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X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems. III.* The Crystal Structure of 8,9-Dihydro-4*H*-cyclohepta[1,2-*b*: 5,4-*b*′]dithiophene-4-one

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8,9-Dihydro-4*H*-cyclohepta[1,2-*b*;5,4-*b*′]dithiophene-4-one, $C_{11}H_8OS_2$, is orthorhombic, space group $Pn2_1a$, with $a=15{\cdot}1520$, $b=4{\cdot}6668$, $c=14{\cdot}2083$ Å, $Z=4$. The structure was refined to an R of 0·037 for 1043 non-zero counter reflexions. The central seven-membered ring deviates considerably from planarity and the planes of the two thiophene rings form an angle of 158 (2)°. The ring angles of the sp^3 carbon atoms are larger than the tetrahedral value.

Introduction

8,9-Dihydro-4*H*-cyclohepta[1,2-*b*: 5,4-*b*′]dithiophene-4-one [denoted (I) in Fig. 1] is a tricyclic system with two thiophene rings connected to a seven-membered ring containing one carbonyl group. The compound was first synthesized by Yom-Tov & Gronowitz (1973), who used it as an intermediate for the synthesis of the dithienotropylium cation (II) and of tricyclic psychoactive drugs. In order to compare the delocalization in some tricyclic systems, Gronowitz, Yom-Tov & Michael (1973) have given a comparison between the C=O stretching frequences of saturated and unsaturated ketones, including the present saturated ketone.

X-ray investigations of compounds similar to the present one have previously been made. Thus the structures of an unsaturated dithienotropylium cation (III) (Aurivillius, 1974*a*) and an unsaturated dithieneborepinyl ether (IV) (Aurivillius, 1974*b*) have been reported. These compounds exhibit planar or nearly planar ring systems with extended π-electron delocalization. The present compound has one double bond less in the central seven-membered ring, and a lower degree of delocalization might be expected. The crystal structure of a saturated dibenzo-annelated compound (V) has been determined (Larsson, 1970) and the central ring of this molecule is found to take a deep boat form. The present investigation was started in order to compare the configurations of molecules of saturated and unsaturated cycloheptadithiophene compounds.

X-ray diffraction work

A specimen was kindly supplied by Dr B. Yom-Tov. The single crystal used for the diffractometer work was a colourless needle of length 0·2 mm in the direction of **b** and with a rectangular (101) cross-section of 0·054 × 0·062 mm.

An Enraf–Nonius (CAD 4) computer-controlled four-circle diffractometer with equatorial geometry was used. The diffractometer was equipped with a graphite monochromator which gave Cu $K\alpha$ (1·5418 Å) radiation. The reflexions were scanned in the $\omega/2\theta$ mode. The scan interval, $\Delta\omega$, varied with the θ value of the reflexions according to $\Delta\omega=(1+0{\cdot}15\tan\theta)°$.

The cell dimensions were determined from 30 reflexions whose θ values were measured with the diffractometer. The Laue symmetry and the systematic extinctions were inferred from preliminary Weissenberg photographs. Some crystal data are given in Table 1.

Table 1. *Crystal data*

$C_{11}H_8OS_2$, M.W. 220·3
Orthorhombic, space group $Pn2_1a$ (No. 33)
$a=15{\cdot}1520$ (5) Å $D_m=1{\cdot}43$ g cm^{-3}
$b=4{\cdot}6668$ (2) $Z=4$
$c=14{\cdot}2083$ (5) $D_x=1{\cdot}46$ g cm^{-3}
$V=1004{\cdot}7$ Å^3 μ(Cu $K\alpha$) = 43 cm^{-1}

Intensities for $\frac{1}{8}$ of the reciprocal sphere were collected in a θ range of 3–75° (1166 reflexions). Of these, 123 were considered unobserved, having $I<2\sigma(I)$. Three standard reflexions were measured at intervals of 60 min. Their intensities showed a linear decay of 4% during the 100 h the crystal was exposed to the radiation. A numerical correction for this decrease was made.

The intensities were corrected for Lorentz, polarization and absorption effects: the transmission factors varied between 0·64 and 0·82. Systematic absences were: $hk0$ with $h=2n+1$ and $0kl$ with $k+l=2n+1$, indicating either the space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62): E statistics confirmed $Pn2_1a$. Symbolic addition was performed and an E map revealed the S atoms clearly.

