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CHEMISTRY AND STRUCTURE OF [1]BENZOTHIENO[2,3-*b*] [1]BENZOTHIOPHENE

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Abstract—The reaction of 1,1-diphenylethylene with sulphur yields [1]benzothieno[2,3-*b*] [1]benzothiopene (I), together with 3-phenylbenzothiophene. Oxidation of I with aqueous peracetic acid gives the corresponding monosulphone (III) and disulphone (IV).

The structures of I and its derivatives were established by chemical reactions and electronic and NMR spectra. The structure of the parent compound I was determined by X-ray analysis.

The aromatic character of the condensed thiophene system (I) was demonstrated by chemical reactions as compared with those of the corresponding sulphones, and from the observed bond lengths obtained from the X-ray analysis of I.

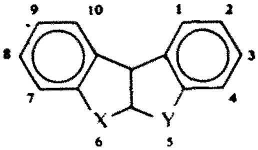
INTRODUCTION

SEVERAL preparations of [1]benzothieno[2,3-*b*] [1]benzothiophene (I) have been reported.[1-3] Cyclizations of 2-(*o*-aminophenylthio)benzothiophene with Cu and 2-(2-benzothienothio)cyclohexanone with P_2O_5, followed by the aromatization of the product with selenium, resulted in low yields of a compound for which the structure I was proposed.[1] The other preparations of I were based on the reactions of 3-phenylbenzothiophene[2] and of 1,1-diphenylethylene[3] with sulphur. The structural proposal which has been made on the basis of these preparations is further supported by the fact that the other possible structure, the isomeric [1]benzothieno[3,2-*b*][1]-benzothiophene (II) undergoes desulphurization with Raney Ni to bibenzyl and tetraphenylcyclobutane.[4] These studies were concerned chiefly with the preparations of I and neither its chemistry nor its physical properties were given due attention.

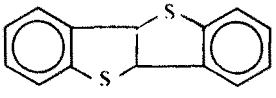
The purpose of the present paper is to describe some chemical reactions of I and of its derivatives, to prove the structures of the reactions products, and to establish the structure of the parent compound (I) by X-ray analysis.

Our study has been guided mainly by the interest in properties which reflect the electronic structure of the thiophene nucleus. Thus, the monosulphone (III) and the disulphone (IV) were prepared, which together with I constitute a series of compounds having the same ring structure but differing from each other in their detailed charge distribution. These differences may have a bearing on the aromatic character of the compounds I, III and IV and thus, attempts have been made to examine the double bond nature of the central C=C bond, by means of several relevant reactions.

On completion of the present study, a detailed investigation, involving 3-dimensional X-ray diffraction data, was undertaken with the aim of comparing the structure of the parent compound (I) with that of its fully oxidized derivative (IV). Since the refinement of the structure of the parent compound is now in its final stages, some results which are relevant to the chemical study described here will be included in the discussion.



I: X = Y = S
III: X = S, Y = SO_2
IV: X = Y = SO_2
VI: X = Y = Se
VII: X = Y = SO



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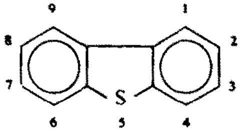
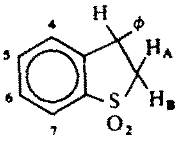
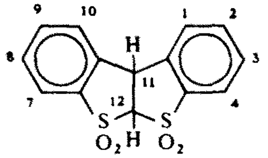


