite-monochromatized Mo $K\alpha$ radiation and a Syntex P2₁ diffractometer. A total of 3767 main Bragg and 7045 satellite reflection intensities were measured and 3346 and 1041, respectively, were used in the data analysis [$R_F(\text{Bragg} + \text{satellite}) = 0.060$]. No absorption corrections were applied ($\mu = 38.4 \text{ cm}^{-1}$, $T_{\text{min}} = 0.57$, $T_{\text{max}} = 0.68$). The triclinic crystal ($P\bar{1}$, $Z = 1$) has cell dimensions (125 K) of $a = 6.561$ (1) \AA , $b = 9.010$ (2) \AA , $c = 15.173$ (2) \AA , $\alpha = 95.09$ (1) $^\circ$, $\beta = 95.95$ (1) $^\circ$, $\gamma = 110.27$ (1) $^\circ$, and $V_c = 829.4$ (2) \AA^3 . The structural modulation gives rise to satellite reflections in the diffraction pattern, which are symmetrically displaced about the main Bragg reflections by the vector $\pm \mathbf{q} = 0.08\mathbf{a}^* + 0.27\mathbf{b}^* + 0.205\mathbf{c}^*$. The superstructure satellite reflections are generally nonequivalent in intensity and may be less, or more, intense than the accompanying Bragg reflection.

of satellite diffraction data is rather complicated if the modulation waves are incommensurate, as is the case for $(\text{ET})_2\text{I}_3$. It was accomplished by use of a new program (JANA),⁸ which allows the description of the main and satellite intensities in a modulated structure in terms of one or more sinusoidal displacement waves with associated phases. We have assumed that both the I_3^- and the ET moieties behave as rigid bodies with respect to the modulation waves. The positional and temperature parameters within the rigidly displaced bodies were varied for all non-hydrogen atoms during the least-squares analysis. Our analysis further assumes that the center of symmetry is preserved in the four-dimensional super space group.

The average crystal structure at 125 K differs mainly from that at 298 K in that the intermolecular S...S distances are contracted by about 2% (Table I). Even at 125 K all but one of the intrastack S...S distances exceed 3.60 \AA . A significant finding is that the displacement vectors for the I_3^- anions and ET molecules are of different directions and magnitudes. While the former is large [0.281 (1) \AA] and directed along the a axis [components in fractional coordinates are 0.0428 (2), 0.0008 (2), -0.0022 (1)] the latter is somewhat smaller [0.124 (3) \AA ; 0.0151 (3), -0.0047 (3), 0.0022 (1)] and directed almost exactly along one of the inertial axes of the ET molecule (see Figure 1 for the orientation of the displacement vectors). The local displacement ($\Delta\mathbf{X}$) of each individual I_3^- anion and ET molecule can be described by the relation $\Delta\mathbf{X} = \mathbf{u} \sin(2\pi\mathbf{q}\cdot\mathbf{r} - \phi)$ (eq 1) in which \mathbf{u} is the displacement vector, \mathbf{r} is the center-of-mass of a molecule relative to an origin, and ϕ is the phase angle. The phase angles are 0° and 13.8 (9) $^\circ$ for the I_3^- and ET species, respectively.

The variation in the derived intermolecular contact distances resulting from the displacive structural modulations depends crucially on the phase angles in eq 1. Since the ET molecule displacement vector is parallel to the molecular plane, local variations in molecular stacking and intermolecular overlap integrals occur. The interstack S...S distances fluctuate by as much as 0.16 \AA in different unit cells (Table I). A local shortening of up to 0.08 \AA is observed. The modulations have a larger magnitude in the I_3^- columns, but are directed such that the I_3^- anions slip relative to each other, with the result that the shortest intermolecular I...I distances change by as much as 0.07 \AA . The local fluctuations of the close intermolecular S...S contacts are very significant, and the effective overlaps between these atoms are expected to change accordingly. Hence, any theoretical treatment of the transport properties of this material below 200 K must take into account the local variations in geometry that result from the observed structural modulations.

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Supplementary Material Available: Summary of crystal data and intensity collection information (Table X1), atom positional parameters, and equivalent isotropic temperature factors (Table X2) (2 pages). Ordering information is given on any current masthead page.

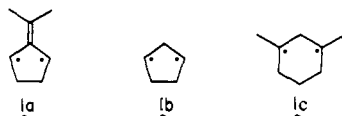
UV-Laser Photochemistry of the Azoalkane 2,3-Diazabicyclo[2.2.2]oct-2-ene: Trapping of the Short-Lived, Triplet Biradical 1,4-Cyclohexadiyl by Molecular Oxygen

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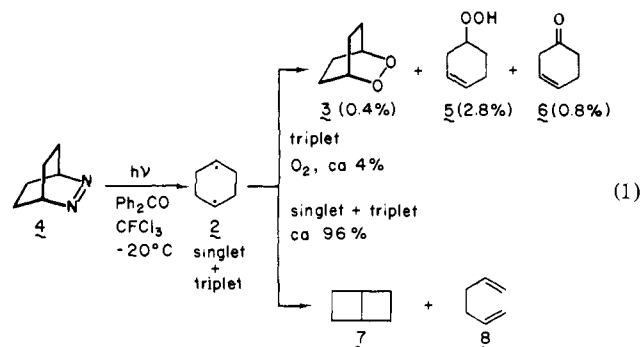
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Trapping of photochemically generated biradicals by molecular oxygen has been demonstrated to serve as an effective and convenient technique for the synthesis of novel peroxides and for the detection and characterization of elusive biradical intermediates. Early examples have been summarized recently,¹ in which the 1,4-preoxetane biradicals derived from the Paterno-Büchi photocyclization of ketones and olefins have been trapped by molecular oxygen to form 1,2,4-trioxanes. More recently the 1,3-biradicals **1a-c** derived from the photolysis of the respective azo compounds



have been trapped with molecular oxygen to form the corresponding bicyclic endoperoxides.² It is significant to note that in all of these cases only the triplet states of the 1,3-biradicals were long-lived enough to be trapped by molecular oxygen.

