X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

V.* The Crystal Structure of 4*H*-Cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one

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$C_{11}H_6OS_2$ is monoclinic, space group $P2_1/c$, with $a = 9.3331$ (13), $b = 8.6930$ (18), $c = 11.9065$ (26) Å, $\beta = 110.098$ (14)° at 173 K, $Z = 4$. The structure was refined to an R of 0.041 for 1135 non-zero counter reflexions at 173 K. The molecule is almost planar; the planes of the two thiophene rings form an angle of 171.6 (8)°. Conjugation is indicated by the short formal C—C single bonds and the long C—O distance. The S—C bonds to the central ring are longer than the outer S—C bonds. A comparison of the detailed conformations of the present and similar molecules is made. The conformations are also correlated with their chemical properties.

Introduction

The cycloheptadithiophenes are tricyclic ring systems with aromatic properties. They have been synthesized and their aromatic properties studied by chemical and spectroscopic methods (Yom-Tov, 1972). A series with decreasing aromaticity is formed by three of these compounds: dithieno[1,2-*b*:5,4-*b'*]tropylium tetra-

* Part I: Aurivillius (1974*a*). Part II: Aurivillius (1974*b*). Part III: Andersson (1975). Part IV: Cynkier (1976).
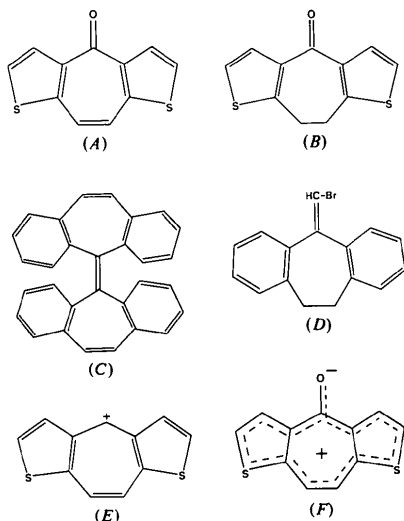

Fig. 1. Schematic drawings of the molecules: (*A*) 4*H*-cyclohepta-[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*B*) 8,9-dihydro-4*H*-cyclohepta-[1,2,-*b*:5,4-*b'*]dithiophen-4-one; (*C*) 2,3;6,7;2',3';6',7'-tetraben-zoheptafulvalene; (*D*) 5-(bromomethylene)-10,11-dihydro-5*H*-dibenzo[*a,b*]cycloheptene; (*E*) dithieno[1,2-*b*:5,4-*b'*]tropylium tetrafluoroborate; (*F*) resonance form.

fluoroborate (*E*) (Fig. 1), the title compound (*A*), and 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (*B*). The ion *E* has a relatively high stability to hydrolysis and was considered to be aromatic and planar. The C—O stretching frequency for the unsaturated ketone *A* is considerably lower than that for the saturated ketone *B* (Gronowitz, Yom-Tov & Michael, 1973). This suggests a high contribution of dipolar resonance form *F*, indicating aromatic character of the system. In view of the similarity in electronic structure between *E* and *F* this is in agreement with the high stability of the tropylium ion *E*. On the other hand, benzo-annelated tropylium ions are drastically less stable to hydrolysis, indicating a low degree of conjugation. In order to correlate chemical properties with molecular conformations the structures of the ketones *A* (this work) and *B* (Andersson, 1975) have been examined by X-ray diffraction and the tropylium ion *E* is under investigation.

X-ray diffraction work

A single crystal of *A* in the form of an approximately rectangular prism 0.07 × 0.07 × 0.20 mm was used for the experimental work. The X-ray data were collected on a four-circle diffractometer (Enraf–Nonius CAD-4) with equatorial geometry and graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The temperature of the crystal was kept at 173 K by a flow of cold nitrogen gas. Ice formation was prevented by heating the outer parts of the laminar nitrogen flow in the outlet nozzle and by keeping the whole diffractometer in a box filled with nitrogen (Danielsson, Grenthe & Oskarsson, 1976).