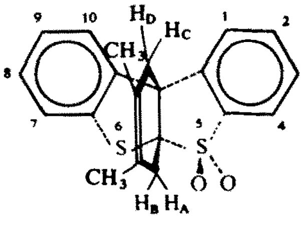
V



VIII



IX



X

RESULTS

The parent compound (I) was prepared in fairly good yields by the reaction of 1,1-diphenylethylene with four equivalents of sulphur. Small amounts of 3-phenylbenzothiophene were also isolated. When lower proportions of S were used, lower yields of I and higher yields of 3-phenylbenzothiophene were obtained. No detectable amounts of either II or of 2-phenylbenzothiophene were found, so that the reaction was not accompanied by rearrangements.[2, 5–7] The NMR spectrum of I shows only three distinct bands in the aromatic region (Table 1). The NMR spectra of dibenzothiophene (V) and of [1]benzoselenopheno[2,3-b][1]benzoselenophene (VI) are similar to that of I. The spectrum of VI had been analysed,[8] and it was found that the lowest field band (8·50 ppm) corresponds to the hydrogens at positions 1 and 10, whereas the band at 7·90 ppm derives from the protons 4 and 7, adjacent to the S atoms. By analogy, it may be assumed that the lowest field bands of both I (8·26 ppm) and V (8·04 ppm) derive from protons 1 and 10, and 1 and 9, respectively; the large deshielding effect on these protons results from ring currents of one benzene ring affecting the ortho hydrogen on the other benzene ring. This observation is, therefore, additional proof for the structure of I.

The parent compound, I, was oxidized with H_2O_2 in aqueous acetic acid, and two products, depending on the concentration of the peracetic acid formed, were obtained: the monosulphone III and the disulphone IV.

In the case of III, the elementary analysis of $C_{14}H_8O_2S_2$ may also fit the disulphoxide VII. The assignment of a monosulphone structure was deduced from the IR spectrum, which shows strong and sharp sulphone peaks at 1152 and at 1300 cm^{-1}, and from the NMR spectrum (Table 1) which shows a distinctive multiplet with relative area 1 at low field (8·20 ppm) which corresponds to hydrogen 4, adjacent to the SO_2 group, together with two other multiplets corresponding to hydrogens 1 and 10 (7·90 ppm) and to the rest of the aromatic H atoms (7·55 ppm).

TABLE 1. NMR DATA

Compound	I			V		
Protons	2,3,8,9	4,7	1,10	2,3,7,8	4,6	1,9
Multiplicity	two superimposed quartets[a]	doublet[a,b]	doublet[a,c]	non-symmetrical quartet[a]	double doublet[a]	double doublet[a]
δ, ppm	7·41	7·84	8·26	7·35	7·78	8·04

Compound	VI			III		
Protons	2,3,8,9	4,7	1,10	2,3,7,8,9	1,10	4
Multiplicity	quintet[a]	doublet[a]	doublet[a]	multiplet	multiplet	multiplet
δ, ppm	7·37	7·94	8·50	ca. 7·55	ca. 7·90	ca. 8·20

Compound	IV		IX		
Protons	1,2,3,8,9,10	4.7	aromatic	11	12
Multiplicity	multiplet	multiplet	multiplet	half of an AB quartet[d]	half of an AB quartet[d]
δ, ppm	ca. 7·98	ca. 8·58		5·72	5·60

[a] with long range splitting; [b] $J = 7{\cdot}0$ c/s; [c] $J = 6{\cdot}5$ c/s; [d] $J = 7{\cdot}0$ c/s.

In addition, desulphurization of III with Raney Ni gave a compound, $C_{14}H_{12}O_2S$ whose IR spectrum shows the two characteristic sulphone absorptions at 1150 and at 1305 cm^{-1}, and a C—H out-of-plane bending of a mono-substituted phenyl at 705 cm^{-1}. The NMR spectrum consisted of two multiplets in the aromatic region, one centred at 7·70 ppm (relative area 1; of proton 7, adjacent to the SO_2 group) and the other one centred around 7·30 ppm, relative area 8, corresponding to the rest of the aromatic protons. As the protons H_A and H_B are non-equivalent, the aliphatic hydrogens appear as a typical ABX pattern, with $H_A = 3{\cdot}40$ ppm, $H_B = 3{\cdot}83$ ppm, $H_X = 4{\cdot}71$ ppm and with $J_{AB} = 13{\cdot}5$ c/s and $J_{AX} = J_{BX} = 7{\cdot}5$ c/s. Hence, the product of the desulphurization is the sulphone VIII, which would be obtained only from III and not from VII.

The IR spectrum of the disulphone IV shows two strong SO_2 peaks at 1330 and at 1135 cm^{-1}; in the NMR spectrum (Table 1), the two H atoms adjacent to the SO_2 group (4 and 7), and the rest of the aromatic hydrogens, can be observed distinctively.