Least-squares refinement of the positions of the S atoms followed by a difference synthesis revealed the positions of all non-hydrogen atoms. Another refinement of the positions of all these atoms followed by a difference synthesis indicated the positions of the H

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* Part I: *Acta Chem. Scand.* (1974). B**28**, 681–688. Part II: *Acta Chem. Scand.* (1974). B**28**, 998–1002.

atoms. A final full-matrix least-squares refinement was performed with anisotropic temperature factors for the non-hydrogen atoms and isotropic for the hydrogens. The weight function was: $w_i^{-1}=\sigma^2|F_o|+0{\cdot}0006|F_o|^2+0{\cdot}1$. The resulting agreement indices were: $R_1=\sum|\Delta F|/\sum|F_o|=0{\cdot}0363$ and $R_2=[\sum w_i(\Delta F)^2/\sum w_i|F_o|^2]^{1/2}=0{\cdot}0446$. The goodness of fit, S, was 1·01. Scattering factors for the non-hydrogen atoms were from Doyle & Turner (1968), those for the H atoms from Stewart, Davidson & Simpson (1965).

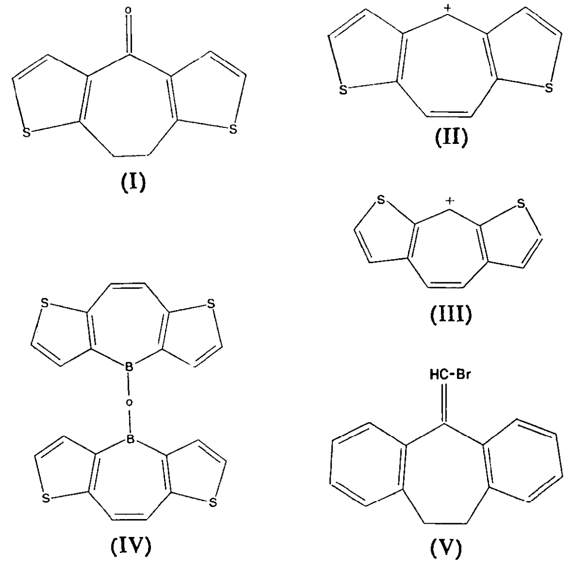

Fig. 1. Schematic drawings of the molecules: (I) 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b*′]dithiophene-4-one, (II) dithieno-[1,2-*b*:5,4-*b*′]tropylium tetrafluoroborate, (III) dithieno-[2,1-*b*:5,4-*b*′]tropylium perchlorate, (IV) bis-(4-dithieno-[3,2:2′,3′-*f*]borepinyl)ether, (V) 5-(bromoethylene)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene.

As the present space group lacks a centre of symmetry, serious errors in the positional parameters can result even for the light elements from the neglect of the imaginary component of the anomalous scattering (Cruickshank & McDonald, 1967). Therefore a correction for anomalous scattering was performed, with figures taken from Cromer & Liberman (1970). The agreement indices were now $R_1=0{\cdot}0371$, $R_2=0{\cdot}0453$ ($S=1{\cdot}03$), and for the inverse model $R_1=0{\cdot}0453$, $R_2=0{\cdot}0567$ ($S=1{\cdot}35$).

Although these results indicate that the corrections for anomalous scattering have not improved the fit, we have chosen to calculate distances and angles from the parameters obtained by the calculation giving $R_1=0{\cdot}0371$. As a result of these corrections the bond distances in the molecule changed less than 2σ, though in such directions that the two halves of the molecule became more alike. The fractional coordinates of the atoms and their thermal parameters are given in Table 2.*

Discussion of the molecular structure

A stereo view of one molecule is given in Fig. 2. The distances, *d*, of the atoms to the best least-squares planes through the thiophene rings are listed in Table 3. For the marked atoms these distances are less than

