Differences in total porphyrin concentration and in light intensity make it difficult to draw a comparison between the flash experiments and the steady-illumination experiments; however, $k_d = 10^3$ sec^{-1} is probably a reasonable estimate of the triplet decay rate in the latter. φ_{isc} is estimated at 0.3–0.7;[19,20,20a] using these values and our measured value of $\varphi_{c\rightarrow t} = 7$ we obtain $k_{et} = 1 - 2.3 \times 10^4$ sec^{-1}. The former value corresponds to $\Delta G^{\ddagger} = 12.3$ kcal/mol from absolute rate theory.

As a test of the proposed scheme we prepared *cis*- and *trans*-1-phenyl-2-(4-pyridyl)propene (PPP) and *cis*- and *trans*-1-(1-naphthyl)-2-(4-pyridyl)propene (NPP), methylated derivatives of 4-stilbazole and NPE which are not expected to have energy minima near the transoid triplet.[2,4,13] Addition of azulene has no effect on the benzophenone-sensitized photoisomerization of 1,2-diphenylpropene,[2,4] and we find similar behavior for PPP.[21,22] For PPP and NPP we would anticipate that selective quenching of the olefin triplet to trans with regeneration of the porphyrin triplet could not occur; consequently $\varphi_{c\rightarrow t}$ should not exceed unity and the stationary state should be richer in *cis*-olefin.

As predicted, the zinc etioporphyrin I sensitized photoisomerization of NPP and PPP is markedly different from that of NPE and 4-stilbazole. Photostationary states measured from both directions give 30% cis for PPP and 31% cis for NPP in contrast to <1% cis for 4-stilbazole and ~4% for NPE. For NPP, $\varphi_{c\rightarrow t} = 0.4$ and $\varphi_{t\rightarrow c} = 0.2$; for PPP, $\varphi_{c\rightarrow t} = 0.1$ and $\varphi_{t\rightarrow c} = 0.05$. Since triplet energy transfer from zinc etioporphyrin I to PPP or NPP should be irreversible, the difference in k_d for a zinc etioporphyrin I–NPP solution and a zinc etioporphyrin I–NPE or zinc etioporphyrin I-pyridine (benzene) solution should provide an estimate of k_{et} for triplet energy transfer to NPP. The value of k_{et} thus determined is 1×10^4 sec^{-1}, in excellent agreement with the value of k_{et} calculated for NPE using eq 12.

Studies on the temperature dependence of isomerization and energy transfer reveal that reaction 5 requires a surprisingly low activation energy.[6] Isomerization yields for zinc etioporphyrin I-*cis*-NPE show very little increase with temperature ($\varphi_{c\rightarrow t}{}^{50°}/\varphi_{c\rightarrow t}{}^{30°} = 1.14$); an Arrhenius plot for k_{et} can be obtained from eq 12 after correcting for the measured small increases of k_d with temperature. The Arrhenius plot (correlation coefficient 0.99) so obtained gives $E_a = 3.2$ kcal/mol; using $\Delta G^{\ddagger} = 12.3$ kcal/mol, we obtain $\Delta S^{\ddagger} = -32$ eu. From k_{et} for zinc etioporphyrin I–*cis*-NPP we obtain an Arrhenius activation energy of 2.5 kcal/mol, and from the preexponential term, $\Delta S^{\ddagger} = -34$ eu. The low E_a values indicate that energy transfer to a >50-kcal/mol "*cis*"-olefin triplet[6] is not important. The high negative entropy of activation appears to be in accord with an interpretation involving energy transfer to yield a distorted olefin triplet.[12,13] Little is known concerning the temperature dependence of k_{et} and the magnitude of $\Delta S^{\ddagger}$ for related intermolecular processes.[5,13] It is not clear whether the observed large negative $\Delta S^{\ddagger}$ will prove to be a general phenomenon or one specific to this system. These points will be more fully discussed in the full paper.[23]

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tions of triplets that bimolecular quenching is negligible and the decay of triplet absorption follows good first-order kinetics.

(18) H. Linschitz and K. Sarkanen, *J. Amer. Chem. Soc.*, 80, 4826 (1958).

(19) G. P. Gurinovich, A. I. Patsko, and A. N. Sevchenko, *Dokl. Phys. Chem.*, 174, 402 (1967).

(20) P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, 31, 1 (1969).

(20a) NOTE ADDED IN PROOF. A recent measurement of $\varphi_{isc} = 0.9$ has been reported; see B. Dzhagarov, *Opt. Spektrosk.*, 28, 66 (1970). Using $\varphi_{isc} = 0.9$, we obtain $k_{et} = 8 \times 10^3$ sec^{-1}.