On bromination of I with bromine in acetic acid, a dibromo compound is obtained. Its IR spectrum is similar in appearance to that of the known dibromo-VI,[9] so that the bromination of I, like that of VI, takes place at the positions 3 and 8, while the central C═C bond remains intact. Attempted brominations on either III or IV did not take place, and only the starting materials could be recovered. I also undergoes electrophilic nitration to a tetranitro compound, probably the 2,4,7,9-tetranitro derivative of I.

The double bond nature of the central C═C bond was also examined chemically. Catalytic reductions of I and of III were accompanied by desulphurizations leading to 1,1-diphenylethane and to VIII, respectively. On the other hand, Pt-catalysed hydrogenation of the disulphone IV lead to the saturation of the central C═C bond, and IX was obtained. Its IR spectrum retains the sulphone features ($\nu = 1140$ and 1320 cm^{-1}), whereas the NMR spectrum (Table 1) shows all the aromatic protons in one broad multiplet, in addition to an AB quartet for the aliphatic H-11 and H-12 protons.

The monosulphone III undergoes a Diels–Alder cycloaddition with 2,3-dimethylbutadiene to form the pentacyclic, 3-dimensional adduct X. Its structure was derived from the NMR spectrum, which consists of a double-doublet with long range splitting at 7·85 ppm (relative area 1; H-4); a multiplet at 7·60 (area 3; H-1,7,10); a singlet at 2·78 ppm (area 4; H-2,3,8,9); an AB quartet of the non-equivalent H_A and H_B [$\delta_{H_A} = 3{\cdot}18$ ppm (area 1), $\delta_{H_B} = 2{\cdot}97$ ppm (area 1), $J_{AB} = 7{\cdot}0$ c/s]; an AB quartet of the non-equivalent H_C and H_D [$\delta_{H_C} = 2{\cdot}81$ ppm, $\delta_H = 2{\cdot}74$, $J_{CD} = 6{\cdot}0$ c/s (total area 2)]; and a singlet at 1·62 ppm, relative area 6, corresponding to the two Me groups. The appearance of the low field, C-4 proton multiplet, serves as an additional proof to the structure of III. Both I and IV do not react with 2,3-dimethylbutadiene. In the case of I, either the absence of an activating group (SO_2) in a position α to the double bond, or the low double-bond character of the central C═C bond, may prevent the addition; in the case of IV, with two activating SO_2 groups on the central bond, steric hindrance is probably the cause of the negative results.

Attempts to add nucleophilic agents to the central bonds of I, III or IV failed; in the first two cases, probably because of the aromatic character of this bond, and in the last case—because of the steric interference with the attack by the nucleophile. Thus, all three compounds failed to react in a Michael-type reaction and are not attacked by Grignard reagents. MeLi failed to react with I and with III, whereas it reduces the disulphone IV to the monosulphone III.

X-ray diffraction study

Crystal data. Crystals of the parent compound, I, were obtained by slow cooling of its solution in petrol ether (b.p. 80–100°). Most of the crystals were twinned, and only a few specimens suitable for study could be selected.

Crystals of the monosulphone, III, were obtained by slow cooling of its solution in dimethylformamide (triclinic modification) and also by slow evaporation of its solution in ethyl acetate (monoclinic modification).

Well formed crystals of the disulphone IV, were obtained by slow cooling of its solution in methyl ethyl ketone.

The unit cell dimensions and the space groups of the compounds I, III and IV were derived from Weissenberg and precession photographs taken with Cu Kα radiation. The Weissenberg photographs were calibrated with powder lines obtained from an 0·2 mm thick copper wire. About 30 independent high angle reflections were measured on each set of photographs and the unit cell dimensions along with their standard deviations were computed by the least squares method. The space groups of IV and of the monoclinic modification of III were uniquely determined by the systematically absent classes of reflections. The space group of I was indicated by the results of a statistical test[10] and by packing considerations while the space group ambiguity in the case of the triclinic modification of III has not been resolved.

The crystal data of the three compounds are summarized in Table 2. The measured densities reported in Table 2 were determined by the flotation method using aqueous solutions of KI and benzene–chloroform mixtures.

