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Isotopically Substituted Bis(ethylenedithio)tetrathiafulvalene at 15 K by Time-of-Flight Neutron Diffraction

DIANNA M. YOUNG,^a ARTHUR J. SCHULTZ,^a ARAVINDA M. KINI^b AND JACK M. WILLIAMS^b

^aIntense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL 60439, USA, and ^bChemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL 60439, USA. E-mail: ajschultz@anl.gov

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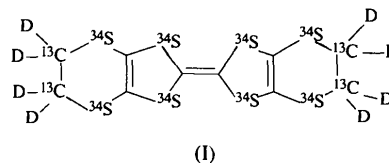
Abstract

The title compound, C₁₀D₈S₈, (ET), has been synthesized whereby all eight S atoms, the four ethylene C atoms and all eight H atoms have been isotopically substituted with ³⁴S, ¹³C and ²H, respectively. Analysis of the neutron scattering lengths derived from single-crystal time-of-flight neutron diffraction data obtained at *T* = 15 K confirms the isotopic distribution. The title phase crystallizes in the space group *P*₂₁/*n* with bond lengths and angles consistent with neutral ET.

Comment

The title compound, (I), (ET), participates as the electron-donor molecule in a large number of organic superconducting salts (Williams *et al.*, 1991). In order to investigate the mechanism for the electron pairing in this class of superconductors, a variety of isotopically substituted ET molecules with different distributions of isotopes throughout the molecule have been synthesized (Kini *et al.*, 1996). Salts of these organic donor molecules have been studied to determine the isotopic effect on *T*_c in the superconducting crystals. In the crystal used in this neutron diffraction experiment, the isotopic substitution of the ET molecule involved the replacement of the four C atoms in the terminal 1,2-ethanedithyl groups with ¹³C, all eight S atoms with ³⁴S and all eight H atoms with deuterium, ²H. The substitution increases the mass of the ET molecule, hereafter denoted by ²H₈¹³C₄³⁴S₈-ET, by 28 a.m.u., which is about 7% of the original mass. From the study by Kini *et al.* (1996), it was shown that the C and S substitution has a normal BCS-like mass (*M*) effect (*T*_c proportional to *M*^{-α}),

whereas deuterium substitution produces an inverse isotopic effect (*T*_c increases). We present here the neutron structure of ²H₈¹³C₄³⁴S₈-ET at 15 K in order to confirm the isotopic distribution and to provide high-precision low-temperature structural parameters.



The only previous structure of neutral ET is the room-temperature single-crystal X-ray structure in space group *P*₂₁/*c* by Kobayashi, Kobayashi, Yukiyoishi, Saito & Inokuchi (1986). We had transformed the atomic coordinates from *P*₂₁/*c* to *P*₂₁/*n* in our previous comparison of the ET structure with the isomorphous Au(DDDT)₂ (DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) crystal structure (Schultz *et al.*, 1987). The transformation of the atomic coordinates from the *P*₂₁/*c* unit cell in Kobayashi *et al.* (1986) to the *P*₂₁/*n* unit cell in this paper is (*x* - *z*, -*y*, -*z*) + (1/2, 1/2, 0).

The *P*₂₁/*n* room-temperature unit cell of neutral ET reported by Kobayashi *et al.* (1986) is *a* = 6.614 (11), *b* = 13.985 (2), *c* = 15.721 (3) Å, β = 93.81 (2)° and *V* = 1451 (5) Å³. The low-temperature data of isotopically substituted ET gave a slightly smaller volume, as expected, of 1416 (1) Å³ and *a* = 6.661 (1), *b* = 13.652 (2), *c* = 15.613 (2) Å, β = 94.281 (2)°. The bond lengths of the low-temperature isotopically substituted ET appear to be slightly longer than those obtained from room-temperature data. Shorter bond distances of the room-temperature neutral ET are probably attributable to anisotropic thermal motion. Isotopically substituted ET bond distances at 15 K are C1—C2 = 1.359 (2), C5—C6 = 1.360 (2), S2—C4 = 1.771 (3) and S4—C6 = 1.769 (3) Å. Kobayashi *et al.* (1986) reported 1.319, 1.328, 1.757 and 1.751 ± (0.007–0.012) Å, respectively.

The ET molecules pack as face-to-face dimeric pairs. Many of the S—S contacts between different molecules have distances close to the sum of the van der Waals radii (3.70 Å). The S···S contacts are listed in Table 2.