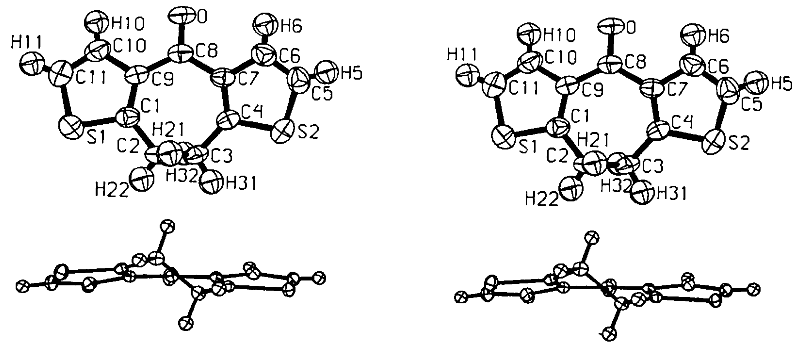

Fig. 2. A stereo view of one molecule of 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b*′]dithiophene-4-one viewed from two different directions. 50% probability ellipsoids are shown in the upper half of the figure.

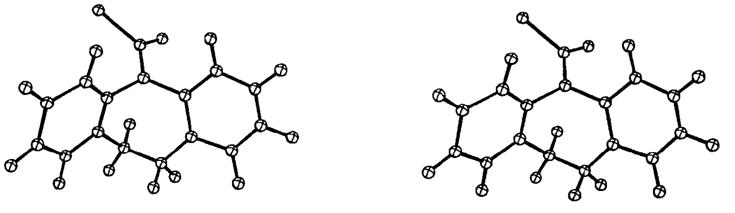

Fig. 3. A stereo view of one molecule of 5-(bromomethylene)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30835 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final positional and thermal parameters*

The estimated standard deviations are given in parentheses. The expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. The β_{ij} values ($\times 10^4$) and the r.m.s. components ($\times 10^3$) are given separately below the other values.

	x	y	z	B (Å)^2
S(1)	0·08939 (7)	$-\frac{1}{4}$	0·60689 (8)	
S(2)	0·46340 (7)	0·29765 (42)	0·72421 (7)	
C(1)	0·1823 (3)	−0·0425 (11)	0·6185 (3)	
C(2)	0·2146 (4)	0·0304 (13)	0·7155 (4)	
C(3)	0·3122 (4)	−0·0341 (12)	0·7260 (3)	
C(4)	0·3686 (3)	0·1675 (11)	0·6722 (3)	
C(5)	0·4901 (4)	0·5020 (13)	0·6289 (4)	
C(6)	0·4300 (4)	0·4743 (13)	0·5593 (4)	
C(7)	0·3602 (3)	0·2815 (11)	0·5832 (3)	
C(8)	0·2932 (3)	0·2084 (11)	0·5110 (3)	
C(9)	0·2152 (3)	0·0307 (10)	0·5322 (3)	
C(10)	0·1625 (4)	−0·0812 (13)	0·4572 (4)	
C(11)	0·0938 (4)	−0·2353 (16)	0·4858 (4)	
O	0·3050 (2)	0·2884 (14)	0·4306 (3)	
H(21)	0·202 (3)	0·225 (11)	0·726 (3)	3 (1)
H(22)	0·184 (4)	−0·079 (14)	0·755 (4)	6 (2)
H(31)	0·328 (3)	−0·020 (11)	0·793 (4)	5 (2)
H(32)	0·324 (3)	−0·223 (12)	0·709 (3)	4 (1)
H(5)	0·539 (4)	0·608 (13)	0·628 (4)	5 (2)
H(6)	0·432 (3)	0·573 (11)	0·500 (4)	4 (2)
H(10)	0·171 (3)	−0·046 (11)	0·395 (4)	4 (2)
H(11)	0·051 (4)	−0·328 (15)	0·449 (4)	6 (2)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	49 (1)	676 (8)	66 (1)	−27 (3)	3 (1)	32 (3)
S(2)	51 (1)	624 (7)	56 (1)	3 (2)	−11 (1)	−31 (3)
C(1)	41 (2)	451 (22)	44 (3)	17 (6)	0 (2)	9 (6)
C(2)	59 (3)	561 (28)	35 (2)	4 (7)	11 (2)	26 (7)
C(3)	59 (3)	457 (23)	34 (3)	8 (7)	−7 (3)	17 (6)
C(4)	45 (2)	400 (18)	38 (2)	19 (6)	−2 (2)	−8 (6)
C(5)	48 (3)	593 (28)	71 (3)	−25 (7)	11 (3)	−48 (9)
C(6)	54 (2)	542 (25)	51 (3)	−14 (7)	12 (2)	−11 (7)
C(7)	47 (2)	391 (19)	38 (2)	12 (7)	6 (2)	0 (6)
C(8)	49 (2)	517 (24)	34 (2)	11 (6)	3 (2)	13 (6)
C(9)	46 (3)	430 (21)	34 (2)	18 (6)	−1 (2)	2 (5)
C(10)	59 (3)	650 (29)	42 (3)	1 (8)	−6 (2)	−10 (7)
C(11)	55 (3)	688 (31)	65 (3)	−21 (9)	−10 (3)	−16 (10)
O	67 (2)	1097 (28)	36 (2)	−58 (8)	−2 (2)	70 (7)