TABLE 2. CRYSTAL DATA

Compound	I	III (monoclinic)	III (triclinic)	IV
a (Å)	9·935 ± 0·003	7·915 ± 0·006	10·309 ± 0·004	11·084 ± 0·006
b (Å)	4·027 ± 0·001	12·380 ± 0·006	8·590 ± 0·001	8·599 ± 0·002
c (Å)	13·622 ± 0·004	13·359 ± 0·007	7·015 ± 0·003	15·325 ± 0·008
α			88·06 ± 0·09°	
β	97·90 ± 0·03°	113·31 ± 0·07°	103·39 ± 0·04°	116·82 ± 0·05°
γ			102·85 ± 0·03°	
D meas. (gr cm^{-3})	1·46	1·51		1·55
D calc. (gr cm^{-3})	1·478	1·504	1·535	1·551
Z	2	4	2	4
Space group	$P2_1$	$P\frac{2_1}{c}$	$P1$ or $P\bar{1}$	$P\frac{2_1}{c}$

Structure determination of I

In view of the short *b* axis of the unit cell it was hoped to solve the structure of I from the projection on the (010) plane. The intensities of the *h*0*l* reflections, required for this purpose, were obtained from a series of timed exposures on an integrating precession camera, taken with Mo Kα radiation. 221 reflections with measurable intensities were observed. The intensities were measured with a recording microdensitometer and after having been placed on a common arbitrary scale they were converted to structure amplitudes by the usual methods.[11] Absorption corrections were not applied at this stage.

The *X* and *Z* coordinates of the two S atoms were determined with the aid of a Patterson projection on the (010) plane. The solution of the vector map for the heavy atom coordinates was not unique and the choice, which later proved to be the correct one, was indicated by packing considerations. A sulphur-phased electron density projection was then computed rejecting those terms for which the ratio between the calculated and observed structure amplitudes was less than $\frac{1}{2}$. In addition to both S atoms, the Fourier map revealed the locations of one of the benzene rings and of both central C atoms. Four cycles of isotropic least-squares refinement, based on the parameters of ten atoms, brought the R factor down to 0·33. The subsequent electron density projection showed all the non H atoms along with a number of spurious peaks.

Additional three cycles of isotropic least-squares refinement based on the parameters of all the non H atoms reduced the R factor to 0·096. The electron density projection computed at this stage is shown in Fig. 1. In addition to the main features of the compound, the projection contains several small peaks whose locations correspond roughly to those expected for the aromatic hydrogens.

Regarding the accuracy of the determination, the average estimated standard deviations of the X and Z coordinates are 0·025 Å and 0·005 Å for the C and S atoms, respectively.

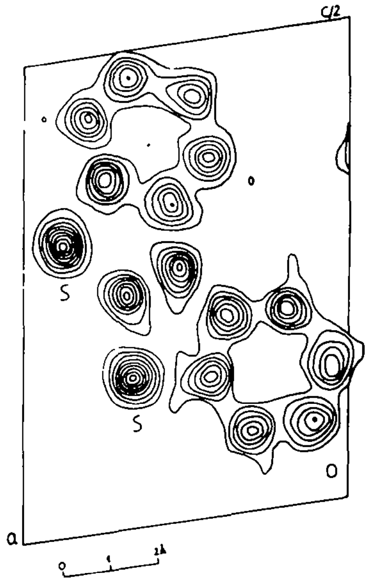


FIG. 1 [1]Benzothieno[2,3-*b*]benzothiophene. Electron density projection along the *b* axis based on the *h* 0 *l* structure factors. Contours at intervals of 1 electron/Å^2 for the carbon atom and at intervals of 3 electrons/Å^2 for sulfur. The first contour represents 1 electron/Å^2.

DISCUSSION

The electron density projection, shown in Fig. 1, confirms the structural assignment of the parent compound I. Moreover, the chemical structures of the various derivatives of I are thereby put on a firm basis, since the reactions involved are mild and rearrangements are very unlikely. The agreement between the observed and the calculated densities of the oxidation products of I (see Table 2) is further supporting evidence for the structures III and IV.