Table 1. *Crystal data*

$C_{11}H_6OS_2$, FW 218·30
Monoclinic, space group $P2_1/c$

$a = 9\cdot3331\,(13)$ Å	$D_m = 1\cdot54$ g cm^{-3}
$b = 8\cdot6930\,(18)$	$D_x = 1\cdot60$
$c = 11\cdot9065\,(26)$	μ(Mo $K\alpha$) $= 5\cdot3$ cm^{-1}
$\beta = 110\cdot098\,(14)°$	λ(Mo $K\alpha_1$) $= 0\cdot70930$ Å
$V = 907\cdot18$ Å^3	$T = 173$ K
$Z = 4$	

The θ values of 45 reflexions were measured (for the method see Danielsson *et al.*), and the cell dimensions calculated by a least-squares procedure. Some crystal data are given in Table 1.

The intensities were measured in the ω–2θ mode with a scan interval $\Delta\omega = (0\cdot90 + 0\cdot50\tan\theta)°$. In a fast prescan the scan time was determined so as to give a total count of approximately 3000. However, for very strong and very weak reflexions this could not be achieved. Reflexions for $\frac{1}{4}$ of the reciprocal sphere within a θ range of 3–27° were collected. Of the 2142 reflexions, 1007 were considered unobserved, having $I < 2\sigma_c(I)$. The intensities of three control reflexions showed no decay during the 84 h the crystal was exposed to the radiation. The intensity control reflexions were measured to a total count of 10 000, which means a counting precision of 1%. However, from the distribution of the actual intensities a real precision of 2 to 5% was estimated. The crystal orientation was checked regularly by a control reflexion.

Determination and refinement of the structure

The intensities were corrected for Lorentz and polarization effects but not for absorption. Systematic extinctions were $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$, indicating space group $P2_1/c$.

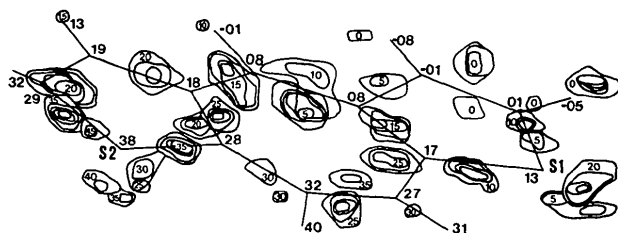The positions of the S atoms were found from a vector map. A subsequent electron density synthesis revealed the non-hydrogen atoms. Least-squares refinement with anisotropic temperature factors for S and isotropic for C gave an R of 0·063 and a subsequent difference synthesis gave the positions of all H atoms.

In the final full-matrix least-squares refinement including all atoms the function minimized was $\sum w(\Delta|F|)^2$, where $\Delta|F| = |F_o| - |F_c|$. The weight function was $w^{-1} = \sigma_c^2(|F_o|) + 0\cdot000625|F_o|^2 + 0\cdot10$. The scattering factors were those of Doyle & Turner (1968) for non-hydrogen atoms, and for H atoms those of Stewart, Davidson & Simpson (1965). For non-hydrogen atoms the anomalous scattering factors were those of Cromer & Liberman (1970). Anisotropic temperature factors were refined for the non-hydrogen and isotropic for the H atoms.

The final $R = \sum|\Delta|F||/\sum|F_o| = 0\cdot041$ and $R_w = [\sum w(\Delta|F|)^2/\sum w|F_o|^2]^{1/2} = 0\cdot044$. The goodness of fit, $S = [\sum w(\Delta|F|)^2/(m - n)]^{1/2} = 1\cdot03$, where m is the number of observations and n the number of parameters varied. The final coordinates are given in Table 2.* A comparison of observed and calculated structure factors showed no apparent extinction. The maximum residual electron density was 0·31 e Å^{-3}, mainly in the region of the bonds (Fig. 2). An attempt to explain the thermal parameters as resulting from the motion of a rigid molecule (Schomaker & Trueblood, 1968) was not successful.

Fig. 2. The residual electron density in the vicinity of molecule A projected from a difference map. The maximum residual electron density is 0·31 e Å^{-3}. Contours are drawn for 0·4, 0·5, ... times 0·31 e Å^{-3}; **b** is pointing towards the reader. Fractional coordinates $\times 10^2$ along **b** for the highest peaks and for the atoms are given.

