The Stereochemistry of Organosulfur Compounds. XIX. The Crystal and Molecular Structure of 10-(1,3-Dithiolan-2-ylidene)-10*H*-indeno[1,2-*f*]-1,2,3,4,5-pentathiepin

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The molecular structure of 10-(1,3-Dithiolan-2-ylidene)-10*H*-indeno[1,2-*f*]-1,2,3,4,5-pentathiepin $S_7C_{12}H_8$, has been determined by single crystal X-ray diffraction. The crystals are triclinic, space group P1, with two molecules in a unit cell of dimensions a = 8.931(2), b = 9.387(2), c = 10.175(2) Å, α = 75.73(2), β = 73.35(1), γ = 64.37(2)°. The structure was solved by direct methods, and refined to a final R value of 3.3% for 1925 independent reflections. The molecule consists of an indene core with a nearly co-planar dithiolane and a fused pentasulfide chain. The S_5C_2 ring is in the chair configuration, with an average S-S distance of 2.052 Å. There is no variation of bond lengths as is frequently seen in multi-sulfur chains. The indenone ring shows no evidence of any delocalization, while the dithiolane ring is disordered at the two methylene positions. No attempt was made to resolve the disorder, since it is frequently seen and has been thoroughly investigated previously.

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Introduction.

Among the longstanding interests of the Houston structural group has been the stereochemical features of sulfur compounds, in general. In the class of organosulfur compounds, we have published a number of studies (1-18) in which we sought to document the stereochemical behavior of such substances in regard to dependence of bond lengths upon changes in bond angles and/or torsion angles, *etc.* The majority of these studies have dealt with mono- and disulfides; however, in a few cases longer chains have been documented (2,5,7). The substance we are describing structurally in this report was synthesized by Z. S. Ariyan, who will publish its synthesis in a separate report. We thank him for providing the crystal used in this study.

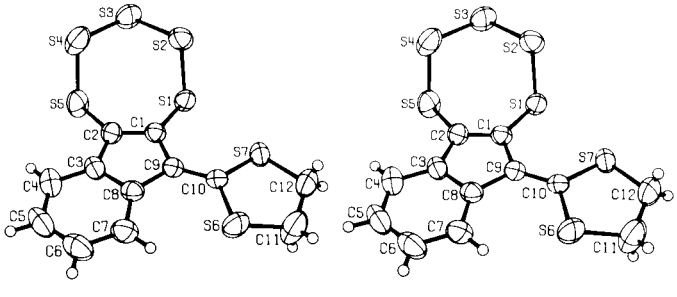

Figure 1. Stereoscopic view of the molecule with the atom labeling scheme. Hydrogens are numbered the same as the carbon to which each is attached. The heavy atoms are shown as 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

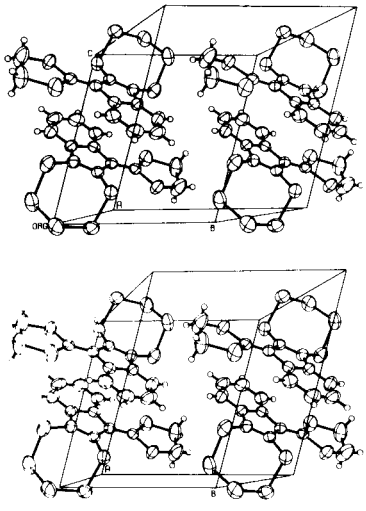

Figure 2. Stereoscopic view of the molecular packing in the unit cell, as viewed into the *a* axis.

EXPERIMENTAL

The single crystal used for data collection was a ruby red block of approximate dimensions 0.52 × 0.38 × 0.32 mm. All measurements were made on an Enraf-Nonius automatic diffractometer using Mo Kα radiation monochromatized by a dense graphite crystal. Final cell constants, as well as other information concerning data collection, are listed in Table 1. The Laue symmetry was determined to be $\bar{1}$, and from the fact that there were two molecules per unit cell, space group $P\bar{1}$ was chosen. Intensity data were collected using the θ-2θ scan technique, with three standard reflections being monitored after every two hours of X-ray exposure time to check crystal stability. In reducing the data, Lorentz and polarization factors were applied.