(21) The benzophenone-sensitized photostationary state in benzene is 41% cis.

(22) The absence of an azulene effect on sensitized photoisomerization of NPP was not verified since we were unable to design an experiment in which direct excitation of NPP could be rigorously excluded.

(23) Support of this work by the National Institutes of Health (Grant No. GM 15,238-03,4) is gratefully acknowledged.

(24) Alfred P. Sloan Foundation Fellow, 1970–1972.

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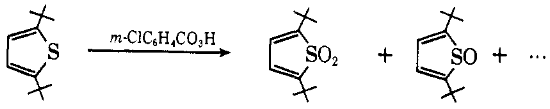
Stable Thiophene Sulfoxides

Sir:

Substituted thiophene sulfones are reasonably well-characterized substances,[1] although the parent, thiophene 1,1-dioxide, may be obtained only in solution.[2] We have isolated two disubstituted thiophene 1-oxides, and here report upon their structure and comment upon the nature of cyclic delocalization in the heterocyclic ring.

Oxidation of 2,5-di-*tert*-butylthiophene (**1**) with 1 equiv of *m*-chloroperbenzoic acid in methylene chloride gave, in addition to 2,5-di-*tert*-butylthiophene 1,1-dioxide (**2**) and some other products, approximately a 5% yield of 2,5-di-*tert*-butylthiophene 1-oxide[3] (**3**), mp 97–98°, isolated by column chromatography (eq 1).



1 **2** **3**

(1)

Interest in this substance centers about the sulfur atom. For optimal contribution to a conventional aromatic sextet, one might think it should be trigonally hybridized, with a formal lone pair of electrons in a 3p orbital perpendicular to the plane of the ring and with the sulfur-oxygen bond in that plane. On the other hand, sulfoxides normally exist exclusively in the pyramidal form, with a sizable barrier to inversion.

Spectroscopic evidence suggests that this sulfoxide is indeed tetrahedrally hybridized. In particular, the sulfur–oxygen stretch in the infrared occurs at λ_{max}^{KBr} 9.5 μ, a normal value. The olefinic ring protons in the nmr resonate in **3** at $\delta_{TMS}^{5\% CCl_4}$ 6.08 (*cf.* **1**, 6.46 **2**, 6.16).[4,5]

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(1) J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 72, 314 (1953); L. G. Vorontsova, *Zh. Strukt. Khim.*, 7, 240 (1966).

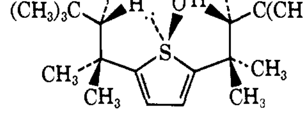
(2) W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 76, 1932, 1936, 1940 (1954).

(3) *Anal.* Calcd for $C_{12}H_{20}SO$: C, 67.89; H, 9.50. Found: C, 67.66; H, 9.54.

(4) However, the couplings between the ring protons (a possible measure of the C(3)–C(4) bond order: M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 91, 6325 (1969)) are: **1**, $J = 3.6$; **2**, $J = 5.0$; **3**, $J = 3.5 \pm 0.1$ Hz (as seen from C-13 satellites). We have elsewhere commented on difficulties of abstracting structural information from the nmr spectra of cyclic sulfones: M. P. Williamson, W. L. Mock, and S. M. Castellano, *J. Magn. Res.*, 2, 50 (1970).

also indicates a similar electronic structure for **2** and **3**. The sulfoxide **3** has two distinct absorptions, $\lambda_{max}^{C_8H_{18}}$ 323 (ϵ 1950) and 251 nm (ϵ 1500); both are shifted in polar solvent, $\lambda_{max}^{CH_3OH}$ 319 (ϵ 2300) and 245 nm (ϵ 1200). For **2** there appears to be a single absorption, $\lambda_{max}^{C_8H_{18}}$ 298 nm (ϵ 2900); however, there is a suggestion of a shoulder upon the end absorption (*ca.* 215 nm) indicating the presence of the second transition. For **1** there is a single absorption, $\lambda_{max}^{C_8H_{18}}$ 238 nm (ϵ 9000).[6] Although the transitions observed in **2** and **3** have not been assigned, we surmise that they arise from related electronic structural features whose effects are more pronounced in the case of **3** (at least in the excited state).[7]

In order to confirm nonplanar hybridization of sulfur in **3** we similarly prepared 2,5-di-*tert*-octylthiophene 1-oxide (**4**) from the corresponding thiophene. The