Table 2. *Positional and isotropic thermal parameters with e.s.d.'s in parentheses*

U (Å^2) is of the form $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

	x	y	z	U
S(1)	0·80931 (11)	0·13326 (14)	0·48515 (10)	
S(2)	0·14049 (11)	0·37944 (14)	0·44851 (10)	
C(1)	0·6175 (5)	0·1685 (5)	0·4595 (4)	
C(2)	0·5827 (5)	0·2731 (5)	0·5381 (5)	
C(3)	0·4429 (5)	0·3231 (5)	0·5317 (4)	
C(4)	0·3011 (4)	0·2844 (5)	0·4416 (4)	
C(5)	0·0244 (5)	0·2893 (6)	0·3233 (4)	
C(6)	0·1023 (5)	0·1895 (5)	0·2785 (4)	
C(7)	0·2614 (5)	0·1837 (5)	0·3451 (4)	
C(8)	0·3601 (5)	0·0783 (5)	0·3084 (4)	
C(9)	0·5268 (5)	0·0819 (5)	0·3624 (4)	
C(10)	0·6169 (5)	−0·0119 (6)	0·3140 (4)	
C(11)	0·7678 (5)	0·0049 (6)	0·3682 (4)	
O	0·3004 (3)	−0·0148 (4)	0·2268 (3)	
H(2)	0·658 (5)	0·314 (5)	0·598 (4)	2·5 (10)
H(3)	0·431 (5)	0·394 (5)	0·587 (4)	3·1 (10)
H(5)	−0·084 (6)	0·319 (6)	0·297 (4)	3·5 (10)
H(6)	0·058 (4)	0·129 (5)	0·206 (4)	1·5 (7)
H(10)	0·573 (5)	−0·080 (5)	0·247 (4)	2·0 (9)
H(11)	0·856 (5)	−0·049 (5)	0·355 (3)	1·6 (8)

Discussion of the structure

A stereoview of the molecule is shown in Fig. 3 and the packing of the molecules is shown in Fig. 4. The molecules are arranged in pairs, within which they are related by a center of symmetry. The distance between the best planes (IV in Table 3) of the molecules in such a pair is 3·54 Å. The shortest intermolecular distances are given in Table 4. Only O—H is somewhat shorter than the van der Waals distance.

The deviations of atoms from some least-squares planes, and interplanar angles are given in Table 3. The deviations of the atoms of the thiophene rings from their respective planes are small, but significant. The atoms in the cycloheptatrienone ring, C(2), C(3) and C(8), nearest the respective thiophene rings show considerably larger deviations from these planes. The

torsion angles are given in Fig. 5(a). Starting with the pair S(1)[C(1)C(9)]C(10) and S(2)[C(4)C(7)]C(6) of the thiophene rings and going clockwise for comparison, a striking similarity between the torsion angles is revealed. This agreement and the deviations of C(2), C(3) and C(8) might be seen as the result of a minor twist of the whole molecule lengthwise.

The seven-membered ring has a boat conformation, as can be seen from the deviations from plane III (Table 3). The conformation is distorted in the way mentioned above, and for this reason a comparison of the torsion angles of the right and the left sides of ring III does not give good agreement (Fig. 5a). Some other planes (IV–VII) in the central ring support this presumption (Table 3). The angle between planes I and II is 171·6 (8)°.
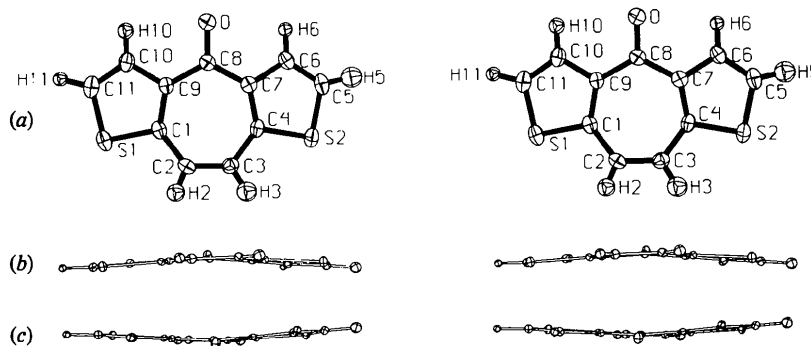
Bond lengths and angles are given in Fig. 5(a). The