	R_1	R_2	R_3
S(1)	221 (2) Å	256 (2) Å	290 (2) Å
S(2)	210 (2)	252 (2)	280 (2)
C(1)	204 (6)	213 (5)	236 (6)
C(2)	174 (6)	249 (7)	271 (6)
C(3)	177 (6)	229 (6)	266 (5)
C(4)	195 (6)	203 (6)	238 (6)
C(5)	222 (6)	229 (7)	303 (7)
C(6)	207 (5)	239 (6)	273 (6)
C(7)	190 (5)	206 (6)	240 (5)
C(8)	182 (5)	230 (6)	250 (6)
C(9)	187 (5)	209 (6)	241 (6)
C(10)	204 (5)	265 (6)	269 (7)
C(11)	225 (7)	277 (6)	282 (7)
O	174 (5)	267 (4)	367 (5)

$3\sigma(d)$. C(2) and C(8) do not deviate very much from the best plane of the S(1) thiophene ring. For the S(2) thiophene ring, C(3) is situated close to the best plane, whereas the deviation of C(8) is quite large. The angle between the best planes of the thiophene rings is 158·2 (3)°. The torsional angle of C(2)–C(3) is 71 (1)°, and as seen from Fig. 2 the conformation around C(2)–C(3) is nearly staggered.

Table 3. *Least-squares planes*

Distances from the planes (Å) are $\times 10^3$. Atoms used to define the planes are marked with asterisks.

Plane I		Plane II	
S(1)	3*	S(2)	−2*
C(1)	−5*	C(5)	1*
C(9)	5*	C(6)	1*
C(10)	−3*	C(7)	−4*
C(11)	0*	C(4)	4*
C(2)	−23	C(3)	22
C(8)	−10	C(8)	−124
H(10)	−57	H(5)	−8
H(11)	−6	H(6)	21

