CONDENSED HETEROCYCLES.

46*. CRYSTAL STRUCTURE OF 3-MERCAPTO-2-BENZO[b]-FURYLIDENE-(p-METHYLPHENYL)AMINE

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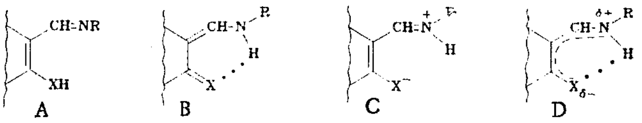
An x-ray structural examination of 3-mercapto-2-benzo[b]furylidene-(p-methylphenyl)amine has been carried out. For the first time, the position of the bridge hydrogen atom in a mercaptoaldimine containing the planar conjugated S═C—C═C—N grouping closed by an intramolecular N—H...S hydrogen bond has been established.

The attention of investigators has in recent times been drawn towards o-hydroxy-, o-mercapto-, and o-selenolaldimines of the aromatic and heteroaromatic series (A):



X=O, S, Se

This is due primarily to their photochromic, thermochromic, complexing, luminescent, and other properties of practical value [2-5]. For this reason, the structures of such compounds, in particular the investigation of prototropic tautomerism, intramolecular hydrogen bonding (X—H...N or X...H—N), etc., is of considerable interest.

Available spectral data provide evidence for the keto (thiono, or selenono)amine structure (B) in these compounds [6, 7]. However, x-ray structural examination of 2-mercapto-3-thenylidenecyclohexylamine (I), carried out at room temperature [8], has shown that the bond lengths in the chelate ring are evened out, but the position of the bridge hydrogen atom was not established, explained by these workers [8] as being due to the simultaneous presence of both the thionoamide (B) and mercaptoimine (A) forms. Shortly after this, NMR and UV spectroscopy was used to show the lack of correspondence between the structures of aldimines and that of (B), and the need to allow for the contribution of resonance form (C) to the tautomeric form (B), such as occurs in the mesomeric structure (D) [9, 10].

In order to establish the position of the bridge hydrogen atom (whether attached to sulfur or nitrogen), and to provide more definite information on the structure of ortho-mercaptoaldimines, we have carried out a low-temperature x-ray structural study of 3-mercapto-2-benzo[b]furylidene-(p-methylphenyl)amine (II).

Atom coordinates are given in Table 1, and valence angles in Table 2. Figure 1 shows a general view of the molecule of (II), with bond lengths.

The C═S distance (1.697(2) Å is close to that of the $C_{sp^2}{=}S$ bond (1.610(9) Å [11]), but is shorter than the single C_{sp^2}—S bond (1.817 Å [12]), which is in accordance with attachment of the hydrogen atom to nitrogen rather than sulfur.

In the approximately planar fragment $S{=}C_{(3)}{-}C_{(2)}{=}C_{(8)}{-}N$ (in which the atoms do not deviate from the mean plane by more than 0.013(2) Å), conjugation is seen, as shown by the decreased $C_{(2)}{-}C_{(3)}$ and $C_{(8)}{-}N$ bond lengths to 1.406(3) and 1.333(3) Å (the standard $C_{(sp^2)}{-}C_{(sp^2)}$ and $C_{(sp^2)}{-}N$ bond lengths are 1.476 [13] and 1.426 (12) Å [14]), and by the increased lengths

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*For communication 45, see [1].