Fig. 3. A stereoview of molecule A from three different directions. In (a) 50% probability ellipsoids are shown, in (b) C(2) and C(3) point towards the reader and in (c) O points towards the reader.
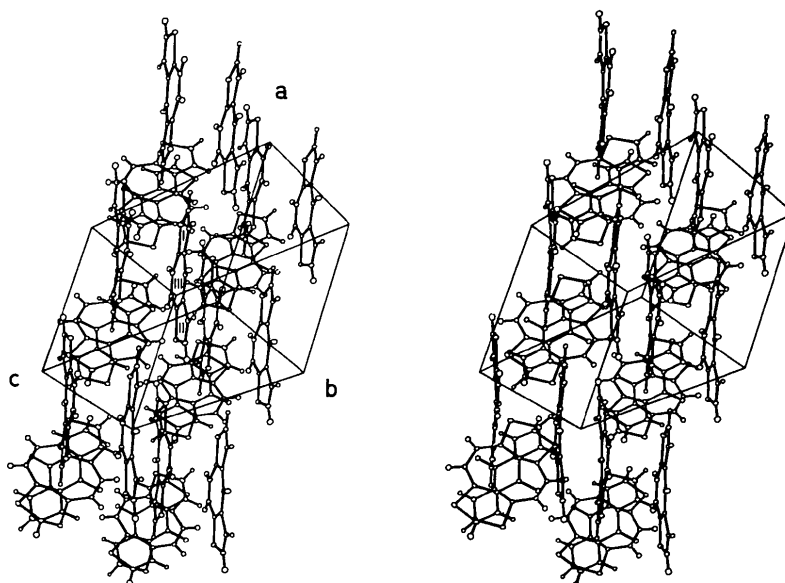

Fig. 4. A stereoview of the stacking of molecules A. The rings of the molecule in the asymmetric part of the unit cell are marked according to Fig. 5(a).

Table 3. Least-squares planes in A

Deviations ($\times 10^3$ Å) of the atoms from the planes, and the angles between them are given. Atoms used to define the planes are marked with asterisks. Weights proportional to the atomic numbers were used.

Plane I		Plane II		Plane III	
S(1)*	1	S(2)*	4	C(1)*	−43
C(1)*	2	C(4)*	−12	C(2)*	14
C(9)*	−7	C(7)*	7	C(3)*	41
C(10)*	10	C(6)*	4	C(4)*	−27
C(11)*	−8	C(5)*	−10	C(7)*	−40
C(2)	31	C(3)	−45	C(8)*	61
C(8)	−37	C(8)	40	C(9)*	−6
H(10)	15	H(6)	−32	O	174
H(11)	36	H(5)	−13	H(2)	20
				H(3)	65

Plane IV				Plane V	
S(1)*	−76	C(9)*	35	S(1)	−11
S(2)*	−27	C(10)*	−30	S(2)	110
C(1)*	35	C(11)*	−117	C(1)	96
C(2)*	126	O*	165	C(4)	151
C(3)*	155	H(2)	153	C(7)*	−3
C(4)*	57	H(3)	202	C(8)*	9
C(5)*	−172	H(5)	−255	C(9)*	−3
C(6)*	−128	H(6)	−225	O*	−3
C(7)*	7	H(10)	−32		
C(8)*	85	H(11)	−137		

Plane	VI	Plane	VII	Angles (°) between the planes	
C(1)*	4	C(1)*	−12		
C(2)*	−8	C(2)	58	I-II	171·6 (8)†
C(3)*	8	C(3)	88	I-III	176·1 (17)
C(4)*	−4	C(4)*	12	II-III	175·4 (17)
H(2)	−44	C(7)*	−14	VII-V	174·7 (32)
H(3)	−16	C(8)	77	VII-VI	176·3 (40)
		C(9)*	14	V-VI	170·9 (39)
		O	180		
		H(2)	71		
		H(3)	121		

† The e.s.d.'s are calculated without considering covariances, in contrast to Waser, Marsh & Cordes (1973).

Table 4. Shortest intermolecular distances (Å) between atoms in A

S—S	3·871 (2)	O—C	3·349 (5)
S—O	3·345 (3)	O—H	2·42 (5)
S—C	3·508 (4)	C—C	3·422 (6)
S—H	3·03 (4)	C—H	2·85 (4)
O—O	>4·0	H—H	2·50 (6)