The crystal for this data collection was obtained from a batch of crystals which underwent mass spectrometry to verify isotopic substitution. In order to confirm the degree of isotopic substitution of this crystal, scattering lengths for each of the atoms were refined. Scattering lengths in units of 10⁻¹² cm from Sears (1986) are: *b*(¹²C) = 0.66511 (16), *b*(¹³C) = 0.619 (9), *b*(³²S) = 0.2804 (2), *b*(³⁴S) = 0.348 (3), *b*(H) = -0.37406 (11), *b*(D) = 0.6671 (4). The average refined scattering length in this structure of the ethanedithyl ¹³C atoms is 0.656 (3) × 10⁻¹² cm, which appears to be closer in magnitude to ¹²C but is also within three standard deviations of the ¹³C scattering length. Thus, the refined ethanedithyl

scattering lengths do not statistically verify the ¹³C substitution and do not permit an assignment of the C isotopes. The deuterium substitution is 96 (2)% and is obtained from an average scattering length of 0.621 (2) × 10⁻¹² cm. Sulfur sites are completely substituted with ³⁴S. The average scattering length is 0.354 (2) × 10⁻¹² cm, indicative of 108 (5)% substitution of ³⁴S.

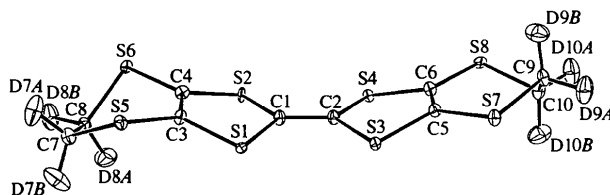


Fig. 1. Molecular structure of isotopically substituted ET with displacement ellipsoids drawn at the 75% probability level.

Experimental

The title compound was prepared according to Kini *et al.* (1996).

Crystal data

C₁₀D₈S₈
M_r = 412.6
 Monoclinic
*P*2₁/*n*
a = 6.661 (1) Å
b = 13.652 (2) Å
c = 15.613 (2) Å
 β = 94.281 (2)°
V = 1416 (1) Å³
Z = 4
D_x = 1.93 Mg m⁻³
D_m not measured

Data collection

IPNS single-crystal diffractometer
 Time-of-flight data
 Absorption correction: spherical
T_{min} = 0.9960, *T_{max}* = 0.9961

Refinement

Refinement on *F*
R = 0.062
wR = 0.058
S = 1.2
 4571 [*F* < 3σ(*F*), *d* > 0.7 Å, *F_o*² < 2*F_c*²] reflections
 274 parameters
 All D atoms refined
w = 4*F_o*²/[σ²(*F_o*²) + (0.04*F_o*²)²]

Pulsed neutron radiation
 λ = 0.7–4.2 Å
 Cell parameters from 1941 reflections
 μ = 0.0355
 + 0.00052(λ) mm⁻¹
T = 15 K
 Rectangular
 3.5 × 1.5 × 1.0 mm
 Red

19 444 measured reflections
 9580 independent reflections
 5405 reflections with *F* > 3σ(*F*)
h = -12 → 13
k = -19 → 9
l = -11 → 22

(Δ/σ)_{max} = 0.02
 Δρ_{max} equivalent to 1% of an S atom
 Δρ_{min} equivalent to 1% of an S atom
 Extinction correction: Becker & Coppens (1974) type I
 Extinction coefficient: 0.91 (2) × 10⁴
 Scattering factors from Sears (1986)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (7)
S1	-0.2580 (4)	0.1167 (2)	-0.0207 (2)	0.0048 (7)
S2	0.1719 (4)	0.1417 (2)	0.0421 (2)	0.0052 (7)
S3	-0.3416 (4)	-0.0046 (2)	0.1534 (2)	0.0052 (7)
S4	0.0890 (4)	0.0116 (2)	0.2124 (2)	0.0046 (7)
S5	-0.2434 (4)	0.2769 (2)	-0.1531 (2)	0.0062 (7)
S6	0.2332 (4)	0.3039 (2)	-0.0878 (2)	0.0052 (7)
S7	-0.4796 (4)	-0.0673 (2)	0.3203 (2)	0.0067 (8)
S8	0.0366 (4)	-0.0507 (2)	0.3929 (2)	0.0057 (7)
C1	-0.0686 (2)	0.0966 (1)	0.0628 (1)	0.0061 (4)
C2	-0.1031 (2)	0.0439 (1)	0.1342 (1)	0.0062 (4)
C3	-0.1212 (2)	0.2096 (1)	-0.0696 (1)	0.0060 (4)
C4	0.0737 (2)	0.2219 (1)	-0.0398 (1)	0.0065 (4)
C5	-0.2757 (2)	-0.0270 (1)	0.2642 (1)	0.0055 (4)
C6	-0.0774 (2)	-0.0198 (1)	0.2911 (1)	0.0065 (4)
C7	-0.0499 (3)	0.2891 (1)	-0.2315 (1)	0.0086 (5)
C8	0.1663 (3)	0.2662 (1)	-0.1989 (1)	0.0070 (5)
C9	-0.3618 (3)	-0.0783 (1)	0.4285 (1)	0.0073 (5)
C10	-0.1570 (2)	-0.1288 (1)	0.4319 (1)	0.0080 (5)
D7A	-0.0647 (3)	0.3652 (1)	-0.2526 (1)	0.0207 (6)
D7B	-0.0956 (3)	0.2409 (2)	-0.2856 (1)	0.0216 (6)
D8A	0.1977 (3)	0.1875 (1)	-0.2011 (1)	0.0185 (6)
D8B	0.2719 (3)	0.3048 (1)	-0.2381 (1)	0.0181 (6)
D9A	-0.4695 (3)	-0.1218 (1)	0.4626 (1)	0.0174 (6)
D9B	-0.3478 (3)	-0.0049 (1)	0.4575 (1)	0.0168 (6)
D10A	-0.1046 (3)	-0.1431 (1)	0.4990 (1)	0.0171 (6)
D10B	-0.1640 (3)	-0.1984 (1)	0.3958 (1)	0.0182 (6)

