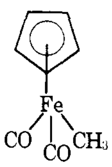
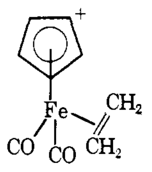


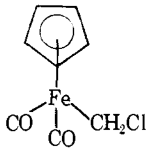
V



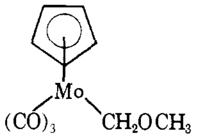
VI

appears to be general and stereospecific; in the presence of *cis*-2-butene reaction of IV with HBF$_4$ produces *cis*-1,2-dimethylcyclopropane, while with *trans*-2-butene the sole cyclopropane product is the *trans*-1,2-dimethyl isomer.

Reaction of the methoxymethyl complex IV and HCl in pentane caused immediate formation of cyclopentadienyl(chloromethyl)iron dicarbonyl (VII).[3] The complex VII reacts instantly with AgBF$_4$, precipitating silver chloride and forming complexes II, V, and VI in solution. When this reaction was performed at −60°, the AgCl was removed and cyclohexene was added to the supernatant and allowed to warm; small amounts of norcarane were produced. These reactions, especially the latter, strongly imply intermediacy of the carbene complex III.



VII



VIII

(CO)$_5$ReCH$_2$OCH$_3$

IX

The chloromethyliron complex VII, upon heating with cyclohexene at 50° for several hours, produces cyclopentadienyliron dicarbonyl chloride and high yields of norcarane (80%). This reaction appears to be analogous to the Simmons–Smith reaction or the pyrolysis of the halomethylmercury systems studied by Seyferth and co-workers.[5,6]

Other transition metal complexes appear to behave in an analogous manner to the iron complex IV. Thus, cyclopentadienyl(methoxymethyl)molybdenum tricarbonyl[3] (VIII) also produces norcarane upon treatment with HBF$_4$ in the presence of cyclohexene.

Although our studies are not yet comprehensive, it appears that the stability of carbene–transition metal complexes will prove to be very dependent upon the nature of the metal and especially its accompanying ligands. An indication of this is seen in the fact that whereas complex IV reacts practically instantly with HCl in pentane to produce the chloromethyl complex VII, (methoxymethyl)rhenium pentacarbonyl[3] (IX) produces the corresponding chloromethyl system only after several hours of treatment with HCl. The manganese compound analogous to IX forms the chloromethyl derivative even more slowly.

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[5] D. Seyferth and M. A. Eisert, *J. Am. Chem. Soc.*, **86**, 121 (1964).

[6] A chloromethyliridium complex appears to act analogously; *cf.* F. D. Mango and I. Dvoretzky, *ibid.*, **88**, 1654 (1966).

[7] The authors thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial assistance. Generous gifts of Fe(CO)$_5$ from General Aniline and Film Corp. are also gratefully acknowledged.

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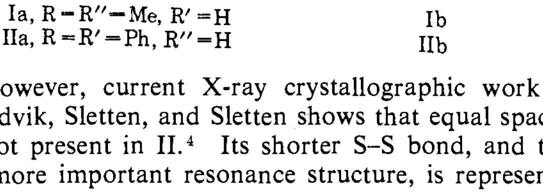
Selenium in the "No-Bond Resonance" System

Sir:

The three sulfur atoms in dimethylthiothiophthene (Ia) are reported to be collinear and equally spaced at 2.36 A. This exceptionally high bond length, as compared to the generally accepted S–S distance of 2.08 A, has been explained in terms of "no-bond resonance" between two equivalent structures, Ia and Ib.[1] This hypothesis has been supported by nmr studies[2] and by the finding that IIa and IIb are not isomers; one and the same compound is given by syntheses that would give both if they had distinct existence.[3]



Ia, R = R″ = Me, R′ = H   Ib
IIa, R = R′ = Ph, R″ = H   IIb

However, current X-ray crystallographic work by Hordvik, Sletten, and Sletten shows that equal spacing is not present in II.[4] Its shorter S–S bond, and thus its more important resonance structure, is represented by IIb; the corresponding S–S bond distance is found to be 2.22 A, 0.14 A above normal. The S–S bond distance corresponding to IIa is 2.51 A, higher than in Ia–Ib but still, of course, much below the van der Waals distance (3.70 A for two sulfur atoms), and thus indicative of a significant contribution from IIa. The obvious explanation for this result is, of course, that the symmetrical sulfur spacing in I is perturbed by unsymmetrical substitution in II. The possibility should also be noted, however, that the results reported for I may be partly due either to random packing of the molecules (since their shape is not altered much upon flipping over) or to an ordered superstructure. This is supported by the anisotropy in the direction of the S–S bonds exhibited by the S atoms as observed in the electron density maps of I. If this were due to a preferred thermal vibration, the much lighter carbon atoms attached to the sulfur atoms might reasonably be expected to move together with them. Yet the electron density distribution of the carbon atoms does not indicate this to be the case,[5] implying dissimilar S–S bonds even in I. The question might be further investigated by low-temperature high-resolution nmr.