The structure was solved *via* MULTAN (19), which yielded all but three of the non-hydrogen atomic positions, and confirmed the choice of space

Table 1

Summary of Data Collection and Processing parameters

Space Group	$P\bar{1}$, triclinic
Cell Constants	a = 8.931(2) Å
	b = 9.387(2)
	c = 10.175(2)
	α = 75.73(2)°
	β = 73.35(1)
	γ = 64.37(2)
Molecular Formula	$S_7C_{12}H_8$
Molecular Weight	376.64
Molecules per Cell	z = 2
Density (Calc.)	ϱ = 1.71 g-cm^{-3}
Absorption Coefficient	μ = 9.70 cm^{-1}
Radiation (MoKα)	λ = 0.71073 Å
Collection Range	$2° \le 2\theta \le 50°$
Scan Width	$(0.70 + 0.35\tan\theta)°$
Maximum Scan Time	120s
Scan Speed Range	0.5 to 10.0° min^{-1}
Total Data Collected	2561
Independent Data with $I > 3\sigma(I)$	1925
Total Variables	202
$R \ldots \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$	0.033
$R \ldots [\Sigma_w(\|F_o\| - \|F_c\|)^2 / \Sigma_w \|F_o\|^2]^{1/2}$	0.036
Weights	$\sigma(F)^{-2}$

group by a nicely centric statistical distribution. Difference Fourier syntheses revealed all the remaining atoms, including hydrogens, despite the large thermal motion of the H11 and H12 types. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table 1. The atomic scattering factors for sulfur and carbon were computed from numerical Hartree-Fock wave functions (20); for hydrogen those of Stewart, Davidson, and Simpson (21) were used. The anomalous dispersion coefficients of Cromer and Liberman (22) were used for sulfur. All calculations were made with the SHELX-76 series of programs (23), and no unusually high correlations were noted between any of the refined parameters. Bond lengths, angles, least squares planes, and torsion angles are presented in Tables 3-6, based on the final position parameters of Table 2. The atom labeling scheme is shown in Figure 1.

Results and Discussion.

As can be seen in Figure 1, the molecule consists of an indene core with an attached dithiolane ring and a fused pentasulfide chain. The indene and dithiolane rings are, as expected, nearly co-planar (see Table 5) as a consequence of maximizing π orbital overlap in the C9-C10 double bond. The S_5C_2 ring is in the chair configuration, which minimizes electronic repulsions.

The indene moiety is quite similar to those found in other indenone derivatives which have been reported (24,25), and shows little, if any, resonance through bond C1-C9. The length of 1.468(4) Å is not significantly shorter than the value of 1.48 Å usually assigned to a C(sp^2)-C(sp^2) single bond (26). There also does not appear to be any conjugation with the C3-C8 ring through bonds C2-C3 and C8-C9, since these bond lengths are not unusual for a single bond between trigonally hybridized carbons, and because there is no alternation of bond lengths in ring C3-C8. Although C5-C6 and C6-C7 do appear to be somewhat shorter than the rest, this is undoub-

Table 2

Atomic Coordinates and Thermal Parameters (x1000, S × 10000)

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
S1	.7501(1)	.0500(1)	.1105(1)	497(4)	490(4)	563(5)	-218(4)	67(4)	-153(4)
S2	.7435(1)	-.0060(1)	-.0698(1)	625(5)	567(5)	486(5)	-105(4)	-12(4)	-107(4)
S3	.9051(1)	-.2414(1)	-.0700(1)	660(6)	593(6)	731(6)	-116(5)	75(5)	-294(5)
S4	.7618(1)	-.3581(1)	.0659(1)	748(6)	565(5)	969(8)	-244(5)	-8(6)	-328(5)
S5	.7662(1)	-.3289(1)	.2583(1)	566(5)	418(5)	784(6)	-51(4)	-124(5)	-10(4)
S6	.1715(1)	.4033(1)	.3635(1)	628(6)	519(5)	772(7)	-128(4)	160(5)	-244(5)
S7	.4825(1)	.3930(1)	.1646(1)	677(5)	404(4)	555(5)	-179(4)	44(4)	-7(4)
C1	.5878(3)	.0039(3)	.2355(3)	40(2)	43(2)	38(2)	-14(1)	-5(1)	-7(1)
C2	.5974(3)	-.1460(3)	.2906(3)	44(2)	41(2)	47(2)	-13(1)	-10(1)	-6(1)
C3	.4465(4)	-.1378(3)	.3969(3)	53(2)	47(2)	42(2)	-25(1)	-14(1)	1(1)
C4	.4014(5)	-.2583(5)	.4837(4)	66(2)	52(2)	65(2)	-30(2)	-18(2)	5(2)
C5	.2501(5)	-.2171(6)	.5807(4)	84(3)	86(3)	50(2)	-59(3)	-14(2)	12(2)
C6	.1498(5)	-.0606(6)	.5899(4)	66(2)	95(3)	51(2)	-50(2)	3(2)	-7(2)
C7	.1921(4)	.0603(5)	.5048(3)	58(2)	66(2)	51(2)	-29(2)	4(2)	-15(2)
C8	.3427(3)	.0240(3)	.4057(3)	47(2)	53(2)	37(2)	-23(1)	-7(1)	-10(1)
C9	.4282(3)	.1206(3)	.3024(3)	44(2)	44(2)	37(2)	-18(1)	-4(1)	-7(1)
C10	.3705(3)	.2835(3)	.2782(3)	47(2)	43(2)	35(2)	-13(1)	-3(1)	-10(1)
C11	.1924(5)	.5885(5)	.3094(6)	66(3)	50(2)	121(4)	-16(2)	0(3)	-24(2)
C12	.3105(7)	.5873(5)	.1795(5)	136(5)	39(2)	83(3)	-9(2)	29(3)	-10(2)
H4	.467(4)	-.349(4)	.473(3)	53(10)					
H5	.233(5)	-.305(5)	.637(4)	97(14)					
H6	.062(5)	-.039(5)	.645(4)	88(14)					
H7	.123(4)	.163(4)	.511(4)	73(11)					
H11A	.093(7)	.661(6)	.302(6)	154(15)					
H11B	.257(6)	.598(6)	.382(5)	154(15)					
H12A	.377(8)	.638(7)	.179(7)	171(18)					
H12B	.240(7)	.606(7)	.113(6)	171(18)					