Table 2. Selected geometric parameters (Å, °)

S1—C1	1.769 (3)	S8—C10	1.812 (3)
S1—C3	1.767 (3)	C1—C2	1.359 (2)
S2—C1	1.767 (3)	C3—C4	1.356 (2)
S2—C4	1.771 (3)	C5—C6	1.360 (2)
S3—C2	1.769 (3)	C7—C8	1.525 (3)
S3—C5	1.778 (3)	C9—C10	1.523 (2)
S4—C2	1.760 (3)	D7A—C7	1.092 (2)
S4—C6	1.769 (3)	D7B—C7	1.092 (2)
S5—C3	1.748 (3)	D8A—C8	1.094 (2)
S5—C7	1.848 (4)	D8B—C8	1.101 (2)
S6—C4	1.751 (3)	D9A—C9	1.096 (2)
S6—C8	1.832 (4)	D9B—C9	1.100 (2)
S7—C5	1.759 (4)	D10A—C10	1.095 (2)
S7—C9	1.817 (4)	D10B—C10	1.102 (2)
S8—C6	1.759 (3)		
C1—S1—C3	93.8 (2)	C4—C3—S1	116.9 (2)
C1—S2—C4	93.3 (2)	S5—C3—S1	118.2 (2)
C2—S3—C5	94.0 (1)	C3—C4—S6	122.0 (2)
C2—S4—C6	94.6 (2)	C3—C4—S2	117.6 (1)
C3—S5—C7	103.4 (2)	S6—C4—S2	120.0 (2)
C4—S6—C8	96.4 (2)	C6—C5—S7	129.6 (2)
C5—S7—C9	101.1 (2)	C6—C5—S3	116.9 (2)
C6—S8—C10	100.1 (2)	S7—C5—S3	113.2 (2)
C2—C1—S1	122.1 (2)	C5—C6—S8	127.2 (2)
C2—C1—S2	123.1 (2)	C5—C6—S4	116.7 (2)
S1—C1—S2	114.6 (2)	S8—C6—S4	115.7 (2)
C1—C2—S4	122.9 (2)	C8—C7—S5	116.6 (2)
C1—C2—S3	123.1 (1)	C7—C8—S6	114.6 (1)
S4—C2—S3	113.9 (2)	C10—C9—S7	113.1 (1)
C4—C3—S5	124.9 (2)	C9—C10—S8	112.3 (1)

Table 3. S...S contacts (Å)

S1...S2 ⁱⁱ	3.593 (4)	3.69†
S1...S3 ⁱⁱⁱ	3.594 (4)	3.62†
S4...S7 ⁱⁱⁱ	3.393 (4)	3.48†
S5...S6 ^{iv}	3.721 (4)	3.69†
S7...S8 ^{iv}	3.503 (4)	3.55†

Symmetry codes: (i) -*x*, -*y*, -*z*; (ii) -*x* - 1, -*y*, -*z*; (iii) *x* + 1, *y*, *z*; (iv) *x* - 1, *y*, *z*.

† Kobayashi *et al.* (1986).