In III, the oxygen analog of I, the remaining S–S bond length is 2.12 A, close to normal.[6] We are investigating other isosteres of thiothiophthene, and report herewith the selenium compound V, obtained in good yield by refluxing IV[3] for 4 hr in chlorobenzene with freshly ground phosphorus pentaselenide; it crystallizes as purple rods from methylcyclohexane, mp 130.5–131.5°.

The absorption spectra of II and IV in hexane conform to the established pattern for such pairs of com-

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[1] S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, **182**, 247 (1958).

[2] H. G. Hertz, G. Traverso, and W. Walter, *Ann.*, **625**, 43 (1959).

[3] E. Klingsberg, *J. Am. Chem. Soc.*, **85**, 3244 (1963).

[4] A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, in press.

[5] M. Mammi, private communication, 1966.

[6] M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282 (1961).

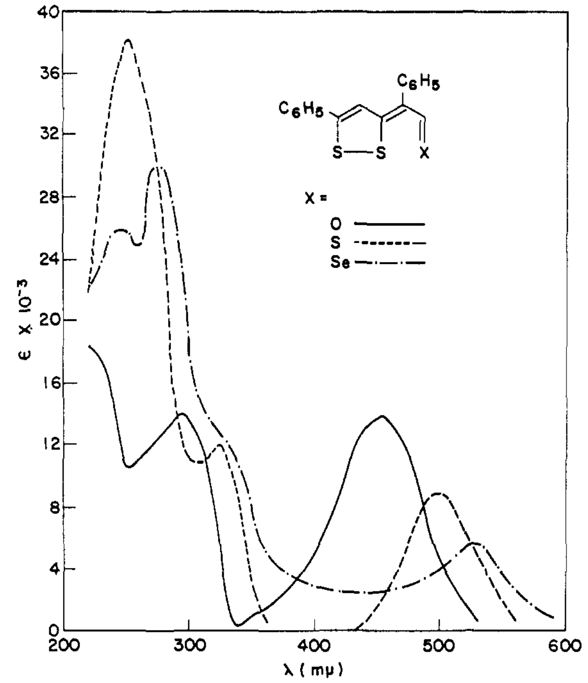


Figure 1.

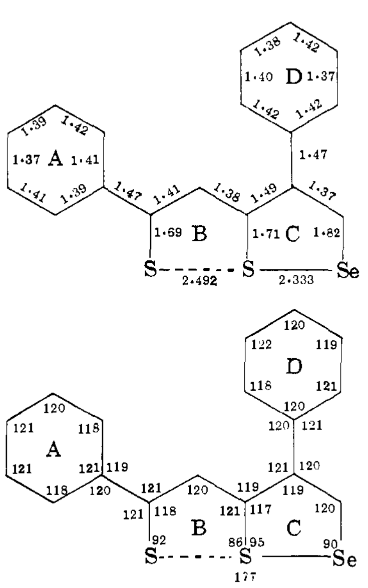
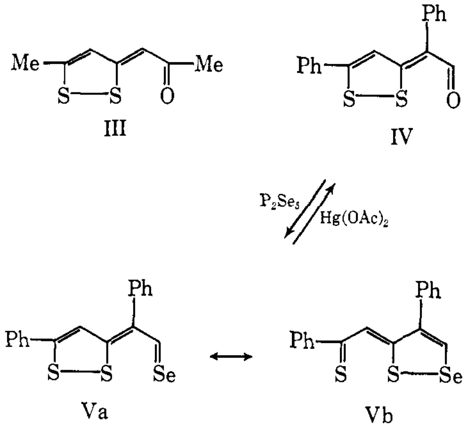


Figure 2. Bond distances: all C–C bonds ±0.02 A; Se–C, S–C ±0.01 A; Se–S, S–S ±0.003 A; average ring A: 1.40 A; D: 1.40 A. Bond angles: all angles ±2°; average ring A: 120°; D: 120°.

pounds.[7] With replacement of oxygen by sulfur, visible absorption is shifted to higher wavelength and weakened, and ultraviolet absorption is shifted to shorter wavelength and greatly strengthened. The selenium-containing system continues this pattern in the visible region: still weaker absorption at still higher wavelength. In the ultraviolet region, however, V is intermediate between II and IV with respect to both position and intensity of absorption (Figure 1).