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TABLE 1. Atom Coordinates (×10^5 for S atoms; ×10^4 for O, N, and C atoms, ×10^3 for H atoms), and Isotropic Equivalent Temperature Parameters for Nonhydrogen Atoms (isotropic for H atoms)

Atom	x	y	z	B_{iso}^{eq} and B_{iso} (Å^2)
S	−27631(7)	69039(5)	6750(3)	1,95(1)
O	1506(2)	7958(1)	−508(1)	1,90(3)
N	1250(2)	5550(2)	867(1)	1,66(4)
$C_{(2)}$	694(3)	7198(2)	10(1)	1,55(4)
$C_{(3)}$	−1278(3)	7539(2)	85(1)	1,53(4)
$C_{(3b)}$	−1702(3)	8563(2)	−422(1)	1,59(4)
$C_{(2b)}$	22(3)	8781(2)	−755(1)	1,68(5)
$C_{(4)}$	−3378(3)	9313(2)	−611(1)	2,06(5)
$C_{(5)}$	−3242(3)	10268(2)	−1114(1)	2,39(5)
$C_{(6)}$	−1483(3)	10470(2)	−1431(1)	2,46(6)
$C_{(7)}$	186(3)	9730(2)	−1261(1)	2,28(5)
$C_{(8)}$	1902(3)	6296(2)	361(1)	1,69(4)
$C_{(9)}$	2317(3)	4602(2)	1279(1)	1,60(5)
$C_{(10)}$	1399(3)	4028(2)	1834(1)	2,00(5)
$C_{(11)}$	2392(3)	3113(2)	2265(1)	2,27(5)
$C_{(12)}$	4323(3)	2749(2)	2157(1)	2,03(5)
$C_{(13)}$	5204(3)	3332(2)	1597(1)	2,00(5)
$C_{(14)}$	4227(3)	4248(2)	1159(1)	1,79(5)
$C_{(15)}$	5391(4)	1739(2)	2619(1)	2,80(6)
H	1(3)	569(2)	95(1)	2,8(5)
$H_{(4)}$	−457(3)	916(2)	−41(1)	2,1(4)
$H_{(5)}$	−440(3)	1078(2)	−124(1)	1,8(4)
$H_{(6)}$	−143(3)	1114(2)	−176(1)	2,8(5)
$H_{(7)}$	141(3)	987(2)	−147(1)	3,2(5)
$H_{(8)}$	330(3)	623(2)	28(1)	2,2(4)
$H_{(10)}$	2(3)	431(2)	190(1)	2,7(5)
$H_{(11)}$	173	271(2)	265(1)	2,7(5)
$H_{(13)}$	653(3)	310(2)	150(1)	2,5(5)
$H_{(14)}$	488(3)	464(2)	79(1)	2,2(4)
$H_{(15.1)}$	680(4)	163(2)	253(1)	5,4(7)
$H_{(15.2)}$	556(4)	196(2)	311(1)	5,3(7)
$H_{(15.3)}$	475(4)	97(3)	255(2)	6,3(8)

TABLE 2. Valence Angles ω (deg)

Angle	ω	Angle	ω	Angle	ω
$C_{(2b)}OC_{(2)}$	105,2(1)	$C_{(4)}C_{(5)}C_{(6)}$	120,9(2)	$NC_{(9)}C_{(14)}$	122,7(2)
$OC_{(2)}C_{(3)}$	111,5(2)	$C_{(5)}C_{(6)}C_{(7)}$	122,1(2)	$C_{(10)}C_{(9)}C_{(14)}$	119,8(2)
$OC_{(2)}C_{(8)}$	117,4(2)	$C_{(6)}C_{(7)}C_{(2b)}$	116,1(2)	$C_{(9)}C_{(10)}C_{(11)}$	120,0(2)
$C_{(8)}C_{(2)}C_{(3)}$	131,1(2)	$C_{(7)}C_{(2b)}C_{(3b)}$	123,2(2)	$C_{(10)}C_{(11)}C_{(12)}$	121,1(2)
$C_{(2)}C_{(3)}C_{(3b)}$	104,7(2)	$C_{(7)}C_{(2b)}O$	125,1(2)	$C_{(11)}C_{(12)}C_{(13)}$	117,8(2)
$C_{(2)}C_{(3)}S$	126,7(2)	$C_{(3b)}C_{(2b)}O$	111,6(2)	$C_{(11)}C_{(12)}C_{(15)}$	121,0(2)
$SC_{(3)}C_{(3b)}$	128,6(2)	$C_{(2)}C_{(8)}N$	121,0(2)	$C_{(15)}C_{(12)}C_{(13)}$	121,1(2)
$C_{(3)}C_{(3b)}C_{(2b)}$	107,0(2)	$C_{(8)}NC_{(9)}$	127,5(2)	$C_{(12)}C_{(13)}C_{(14)}$	121,8(2)
$C_{(3)}C_{(3b)}C_{(4)}$	133,5(2)	$C_{(8)}NH$	114(1)	$C_{(13)}C_{(14)}C_{(9)}$	119,5(2)
$C_{(2b)}C_{(3b)}C_{(4)}$	119,5(2)	$C_{(9)}NH$	118(1)		
$C_{(3b)}C_{(4)}C_{(5)}$	118,1(2)	$NC_{(9)}C_{(10)}$	117,5(2)		