Table 4. Refined scattering lengths (10^{-12} cm)

C1	0.646 (6)	S4	0.359 (5)
C2	0.644 (5)	S5	0.356 (5)
C3	0.647 (5)	S6	0.357 (5)
C4	0.640 (5)	S7	0.352 (5)
C5	0.648 (5)	S8	0.355 (5)
C6	0.653 (5)	D7A	0.620 (6)
C7	0.660 (6)	D7B	0.616 (7)
C8	0.651 (6)	D8A	0.621 (6)
C9	0.650 (6)	D8B	0.620 (6)
C10	0.661 (6)	D9A	0.620 (6)
S1	0.355 (5)	D9B	0.617 (6)
S2	0.354 (5)	D10A	0.624 (6)
S3	0.346 (5)	D10B	0.626 (6)

A detailed description of the IPNS SCD has been published and described elsewhere (Schultz, 1993). Since the IPNS is a pulsed neutron source, data are obtained by the time-of-flight (TOF) Laue technique utilizing an area position-sensitive ^6Li -glass scintillator detector with an active area of $30 \times 30 \text{ cm}^2$ and a wavelength range of 0.7–4.2 Å. Each detected neutron is stored in a three-dimensional histogram with coordinates x , y , t corresponding to horizontal and vertical detector positions and the TOF, respectively. 32 histograms with different χ and φ crystal settings were required to cover a unique quadrant of reciprocal space. Counting time per histogram (*i.e.* per χ and φ setting) was approximately 6.5 h. Since all peaks were counted during each pulse no standards were required, only scaling between different crystal orientations.

The lattice parameters were refined from the observed positions and wavelengths of 1941 reflections. Bragg peaks were integrated in three dimensions (x , y , t) about calculated peak positions from an orientation matrix. Data were corrected for the Lorentz factor, absorption, the incident source spectrum and the detector efficiency. Linear absorption coefficients at each wavelength were calculated from the sum of the wavelength-dependent true absorption and the wavelength-independent total scattering: $\mu = 0.355 + 0.0052 \times \lambda$, with μ in units of cm^{-1} and λ in units of Å.

The programs used to analyze the data were as follows: *PEAKS*, to search the histogram for Bragg peaks (Jacobson, 1986); *BLIND*, an autoindexing program for time-of-flight data (Jacobson, 1986); *LSQRS*, to determine unit cell and orientation matrix least squares (Argonne program); *INTEGRATE*, which integrates Bragg peaks (Argonne program); *ANVRED*, for data reduction (Argonne program); *ANVLS*, for least-squares structure refinement with multiwavelength data (Argonne program), based on *ORFLS* (Busing, Martin & Levy, 1962); *ORTEPIII*, for molecular graphics (Burnett & Johnson, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1170). Services for accessing these data are described at the back of the journal.

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Two Related Benzylcamphor Dimers

IL-HWAN SUH,^a SUNGJO CHOI,^b DAVID E. LEWIS^b AND WILLIAM P. JENSEN^b

^aDepartment of Physics, Chungnam National University, Taejeon 305-764, Korea, and ^bChemistry Department, South Dakota State University, Brookings, SD 57007, USA. E-mail: jensenb@mg.sdstate.edu

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Abstract

The crystal structures of two related dimeric 3-benzylcamphors, namely, (1*R*,3*R*,4*R*,1'*R*,3'*R*,4'*R*)-3,3'-[(1*R*,2*R*)-1,2-diphenylethylene]bis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), (1), and (1*R*,3*R*,4*R*,1'*R*,3'*S*,4'*R*)-3,3'-[(1*R*,2*S*)-1,2-diphenylethylene]bis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), (2), both $\text{C}_{34}\text{H}_{42}\text{O}_2$, are reported. Compound (1) possesses C_2 molecular symmetry; it adopts a conformation in the crystal in which the two phenyl rings are *gauche* with respect to one another and *anti* to the C3—C4 bond (terpene numbering) of the camphor ring system. Compound (2) lacks a molecular C_2 axis of symmetry; it adopts a conformation in the crystal where the two phenyl rings are *anti* with respect to one another, and in which one phenyl ring is partially in the *endo* cavity of the camphor ring system. In both compounds, C3 of both camphor ring systems (terpene numbering) is distorted to trigonal pyramidal from tetrahedral; the C—C—C bond angles about C3 in both camphor rings are considerably expanded from idealized tetrahedral values and the dihedral angle between the benzyl C atom and the carbonyl O atom is reduced from the idealized value of 60° to less than 48° .

Comment

The ^{13}C NMR spectrum of the minor isomer (1) exhibits only ten resonances typical of sp^3 -hybridized C atoms