distances and angles for corresponding bonds in the right and left parts of the molecule are not significantly different. The half-normal probability plot method (Hamilton, 1974) indicates that the standard deviations of the bonds and angles are overestimated by a factor of 0·7.
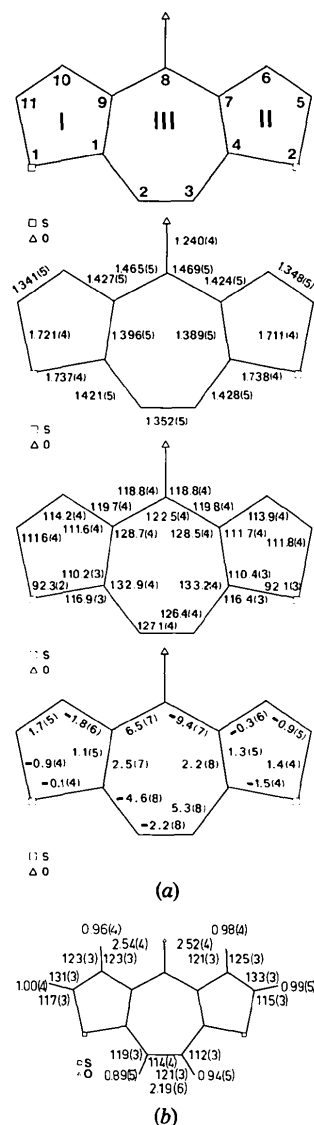

Fig. 5. Compound A. (a) Schematic diagrams showing the non-hydrogen atoms. The numbering of the ring system and the atoms, as well as selected distances (Å), bond angles (°) and torsion angles (°) are presented. The e.s.d.'s are given in parentheses. (b) Distances (Å) and angles (°) to H atoms.

Thus, we conclude that the molecule has an approximate mirror plane. Within each half of the molecule the S—C bond to the central ring is longer than the outer S—C bond. The formal double bonds of the central ring C(1)—C(9) and C(4)—C(7) are longer than the other double bonds of the molecule, all of which have the same length. Similarly, the formal single bonds of the central ring C(7)—C(8) and C(8)—C(9) are longer than the other single bonds. The C—O distance is rather long, 1·240 (4) Å. The angles of the ring systems differ from the ideal values for five- and seven-membered rings, especially in ring III at C(1), C(4) and C(8).

The H atoms are not significantly out of their respective planes (Table 3). Bond distances and angles involving H atoms are given in Fig. 5(*b*).

Comparison with *B*

In the light of the present structure (*A*), the corresponding cycloheptadienone structure, 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (*B* in Fig. 1) (Andersson, 1975), will be discussed. For convenience a stereoview of *B* is reproduced in Fig. 6. From this drawing and Fig. 3 it can be seen that the conformations of the compounds are remarkably similar; *B* might be thought of as resulting from *A* by exchanging the double bond C(2)—C(3) for a single bond, thereby twisting the rigid thiophene parts to each side. *A* has a slightly bent shape, but it is difficult to decide whether this deviation from the plane is transferred to *B*.

The precision in the determination of the structure of *A* is much higher than that of *B* (see below). In *B* the thiophene rings are planar within experimental error. In fact, the deviations from the planes I and II are markedly less in *B* than in *A*. However, C(8) (ring III) in *B* has a quite large deviation of 0·12 Å from plane I. Thus *B* is distorted from idealized C_2 symmetry, possibly depending on thermal motion. The cycloheptadienone ring in *B* has a twisted form with an angle between the thiophene planes of 158·2 (3)°. The torsion angles of *B* (Fig. 7) have about the same values as those of *A*, except for the C(1)—C(2)—C(3)—C(4) bonds.

The bond distances in *B* show differences between the right and left parts of the molecule; a half-normal probability plot indicated that the standard deviations of the bonds are underestimated by a factor of 1·6. This is taken into consideration in the comparison of *A* and *B*. The C(1)—C(2)—C(3)—C(4) bonds in *B* compared to those in *A* are quite different, but some other smaller differences also exist. Thus, in *B* the formal double bond C(1)—C(9) in the seven-membered ring, the carbonyl group and the annelated S(1)—C(1) bonds are

shorter than those in *A*. Some caution is appropriate as the structure of *A* in contrast to *B* was determined at low temperature and is likely to have smaller thermal motion. Large thermal motion of the molecules can give systematic errors often appearing as an apparent shrinkage of bond lengths. The angles in *A* and *B* show only small differences; the values of C(2)—C(1)—C(9) and C(3)—C(4)—C(7) in *B* are significantly smaller, however.