To the best of our knowledge³ it has not been possible to trap simple, unstabilized triplet 1,4-biradicals such as 1,4-cyclohexadiyl (**2**) to produce the corresponding bicyclic endoperoxide **3** (eq 1).



In this report, we describe the results of the oxygen trapping of triplet 1,4-cyclohexadiyl (**2**) generated from the photoextrusion of nitrogen from 2,3-diazabicyclo[2.2.2]oct-2-ene (**4**).⁴ Azoalkane

4 constitutes the first of a rather extensive class of photoreluctant azoalkanes to be studied using this oxygen-trapping technique and the results reported here demonstrate that even inaccessible triplet biradicals such as **2** derived from photoreluctant azoalkanes can be trapped successfully and studied by this method.

Due to the low quantum yield for nitrogen loss ($\Phi \sim 1.4\%$) from the triplet state of this photoreluctant azoalkane **4**,⁵ it was essential to employ an intense laser source; a Coherent Radiation Model 18 Super Graphite argon ion laser with an output of ca. 3 W in the UV region of interest was used. Adjustment of experimental parameters such as azoalkane concentration, oxygen pressure, and irradiation time was critical in order to obtain optimal results. In a typical experiment, the azoalkane **4** (0.09 M) and benzophenone (0.11 M) in 15 mL of CFCl_3 was placed in a Griffin-Worden tube and pressurized to 10 atm with oxygen. After being equilibrated for ca. 1 h, this solution was irradiated with the 363.7-nm line of the laser at -20°C for 8 h. During this period ca. 65% of the azoalkane **4** had been consumed. Careful removal of the solvent and chromatography on silica gel at -20°C , eluting with CH_2Cl_2 , afforded the mixture of oxygen trapping products **3**, **5**, **6**, and the mixture of hydrocarbon products **7** and **8** (eq 1).⁵ The relative yields in eq 1 were estimated by capillary GLC and ^1H NMR. Traces of 2-cyclohexenone, arising from the facile isomerization of the 3-cyclohexenone (**6**), were detected also.⁶

The structure of endoperoxide **3**⁷ was confirmed by comparison of capillary GLC retention times, capillary GLC-MS fragmentation patterns, and 400-MHz ^1H NMR spectra with authentic material. The hydroperoxide **5** was too labile for purification by GLC as it decomposed to a mixture of enone **6** and 3-cyclohexenol.⁸ Consequently, NaBH_4 reduction of the hydroperoxide sample isolated by chromatography on silica gel afforded 3-cyclohexenol, which was fully characterized by comparison of its MS and ^1H NMR spectral properties with reported values.⁹ Due to the ease of isomerization of enone **6** into its conjugated isomer, 2-cyclohexenone, **6** could not be isolated in pure form. However, its MS and ^1H NMR spectral properties¹⁰ were consistent with the proposed structure.⁶ Finally, control experiments showed that the oxygen-containing products **3**, **5**, and **6** were not derived from the hydrocarbon products **7** and **8**, since the latter were stable under the conditions used in the irradiation of the azoalkane **4**.

It must be emphasized that the azoalkane **4** n, π^* transition¹¹ occurs in the same spectral region as the benzophenone n, π^* transition, i.e., 350–400 nm. Thus, it is not possible to excite only the benzophenone sensitizer without populating the singlet excited state of **4** to some extent. It is known further that both the singlet and triplet states of **4** lose nitrogen in temperature-dependent processes which occur with about equal but very low probability (ca. 0.1% at -20°C).¹² In addition, the singlet state of **4** is exceptionally long-lived (434 ns at 25°C).¹² In the presence of oxygen (air-saturated solutions), oxygen-induced intersystem crossing of singlet to triplet **4** is thought to proceed quantitatively.⁵ Consequently, in this work, the combination of high oxygen pressure and benzophenone sensitization should ensure that singlet **4** is completely converted to triplet **4** and, hence, that the triplet 1,4-biradical **2** is formed quantitatively. If the 1,4-biradical **2**

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(10) MS (70 eV), m/e 97 (4%, M + 1), 96 (69%, M), 95 (1%), 81 (5%), 69 (1%), 68 (19%), 67 (22%), 66 (2%), 65 (3%), 63 (1%), 62 (1%), 55 (5%), 54 (100%, M - 42), 53 (23%), 52 (2%), 51 (4%), 50 (3%), 43 (1%), 42 (11%), M - 54, 41 (10%); ^1H NMR (CDCl_3 , 400 MHz) δ 2.45 (m, 4 H), 2.85 (m, 2 H), 5.75 (m, 1 H), 5.90 (m, 1 H).

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