tedly due to the lack of a librational correction for these peripheral atoms. As can be readily seen in Figure 1, C5 and C6 show much larger thermal motion than the other ring atoms, and it is in an attitude which would tend to artificially shorten the interatomic distances involving them.

The angles throughout the indene ring are remarkably similar to those in another 2,3-substituted indenone in the literature (24), including the inequality of the two angles S5-C2-C3 and S5-C2-C1. Such comparison shows that the reason for the apparent bending away of the S5 atom (NH in the other case) is not due to ring strain through the pentasulfide system, but rather to some steric pressures associated with the indene itself.

The geometry of the 1,3-dithiolane ring also shows excellent agreement with literature values (27-30). The literature averages for S-C(sp^2) and S-C(sp^3) bonds in these rings are about 1.74 Å and 1.80 Å, respectively, as compared with the theoretical single bond distances of 1.78 Å and 1.81 Å (26,31). The only significant discrepancy with our results is the unusually short S6-C11 bond, which is very nearly the same as in a previously reported case (29). In both instances, the C11-C12 bond is excessively short, the explanation for which is a static disorder between two equally stable conformational sites for the carbons. Much as in the case of C5 and C6 mentioned above, the lack of inclusion of a disordered model for the C11, C12 site makes the bond lengths determined unreliable for purposes of detailed analysis. Other researchers have made attempts to unravel this disorder *via* the use of partial occupancies (27) and corrections for "thermal motion" (28), each method producing bond parameters which are more pleasing from a structural standpoint. After correction, the C11-C12 bond averages 1.499 Å, with the two carbons oppositely displaced from the SCS plane by about 0.33 Å. Our values, uncorrected, are 1.431 Å and 0.25 Å. The theoretical torsion angles about the ring are SCSC: -11.5°, CSCC: 35.8°, and SCCS: -47.3° (32); whereas our values are -8.0°, 26.1°, and -34.7°. The puckering to relieve eclipsing of the methylene hydrogens is apparent, but the percentage of each of the two possible disordered components which contribute is unknown.

The S-S distances in the pentasulfide chain average 2.052 Å, with the maximum deviation from the average

Table 3
Intramolecular Bond Distances (Å)

S1-S2	2.051(1)	C4-C5	1.386(5)
S2-S3	2.052(1)	C5-C6	1.361(6)
S3-S4	2.050(1)	C6-C7	1.370(5)
S4-S5	2.055(1)	C7-C8	1.392(4)
C1-S1	1.767(3)	C8-C9	1.476(4)
C2-S5	1.756(3)	C9-C10	1.368(4)
C10-S6	1.745(3)	C11-C12	1.434(6)
C11-S6	1.764(4)	C4-H4	0.81(3)
C10-S7	1.741(3)	C5-H5	0.93(4)
C12-S7	1.814(4)	C6-H6	0.80(4)
C1-C2	1.355(4)	C7-H7	0.90(3)
C1-C9	1.468(4)	C11-H11A	0.87(5)
C2-C3	1.452(4)	C11-H11B	1.09(5)
C3-C4	1.385(4)	C12-H12A	0.91(5)
C3-C8	1.406(4)	C12-H12B	0.99(5)