of the $C_{(2)}=C_{(8)}$ and $C_{(3)}$ = S bonds to 1.373 (3) and 1.697(2) Å (the standard $C_{(sp^2)} = C_{(sp^2)}$ bond length is 1.333 Å [13]). The length of the C=S bond in (II) is the same as the mean value of the C=S bond length in (I) 1700 Å (two symmetrically independent molecules). The bond length distribution in the planar conjugated SCCCN grouping observed in (II) is also shown by (I). The possible involvement of the unshared electron pair of the nitrogen atom in (II) in conjugation with the π-system of the $C_{(2)} = C_{(8)}$ double bond is confirmed by its planar geometry (the sum of the valence angles is 359.5°). The N-H...S hydrogen bond closes the S = $C_{(3)}$–$C_{(2)}$=$C_{(8)}$–N fragment into a six-membered ring [N–H 0.88 (2), H...S 2.29 (2) Å, N–H...S 147(2)°]. The distance between the N and S atoms in (11) is 3.060(2) Å, and in (I) it is 3.005(7) Å, which would also permit the presence of a hydrogen bond in the ring, although the position of the hydrogen atom has not been established in this instance.

The O–$C_{(2)}$ and O–$C_{(2b)}$ bond lengths in the furan moiety are different. The O–$C_{(2b)}$ bond length of 1.371(2) Å is in agreement with the value of 1.368(5) Å in furan [15], but the O–$C_{(2)}$ bond length of 1.405(2) Å is considerably greater than this. This difference appears to be due to greater participation of the unshared electron pair of the oxygen atom in conjugation with the annelated benzene ring than with the S=C–C=C–N grouping [16]. Indeed, the

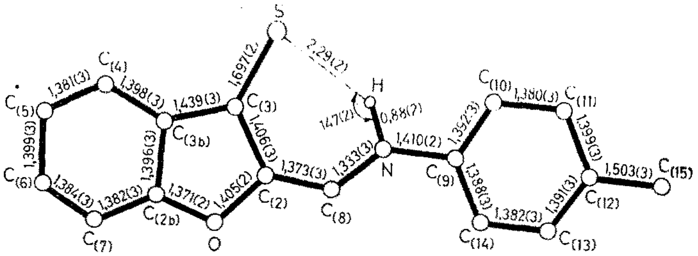

Fig. 1. Structure of the molecule of (II). The broken line shows the intramolecular hydrogen bond N—H...S.

oxygen atom is coplanar with the benzene ring, favoring p—π conjugation, whereas it departs from the plane of the S=C—C=C—N grouping by 0.046(1) Å.

The $C_{(9)}...C_{(14)}$ benzene ring is virtually coplanar with the conjugated grouping $S{=}C_{(3)}{-}C_{(2)}{=}C_{(8)}{-}N$ [the $C_{(8)}NC_{(9)}C_{(10)}$ torsion angle is 173.4(3)°]. The $N{-}C_{(9)}$ bond length of 1.410(2) Å is close to the standard value for the $C_{(sp2)}{-}N$ bond (1.426(12) Å [14].