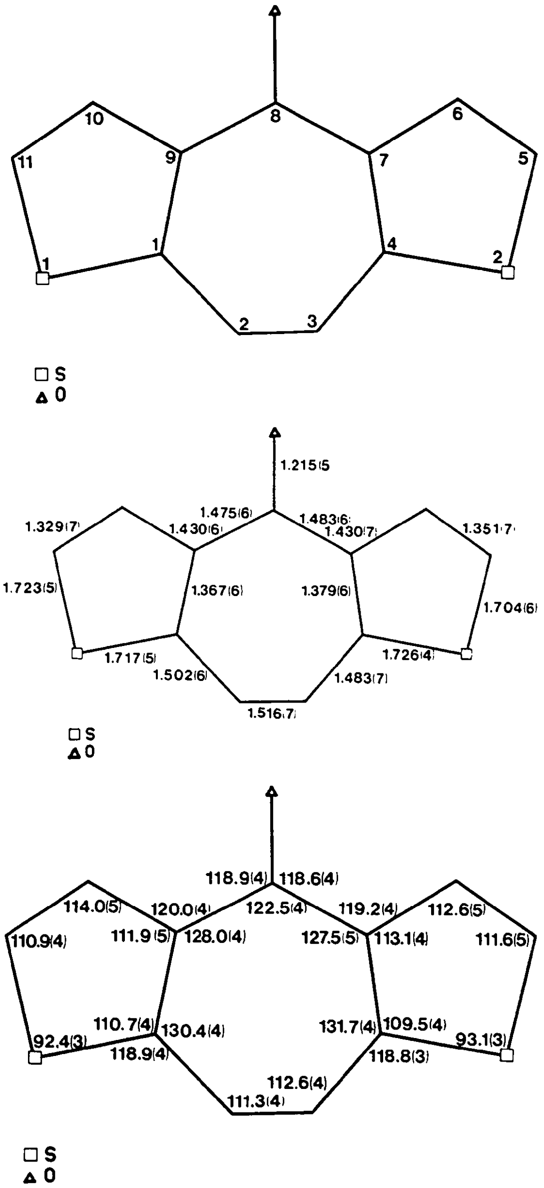

Fig. 4. Schematic pictures of one molecule of 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b*′]dithiophene-4-one showing the non-hydrogen atoms. Numbering of the atoms, selected distances (Å) and angles (°) are presented. Remaining values can be found in Table 4. The estimated standard deviations are given in parentheses.

A benzene analogue of the present system, 5-(bromomethylene)-10,11-dihydro-5*H*-dibenzo[*a*,*b*]cycloheptene, denoted (V) in Fig. 1, has been studied by X-ray methods (Larsson, 1970). A stereo view calculated from the data given by this author is presented in Fig. 3, from which it may be seen that the seven-membered ring has a deep boat form. The two C atoms adjacent to a benzene ring are situated in the best plane of the benzene ring. The planes of the benzene rings form an angle of 119·9 (1)°. The torsional angle of C(2)–C(3) is 64 (4)° for the bromo compound. (The numbering of the atoms in the seven-membered ring is the same as that used for the thiophene compound.)

Table 4. *Distances* (Å) *and angles* (°) *involving the hydrogen atoms*

The estimated standard deviations are given in parentheses.

C(2)—H(21)	0·94 (5)	C(2)—C(3)—H(31)	109 (3)
C(2)—H(22)	0·89 (6)	C(2)—C(3)—H(32)	110 (3)
C(3)—H(31)	0·98 (5)	C(4)—C(3)—H(31)	108 (3)
C(3)—H(32)	0·93 (6)	C(4)—C(3)—H(32)	111 (3)
C(5)—H(5)	0·89 (6)	H(31)–C(3)—H(32)	106 (4)
C(6)—H(6)	0·96 (5)	S(2)—C(5)—H(5)	121 (4)
C(10)–H(10)	0·90 (5)	C(6)—C(5)—H(5)	127 (4)
C(11)–H(11)	0·94 (6)	C(5)—C(6)—H(6)	125 (3)
C(1)—C(2)—H(21)	107 (3)	C(7)—C(6)—H(6)	122 (3)
C(1)—C(2)—H(22)	106 (4)	C(9)—C(10)–H(10)	125 (4)
C(3)—C(2)—H(21)	112 (3)	C(11)–C(10)–H(10)	121 (4)
C(3)—C(2)—H(22)	110 (4)	S(1)—C(11)–H(11)	120 (4)
H(21)–C(2)—H(22)	110 (5)	C(10)–C(11)–H(11)	129 (4)

Bond lengths and angles are given in Table 4 and in Fig. 4. Corresponding distances and angles in the two halves of the molecule differ at most at a level of $\Delta/\sigma(\Delta)=3{\cdot}0$. C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are larger than the tetrahedral value. The S–C distances in the S(1) thiophene ring have $\Delta/\sigma(\Delta)=1$, while in the S(2) thiophene ring S(2)–C(4) is longer than S(2)–C(5), $\Delta/\sigma(\Delta)=3$. Both for the S(1) and S(2) thiophene rings, the formal fused double bonds C(1)–C(9) and C(4)–C(7), respectively, are significantly longer than the purely thiophenic double bonds, C(10)–C(11) and C(5)–C(6). Differences of the same order of magnitude exist in the related unsaturated compounds dithieno-[2,1-*b*: 5,4-*b*′]tropylium perchlorate, (III) in Fig. 1 (Aurivillius, 1974*a*), dithieno[1,2-*b*: 5,4-*b*′]tropylium tetrafluoroborate, (II) (Andersson, J.-E., in preparation) and bis-(4-dithieno[3,2: 2′,3′-*f*]borepinyl)ether, (IV) (Aurivillius, 1974*b*). The bond distance of the conjugated carbonyl group is rather short, 1·216 Å. There are no intermolecular distances shorter than the sums of the pertinent van der Waals radii.

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