Conformations and properties

For comparison of the seven-membered ring in different conformations (planar and boat forms), two more compounds (*C* and *D* in Fig. 1) will be discussed. *syn*-TBHF (*C*) (Dichmann, Nyburg, Pickard & Potworowski, 1974) has three double bonds in the central ring, which is also the case for *A*. 5-(Bromomethylene)-10,11-dihydro-5*H*-dibenzo[*a,b*]cycloheptene (*D*) (Larsson, 1970; stereoview, Andersson, 1975) has two double bonds (as in *B*). The seven-membered ring in the boat form (*C*) has almost planar ethylene units and torsion mainly in the single bonds. *A* is only slightly twisted in the single bonds. The same is valid for *D* compared to *B* if the bonds C(1)—C(2)—C(3)—C(4) are not taken into account. This indicates a greater overlap of *p* orbitals in *A* and *B* compared to *C* and *D*, and this is especially marked for C(7)—C(8) and C(8)—C(9),
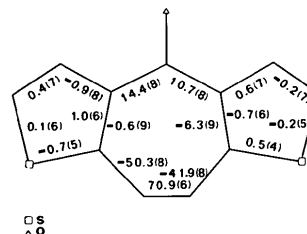

Fig. 7. Compound *B*. A schematic diagram showing the torsion angles (°). The numbering of the ring system and the atoms are as in Fig. 5(*a*).
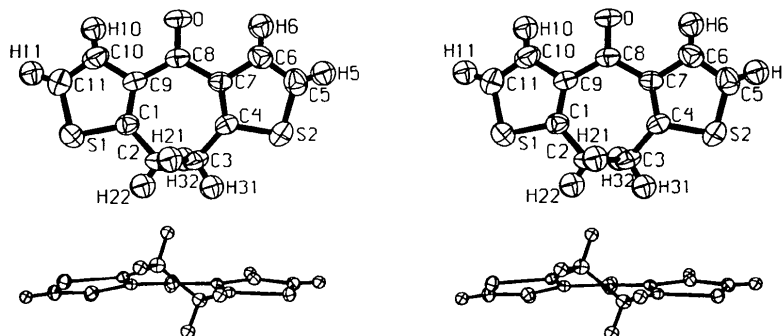

Fig. 6. Compound *B*. A stereoview of one molecule viewed from two directions. 50% probability ellipsoids are shown in the upper drawing.

where, in fact, the bond distances do not differ very much between the planar and boat forms.

The bond lengths of A, B and C are compared with those accepted for single and double bonds in Table 5. For A, the lengths of the double bond C(1)—C(9) and the single bond C(1)—C(2) are equal to the lengths of an aromatic bond and of C—C in graphite respectively. The double bond C(2)—C(3) is longer and the single bond C(7)—C(8) shorter than the corresponding reference values. This indicates that there is some conjugation in the system. The short single bond C(1)—C(2) is remarkable. For B the bond lengths are closer to the reference values. The C—O and the C(1)—C(9) distances are shorter compared to those of A, in good agreement with the C—O stretching frequencies. This is an indication of less delocalization for B than for A. Also, for C the bond distances are clearly closer to the reference values than for A [except for C(1)—C(9)] and this is particularly apparent for C(1)—C(2). The torsion angles are much greater for C. Thus the bond alternation and torsion of the bonds indicate decreasing conjugation in the order A/B and A/C. For all the compounds the distances C(1)—C(9) and C(8)—C(9) in

Table 5. *Mean values of bond distances* (Å)

The e.s.d.'s for A and B are multiplied by 0·7 and 1·6 respectively (see text). Notation: s = single bond, d = double bond. The reference distances are taken from *International Tables for X-ray Crystallography* (1962) and from Kitaigorodsky (1973).