In the crystal, intermolecular contacts $C_{(3)}...C_{(9)}$ 3.399(3) Å and $C_{(9)}...C_{(15)}$ 3.310(3) Å are seen between the original molecule of (II) and the molecules derived from it by symmetry transformations ($\bar{x}$, 1 − y, $\bar{z}$) and (1 − x, y + 1/2, 1/2 − z) respectively, these being approximately twice the van der Waals radius of the carbon atom, 3.40 Å [17]. The planar molecules of (II) form stacks along the b-axis with an interplanar distance of 3.60 Å.

These x-ray studies have therefore shown that the C=S bond is double, the hydrogen atom is located at the nitrogen atom rather than sulfur, and the conjugation in the S=C—C=C—N grouping shows that the molecular geometry is described by the mesomeric form (D).

EXPERIMENTAL

Compound (II) was obtained by successive treatment of 3-chloro-2-benzo[b]furfural with sodium hydrogen sulfide and p-toluidine hydrochloride, as described in [18].

The crystals of (II) were monoclinic: a = 6.775(4), b = 10.596(8), c = 18,396(14) Å, β = 96.254(60)°, V = 1312.7(1.6) $Å^3$, d_{calc} = 1.353 g/cm^3, z = 4, space group $P2_1/c$. The cell parameters and the intensities of 2242 independent reflections with $I \geq 2\sigma$ were measured on a Syntex $R2_1$ automatic four-circle diffractometer at —120°C (λMoK_α, graphite monochromator, θ/2 scanning, $2\theta \geq 60°$). The structure was calculated directly using the MULTAN program, all the nonhydrogen atoms being visualized, and refined by full-matrix least squares in anisotropic approximation for the nonhydrogen atoms. All the hydrogen atoms were visualized by difference synthesis, and refined isotropically. The final values of the divergence factors were R = 0.044 and R_W = 0.045. All calculations were carried out on an Eclips S/200 computer using INEXTL programs [19].

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MASS-SPECTROMETRIC BEHAVIOR OF BENZO-SUBSTITUTED DIBENZO-18-CROWN-6 ETHERS

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It was shown that the intensity of the peak of the molecular ion in the mass spectra of dibenzo-18-crown-6 derivatives depends to a marked extent on the electronic properties of the substituents on the benzene ring. Fragmentation of the substituents is observed after the decomposition of the polyether ring. This permits the proposition that the preferred localization of the charge in the molecular ion and the fragment ions is on the oxygen-containing part of the molecule. The analysis of the mass spectra of benzo-substituted crown ethers renders possible the determination of substituents occurring in the aromatic part of the molecule and their steric position.

Crown ethers and macrocyclic compounds similar to them have received a very widespread attention in differing areas of organic and analytical chemistry in recent years. The dibenzocrown ethers are especially promising since the introduction of different substituents into the benzene ring and their modification in the prepared macrocyclic molecule permit the variation in the properties of such compounds over a wide range [1-3].

The determination of the structure of the macrocycles obtained in this way often represents a difficult problem. In connection with this, the crown ethers and compounds structurally similar to them have become the object of a series of mass spectrometric investigations [4-7] in recent years.

However, the benzo-substituted crown ethers have been little studied by this method until now. Therefore, we also undertook investigations of a series of substituted dibenzo-18-crown-6 ethers containing electron-donor or electron-acceptor groups in the benzene nuclei, as well as the heterocyclic ring of 2-methylimidazole and 2-aminothiazole ring-fused to benzene. A series of compounds was obtained in the form of two isomers differing in the syn or anti disposition of the same substituents in the different benzene rings relative to each other.

The analysis of the mass spectra (Table 1) permits it to be noted, first of all, that the molecular ion M^{+} was registered in all cases; the intensity of the peak of the molecular ion depends to a marked degree on the electronic properties of the R^1 and R^2 substituents. The stability of the molecule (Table 2) to electron impact is higher in the case of electron-donor substituents and lower in the case of electron-acceptor substituents or ring-fused heterocyclic nuclei.

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