The assessment of the results of the present study has led to detailed investigations of the structures of the parent compound I and of its disulphone, IV. As mentioned in the introduction, the refinement of the structure of the parent compound is nearing completion. In view of the rather satisfactory values of the reliability index (R_{hkl} = 0·075 for 960 observed reflections) and of the standard deviations of bond lengths (0·015 Å and 0·0095 Å for C—C and S—C bonds, respectively) it seems both justifiable and advisable to present some relevant preliminary results here.

The molecule of the parent compound is very nearly planar and the bond lengths within the benzene rings are those normally found in aromatic compounds. The central C—C bond length is 1·39 Å while the C—C bonds connecting one of the central C atoms to the neighbouring ring carbons are 1·43 Å long.

These results indicate that the resonating system is spread throughout the molecule and hence its behaviour towards some of the reactions described in the previous section can be accounted for. A more detailed analysis involving the consideration of intramolecular non-bonded interactions will be published along with the complete description of the structure.[13]

The relative stability of thiophene towards addition reactions, compared to that of its corresponding sulphone, is well known. In fact, pure thiophene-1,1-dioxide cannot be obtained at all as a result of the high reactivity of its double bonds, which act both as a diene and a dienophile. In our systems, however, a dienic system is impossible, so that the sulphones are quite stable. In addition, the O atoms of the sulphone groups, projecting above and below the molecule's plane, interfere sterically with an attack on the central C—C bond by bulky groups. Hence, the disulphone IV is remarkably stable towards the ordinary reactants (the phenyl rings, too, are inert due to the deactivating effect of the SO_2 groups). A small atom, viz. H, however, can penetrate the steric barrier and so the catalytic hydrogenation of IV leads to the saturation of the central C═C bond with the formation of IX.

The less hindered monosulphone III may add groups bulkier than hydrogen, and it undergoes a Diels–Alder cycloaddition.

The central C—C bond of the parent compound I is also quite inert to additions due to its aromatic character, a property indicated by its length, which is about equal to that of benzene. On the other hand, I is susceptible to electrophilic substitutions on the phenyl groups.

EXPERIMENTAL

All m.ps reported are corrected. IR spectra were measured on a Perkin–Elmer 337 grating spectrophotometer. UV spectra were recorded on a Perkin–Elmer 137 UV spectrophotometer. NMR spectra were measured on a Varian HA 100 Spectrometer with TMS as an internal standard. Chemical shifts are expressed in ppm from TMS.

The cameras used for recording the X-ray patterns were a Weissenberg camera produced by Stoe and an integrating precession camera produced by Enraf-Nonius. Cu Kα and Mo Kα radiation was obtained from Phillips fine-focus X-ray tubes. The intensities of the reflections were measured by a Joyce–Loeble Mark IIICS recording microdensitometer.

Most of the computer programs used were obtained from Dr. D. Rabinowich of the Weizmann Institute of Science and were adapted by us to the CDC-3400 computer at the Tel-Aviv University Computation Center, where the calculations were carried out.

[1]*Benzothieno*[2,3-b][1]*benzothiophene* (I). A mixture of 1,1-diphenylethylene (36 g, 0·2 moles) and S (27·2 g, 0·85 moles) was heated for 5 hr at 240°. After cooling, the dark tarry mixture was extracted 4–5 times with boiling AcOH, and the soln was evaporated. The residue was crystallized from EtOH or from acetone, 26 g (54%) of colourless crystals, m.p. 141–142° (lit.[3] 140–141°) were obtained. (Found: C, 70·04; H, 3·36; S, 26·56. Calc. for $C_{14}H_8S_2$: C, 69·97; H, 3·35; S, 26·68%).

After evaporation and vacuum distillation, the mother liquor yielded 11 g (24%) of 3-phenylbenzothiophene, b.p.132–135° at 1·0 mm (lit.[7] 100–120° at 0·1 mm); its sulphone, obtained in 90% yield by oxidation with 1:1 30% H_2O_2: AcOH, had after recrystallization from AcOH m.p. of 152° (lit.[5] 152°).

When the reaction was carried out with 19·2 g (0·6 moles) of S, I and 3-phenylbenzothiophene were obtained in yields of 25% and in 55·5%, respectively.