Table 4
Intramolecular Bond Angles (Å)

C1-S1-S2	104.5(1)	C1-C9-C10	128.3(3)
S1-S2-S3	104.4(1)	C9-C10-S6	121.6(2)
S2-S3-S4	102.8(1)	C9-C10-S7	125.3(2)
S3-S4-S5	104.4(1)	S6-C10-S7	113.1(2)
S4-S5-C2	104.7(1)	S6-C11-C12	110.7(3)
C10-S6-C11	98.3(2)	C11-C12-S7	111.9(3)
C10-S7-C12	96.2(2)	C3-C4-H4	116(2)
S1-C1-C2	124.7(2)	C5-C4-H4	125(2)
S1-C1-C9	125.5(2)	C4-C5-H5	113(2)
C2-C1-C9	109.7(2)	C6-C5-H5	127(2)
S5-C2-C1	128.8(2)	C5-C6-H6	119(3)
S5-C2-C3	121.7(2)	C7-C6-H6	119(3)
C1-C2-C3	109.3(2)	C6-C7-H7	121(2)
C2-C3-C4	130.5(3)	C8-C7-H7	120(2)
C2-C3-C8	108.0(2)	S6-C11-H11A	107(4)
C4-C3-C8	121.5(3)	S6-C11-H11B	107(3)
C3-C4-C5	118.8(4)	C12-C11-H11A	111(4)
C4-C5-C6	119.9(4)	C12-C11-H11B	103(3)
C5-C6-C7	122.2(4)	H11A-C11-H11B	118(5)
C6-C7-C8	119.8(4)	S7-C12-H12A	95(4)
C7-C8-C9	134.1(3)	S7-C12-H12B	108(3)
C7-C8-C3	117.9(3)	C11-C12-H12A	111(4)
C3-C8-C9	107.9(2)	C11-C12-H12B	102(4)
C8-C9-C10	126.6(3)	H12A-C12-H12B	129(5)
C8-C9-C1	105.0(2)		

Table 5
Least Squares Planes and Out-of-Plane Distances (Å)

Plane A:	S1, S2, S4, S5				
	S3 1.21	C1	-1.33	C2	-1.31
Plane B:	C1-C9				
	S6 0.09	S7	-0.16	S1	-0.16
	S5 -0.14	C10	-0.02		
Plane C:	S6, C10, S7				
	C11 -0.26	C12	0.23		
Interplanar Angles:					
	A-B	117.1°			
	A-C	112.9°			
	B-C	5.1°			

Table 6
Selected Torsion Angles (°)

C1-S1-S2-S3	-89.4
S1-S2-S3-S4	77.9
S2-S3-S4-S5	-76.8
S3-S4-S5-C2	86.9
S1-C1-C2-S5	1.2
S1-C1-C9-C10	3.2
C10-S6-C11-C12	26.4
C10-S7-C12-C11	25.8
S6-C11-C12-S7	-34.7
S6-C10-S7-C12	-7.4
S7-C10-S6-C11	-8.6

value being 0.003 Å. This compares quite well with the value of 2.06 Å found in a TiS_5 ring (33), in 1,2,3,4-tetrathiadecalin (34), and in three allotropes of elementary sulfur (35). In each case, there is little deviation from the mean in any of the individual values. Although 2.08 Å is generally used for an S-S single bond length (36), Steudel has suggested that 2.06 Å is a more accurate value (37), and this would be supported by our results since there is no formal reason for any partial double bond character in any of the S-S bonds. Since there may be a favorable orientation of *d* orbitals between adjacent atoms, however, as suggested earlier (33), the possibility of some degree of multiple bonding cannot be totally ruled out, leaving this question open. It is also curious that the above-mentioned sulfur chains, as well as ours, show little variation in bond length, while many other determinations exhibit clear alternation (8,38-40).

The S-C bond lengths in our C_2S_5 ring average 1.762 Å, as compared with 1.78 Å for an S-C(sp^2) single bond (26,31). As stated above, this could be due to a slightly too large value of the "accepted" single bond sulfur radius, or to a $p\pi$-$d\pi$ interaction between the C-C double bond and the sulfurs. In any case, the value is very nearly the same as that observed in several compounds between sulfur and phenyl rings (1,18,41). Under these circumstances, there is usually an interaction postulated between the sulfur *d* orbitals and the aromatic system.

Figure 2 shows the molecular packing in the unit cell, in which it can be seen there are no unusually close intermolecular contacts. The molecules oppose each other in pairs across inversion centers of the type (½,0,½), and form interlocking sheets separated by repulsions between the aromatic rings.

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