III IV

Va Vb

A single-crystal X-ray analysis has yielded interesting results. The material was found to be monoclinic, and to belong to the space group $P2_1/a$ with four molecules in the unit cell of dimensions a = 17.532 A, b = 11.272 A, c = 8.099 A, β = 110.08°. The observed density of 1.56 g cm^{-3} agrees well with the calculated value of 1.59 g cm^{-3} which is based on the assumption of four molecules per unit cell. Intensity data were obtained with Cu Kα radiation on a General Electric XRD-6 equipped with eulerian cradle, and measuring the peak heights with a wide open aperture, balanced filters, and pulse-height discrimination. Of the 1530 possible reflections which were monitored with a range of θ between 0 and 53° ($d_{\min}$ = 1 A), 1072 were considered to be observable.

A sharpened three-dimensional Patterson function revealed the positions of the selenium atom and also provided probable positions for the two sulfur atoms. From a subsequent three-dimensional density map using only the stronger reflections with signs based on the selenium positions, these sulfur positions could be confirmed. A second electron-density map phased by the sulfur and selenium atoms resulted in a density distribution which could be interpreted completely in terms of structure V.

Subsequent isotropic refinement of the positional parameters and, after R had decreased to 0.17, of anisotropic thermal coefficients as well, reduced the discrepancy factor, R, to 0.075 ($R = \Sigma|k|F_o| - |F_c||/\Sigma|F_c|$).

The bond distances and bond angles as they were obtained after the refinement had converged are given in Figure 2.

The rings A, B, C, and D are all planar within the estimated standard deviations, and the angles of twist between rings A–B and C–D are 35.5 and 58.7°, respectively. Rings B and C make an angle of 6.6° with each other. In view of the internal consistency of the observed bond distances within the ring systems, it seems reasonable to consider the calculated standard deviations of 0.01 A for the C–C distances, which give an uncertainty of ±0.02 A at the 95% confidence level, as a good measure of the accuracy of the structure. The error in the S–S and Se–S distances is estimated at 0.003 A, and in the Se–C and S–C distances at 0.01 A.

The S–S bond distance of 2.49 A is appreciably higher than the 2.36 A reported for both S–S bonds in I, but almost exactly equal to the corresponding S–S bond in IIa (2.51 A). Evidently the replacement of one sulfur atom by selenium has negligible effect on the remaining S–S bond. Furthermore, the S–Se

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[7] H. Behringer, M. Ruff, and R. Wiedenmann, *Chem. Ber.*, **97**, 1732 (1964); H. Behringer and D. Weber, *ibid.*, **97**, 2567 (1964).

distance of 2.333 A seems to be too high for a normal single bond, much like the corresponding S–S bond in IIb, since the sum of the single-bond covalent radii for S and Se (1.04 and 1.17 A, respectively[8]) is 2.21 A. (Comparable S–Se bond lengths in other compounds have apparently not been determined experimentally.) Similarity to IIb is also shown in the smooth elimination of *selenium* on treatment with mercuric acetate in acetone–acetic acid at room temperature, regenerating IV in high yield. Peracetic acid gives the same result. On the whole it seems apparent that Vb contributes more than Va to the structure, just as IIb is more important than IIa; the S–Se bond distance is *less* than the S–S distance, whereas the "normal" S–Se distance of 2.21 A (sum of covalent radii) is *greater* than the normal S–S bond distance of 2.08 A. Selenium is accommodated in the thiothiophthene system without distortion.[9]

Acknowledgment. The authors are indebted to Mrs. Maryellen Kish and Mr. N. R. Nelson for technical assistance.

(8) S. C. Abrahams, *Quart. Rev.* (London), **10**, 417, 429 (1956).

(9) Selenium compounds that may be related to thiothiophthene have been reported, without structure analysis, by G. Traverso [*Ann. Chim.*, 47, 3 (1957)] and M. Sanesi and G. Traverso [*Chem. Ber.*, **93**, 1566 (1960)].