Seven-membered ring

| | | C(1)—C(9) | C(1)—C(2) | C(7)—C(8) |
	C(2)—C(3)	C(4)—C(7)	C(3)—C(4)	C(8)—C(9)
Compound	d or s	d	s	s
A (173 K)	1·352 (4)	1·393 (3)	1·425 (3)	1·467 (3)
B (295 K)	1·516 (12)	1·373 (7)	1·493 (8)	1·479 (7)
C (*c:a*, 295 K, molecule 1)	1·341 (5)	1·406 (4)	1·456 (4)	1·489 (3)

Reference bonds	Double (simple) 1·337 (6) Single (partial) 1·507	Aromatic 1·395 (3)	Graphite 1·4210 (1)	Single (partial) 1·476

Thiophene rings and the carbonyl bond

| | C(10)—C(11) C(5)—C(6) | C(9)—C(10) C(6)—C(7) |
	d	s
A (173 K)	1·345 (4)	1·426 (4)
B (295 K)	1·340 (8)	1·430 (8)

| | S(1)—C(1) S(2)—C(4) | S(1)—C(11) S(2)—C(5) | |
	s	s	C—O
A (173 K)	1·738 (3)	1·716 (3)	1·240 (3)
B (295 K)	1·722 (6)	1·714 (7)	1·215 (8)

the central ring are longer than the other double and single bonds respectively. The annelated S—C bonds of A are longer than the outer S—C bonds.

In the approximately planar molecules A and B, the angle at the carbonyl bond C(7)—C(8)—C(9) is 122·5° and the mean value of the other angles of the seven-membered ring is 129·5°. In the central ring of C (boat form), the C(7)—C(8)—C(9) angle is 114·3° and the mean value of the other angles (123·6°) is much less than in A and B. Thus, angular strain is much less in the boat form. The annelation of a five-membered ring such as thiophene decreases the angular strain, as pointed out by Gronowitz *et al.* (1973). This is more pronounced than for a six-membered ring, such as benzene. The angle C(2)—C(1)—C(9) of A (132·9°) is greater than the corresponding angle of B (130·4°).

Intramolecular interactions are not large in A, B and C. They are mainly between the *peri* atoms of the central ring and the annelated rings and are thus dependent on their types. However, steric factors such as intramolecular H—H and H—C interactions are probably important in determining the conformations of C and D. In a fictitious planar form of C there would be large interactions, assuming normal C—H distances and C—C—H angles. In a boat form these interactions, as well as the angular strain, are minimized and this is probably also valid for D. Such interactions are small in the thiophene compounds.

Thus the properties of the above compounds, observed by chemical and spectroscopic methods, agree well with the detailed geometry of the molecules in the crystalline state. Preliminary structural results on the tropylium ion E (Fig. 1) also follow these trends in properties and structural details.

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Experimental and Theoretical Difference Densities for Urea.
A Simple Refinement of Density Distributions of Bonding Electrons VII.
Comparison of Observed and Calculated Electron Densities IX

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From a recently refined model of the electron density distribution in the urea molecule, dynamic and static density sections are calculated and presented as difference densities ρ(molecule) $- \rho$(isolated atoms). The sections obtained are compared to corresponding sections derived from a quantum-chemical calculation of 4-31G quality. In addition, a direct examination of this theoretical density distribution with the X-ray data is described.

Introduction

Mullen & Hellner (1978) measured X-ray data for urea at 123 K and determined the density distribution in the molecule by an empirical model (Hellner, 1977). In this paper the dynamic and static difference densities, obtained from Mullen & Hellner's refinement, are presented. Furthermore, a quantum-chemical calculation of the density distribution in the urea molecule, with a 4-31G basis set, has been carried out and dynamic and static difference densities for the theoretical model are presented. In addition, a test of this theoretical density distribution against the X-ray data by structure factor calculations and $F_o - F_c$ synthesis is reported. The procedure for thermal deconvolution and the treatment of series-termination effects have been described (Scheringer, 1977a; Scheringer, Mullen & Hellner, 1978).

Results

The experimental dynamic and static difference densities are presented in Fig. 1, the corresponding theoretical difference densities in Fig. 2.

The experimental densities are based on Mullen & Hellner's (1978) model. R for the 288 X-ray data is 1·60%, obtained with 63 density parameters and one scale factor. The $F_o - F_c$ synthesis based on the final model is nearly flat and shows positive and negative peaks up to 0·1 e Å^{-3}. The random error in the $\Delta\rho$ map, based on Rees's (1976) formula (10), is $\sigma(\Delta\rho) = 0\cdot033$ e Å^{-3} where the term $\sigma(\rho_c)$ and the scale factor term $\sigma(k)/k$ have been neglected. The positional and thermal parameters of the C, N and O atoms were obtained by determining the parameters of the respective $1s^2$ orbital products (Kutoglu & Hellner, 1978). Similarly, the positional and isotropic thermal parameters of the H