[1]Benzothieno[2,3-b][1]benzothiophene 5,5-dioxide (III). 200 ml of 30% H_2O_2 were added to a warm 60–70°) soln of 5·5 g (0·02 ml) I in 200 ml AcOH, and the resulting mixture was left overnight at room temp. After filtration and crystallization from AcOH, 4·2 g (67·5%) of bright yellowish crystals, m.p. 234–235°, were obtained. (Found: C, 61·58; H, 2·98; S, 23·80. Calc. for $C_{14}H_8O_2S_2$: C, 61·74; H, 2·96; S, 23·55%).

[1]Benzothieno[2,3-b][1]benzothiophene disulphone (IV). A soln of I (5·5 g, 0·02 moles) in a mixture of 100 ml AcOH and 100 ml Ac_2O, in a 2 l. beaker, was heated to 70° and 60 ml 30% H_2O_2 was added rapidly with stirring. After about 5 min, an exothermic reaction started and the solid dissolved. On cooling, yellow needles of the disulphone precipitated, which, after recrystallization from dioxan, yielded 4·8 g (69%) of yellow crystals, m.p. 312–315°. (Found: C, 55·34; H, 2·67; S, 21·78. Calc. for $C_{14}H_8O_4S_2$: C, 55·25; H, 2·65; S, 21·07%).

3-Phenyl-2,3-dihydro-1-benzothiophene (VIII). A mixture of 0·5 g III and a spoonful (about 6 g) of 6 months' old Raney Ni in 100 ml EtOH was refluxed with stirring for 5 hr. After filtration, the clear, colourless soln was evaporated to dryness in vacuum and chromatographed on silica. 150 mg (34%) of a colourless oil was isolated, which after crystallization from benzene–petrol ether gave colourless crystals, m.p. 119–121° (lit.[12] 122·5–123°).

Bromination of I. 1 g of I was dissolved in 20 ml AcOH. To the warm (60°) soln, an excess of 5% soln of Br_2 in AcOH was added. After 2 hr, the mixture was filtered and washed with AcOH. On crystallization from DMF, 1·4 g (85%) of colourless, cotton-like crystals, m.p. 279–281°, were obtained. (Found: C, 42·32; H, 1·52; Br, 39·85; S, 16·03. Calc. for $C_{12}H_6Br_2S_2$: C, 42·23; H, 1·52: Br, 40·14; S, 16·11%).

Nitration of I. 5 g of powdered I were added in portions to a cold (−10°) stirred mixture of 100 ml HNO_3 and 100 ml H_2SO_4. Stirring was then continued for 1 hr, the temp being kept below 0°. The soln was then poured onto ice, and filtered after 12 hr. After drying the orange-red powder, it was crystallized from a large volume of dioxan, and 7·8 g (89%) of small orange crystals, m.p. 340–345° dec, were obtained. (Found: C, 40·23; H, 1·59; N, 13·86; S, 14·89. Calc. for $C_{14}H_4N_4O_8S_2$: C, 40·00; H, 0·96; N, 13·31; S, 15·23%).

Reduction of IV *to* IX. A mixture of 1 g IV, 100 ml EtOAc and 0·2 g PtO_2 were hydrogenated in a Parr hydrogenator at 3–4 atm H_2 and at room temp. Filtration, evaporation and crystallization from EtOH or from acetone–petrol ether yielded 0·87 g (88%) of IX, m.p. 279–280°. (Found: C, 54·74; H, 3·48; S, 20·18. Calc. for $C_{14}H_{10}O_4S_2$: C, 54·88; H, 3·30; S, 20·93%).

Formation of X. In a sealed tube, 1 g of III, 5 ml freshly distilled 2,3-dimethylbutadiene, and 20 ml dry toluene were heated for 12 hr at 160°. The cold mixture was filtered. The solid residue (750 mg) was identified as unreacted IV. Another 50 mg of IV were recovered by concentrating the soln. The remaining soln, after evaporating and repeated recrystallizations from EtOH, yielded 85 mg (6·5%) of solourless crystals, m.p. 213°. (Found: C, 67·52; H, 5·61; S, 17·42. Calc. for $C_{20}H_{18}O_2S_2$: C, 67·76; H, 5·12; S, 18·09%).

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