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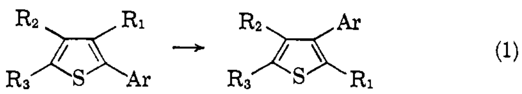
The Photochemistry of Thiophenes. III. Photochemical Rearrangements of Arylthiophenes

Sir:

The results of photochemically induced rearrangement of a large number of unsymmetrically disubstituted arylthiophenes coupled with previous ^{14}C evidence[1] allow significant extension and refinement of our recent mechanistic proposals.[1–3]



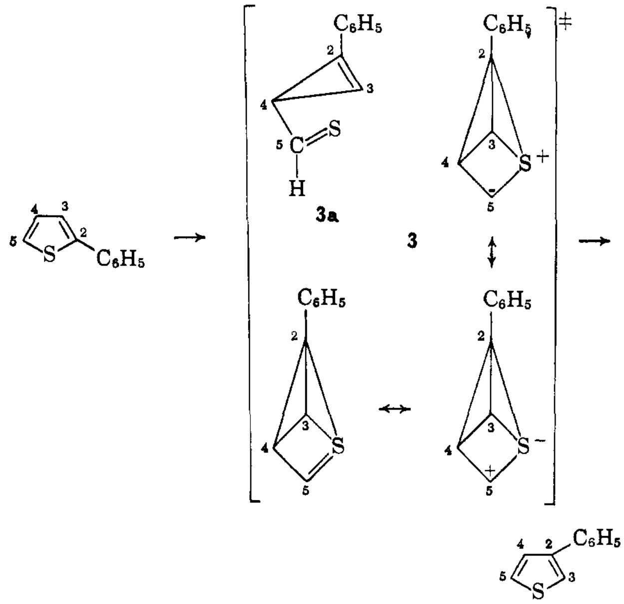
(1)

1 2

a, Ar = C_6D_5, R_3 = D, $R_1 = R_2$ = H
b, Ar = C_6H_5, R_3 = CH_3, $R_1 = R_2$ = H
c, Ar = C_6H_5, R_2 = CH_3, $R_1 = R_3$ = H
d, Ar = C_6H_5, R_1 = CH_3, $R_2 = R_3$ = H
e, Ar = C_6H_5, R_2 = C_6H_5, $R_1 = R_3$ = H

With 2-arylthiophenes **1a–e**, products **2a–e** account for 80% or more of the rearranged materials (eq 1);[4] the balance of the products are the other positional isomers and starting material.[5] The major rearrangement path (80% or more) thus involves, as shown in eq 1, specific C_2–C_3 inversion without concomitant C_4–C_5 inversion of the thiophene ring carbons.

A prediction, at this stage, of the exact geometry of the state(s) responsible for rearrangement is difficult.[6] A series of sufficiently complex equilibria between postulated valene, Dewar, and/or prismane type structures[1–3] allow rationalization of the products formed (or indeed of any rearrangement products!) but fail to predict adequately the observed specificity of this photoreorganization. More logical, we think, are structures **3a** and **3** which provide a useful qualitative framework for rationalization of the observations. Form **3a**, a thioaldehyde, would clearly offer the simplest explanation though little ground-state stability would be predicted.[7] Structures **3** involve active participation of the sulfur 3d orbitals.



In unsymmetrically disubstituted 3-phenylthiophenes further changes in the carbon atom sequential order occur, as shown in eq 2–4.[4,5,8] Selectivity of rearrangement is again observed, but is of a different nature than that observed with 2-phenylthiophenes. In these rearrangements intermediates similar to **3** could play an important role but do not provide a necessarily unique rationalization of the results.

In the superficially similar rearrangement of an isoxazole to an oxazole, Ullman and Singh[9] have isolated, as a true photochemical intermediate, an azirine analogous to **3a**. Participation of the sulfur 3d orbitals of our **3a** with the carbon–carbon double bond

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(1) The phenyl group remains attached to the same carbon atom during rearrangement. H. Wynberg and H. van Driel, *Chem. Commun.*, 204 (1966). We assume this holds true for all arylthiophenes although this is unequivocally proved only with 2-phenylthiophene.

(2) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, 87, 3998 (1965).

(3) H. Wynberg and R. M. Kellogg, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 10–16, 1966.

(4) Photolysis conditions were approximately those previously described.[2] Extrapolation of product ratios to zero time indicated products 2 to be the first products of rearrangement and not those of secondary photolysis. Small quantities of the other isomers appear to be formed in the primary photolysis.

(5) All products have been unambiguously identified by comparison of infrared, ultraviolet, and/or nmr spectra with those of authentic samples. The synthesis, separation, and identification will be included in the full paper.

(6) This is particularly true if rearrangement occurs in an excited state or even in a highly vibrationally excited ground state. Thus far we have been unable to detect any ground-state intermediates either directly or by trapping experiments. Lacking other evidence, we assume rearrangement through an energetic species.

(7) For a representative reference on thioaldehydes, see W. Schroth, F. Billig, and H. Langguth, *Angew. Chem.*, 77, 919 (1965).

(8) For 3-phenylthiophene itself these rearrangements become examples of photochemical "no-reaction" reactions.

(9) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966). See also a sydnone rearrangement: C. H. Krauch, J. Kuhls, and H. J. Piek, *Tetrahedron Letters*, **34**, 4043 (1966).