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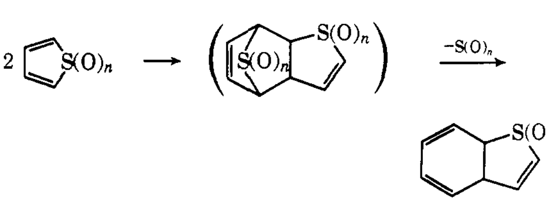
spectroscopic properties of **4** parallel those of **3**; however, the nmr spectrum is uniquely informative. At −10° the geminal methylene protons in the side chain of **4** are magnetically nonequivalent; $\delta_{TMS}^{CCl_4}$ 1.68, 1.98 (d, $|J|$ = 14.8 Hz).[8] We believe that the source of the anisotropy must be the sulfoxide functionality, which therefore must be pyramidal. As the temperature is raised, this quartet broadens and fuses (reversibly), becoming a singlet above 60°. The most reasonable explanation of this phenomenon is rapid inversion of the sulfoxide function, proceeding through a planar transition state (or intermediate). Alternative explanations seem less likely in that these resonances remain a singlet in the corresponding thiophene and sulfone down to −45° (the lowest temperature at which compounds in this series were examined).

At the coalescence temperature (26°) the rate constant[9] for the process under observation is k = 90 sec^{-1}. The derived free energy of activation is $\Delta G^{\ddagger}_{26}$ = 14.8 kcal mol^{-1}; the latter number is also a reasonable estimate for the enthalpy of activation ($\Delta H^{\ddagger}$).[10] This is to be contrasted to the configurational stability ordinarily exhibited by this functional group; for diaryl sulfoxides[11] $\Delta H^{\ddagger}$ for inversion is on the order of 36 kcal mol^{-1}. It is attractive to equate the lowering of the inversion barrier (by *ca.* 20 kcal mol^{-1}) to a delocalization energy of planar thiophene sulfoxide; similar stabilization of the transition state for inversion in the phosphole ring system was recently ascribed to this origin.[12]

However, a comment regarding chemical reactivity in the thiophene oxides is in order. A common feature, which prevents isolation of less sterically hindered thiophene sulfoxides (and thiophene sulfone[2]), is ready Diels–Alder dimerization (eq 2). The facility of this reaction, which incidentally is characteristic of certain antiaromatic systems, is in general a consequence of a reduced energy gap between the highest filled ("valence electrons") and lowest unfilled energy levels of the conjugated system, such that the transition state for dimerization is stabilized by effective mixing of these orbitals.[13] The occurrence and the relative positions of the long-wavelength uv absorptions in **2** and **3** are consistent with this concept and with apparently greater reactivity of the sulfoxide ring. We would note, therefore, that the low activation energy requirement for forming a planar sulfoxide in the case of this thiophene system might equally well be thought of as a consequence of relief from a destabilization energy associated with the (antiaromatic) pyramidal form in the course of inversion.



(2)

This conceptual ambivalence is eased by the hypothesis of valence shell expansion of sulfur, wherein 3d orbitals are utilized. Presumably, the various available d orbitals will be used simultaneously for sulfur–oxygen bonding and for cyclic conjugation within the ring, in both planar and pyramidal forms of the heterocycle.[14] Since it is the resultant of all the filled molecular orbitals which determines configuration, it is probably unjustified to select out any partial feature, such as a trio of electron pairs forming an "aromatic sextet," to explain the properties of this ring. On the other hand, there is indicated a possibility for elucidation of the conjugative interactions of sulfoxides and sulfones with the aid of simple symmetry concepts,[13,14] which will be pursued elsewhere.

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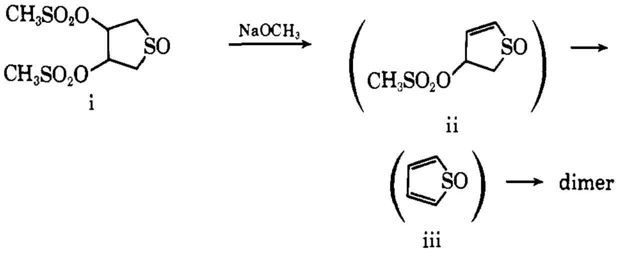
(5) For the *tert*-butyl groups the following chemical shifts ($\delta_{TMS}^{CCl_4}$) are observed: **1**, 1.35; **2**, 1.35; **3**, 1.4.

(6) R. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, 3136 (1965); H. Wynberg and U. E. Wiersum, *J. Org. Chem.*, 30, 1058 (1965).

(7) Detection of the parent thiophene sulfoxide (iii) in solution has been claimed: M. Prochazka, *Collect. Czech. Chem. Commun.*, 30, 1158 (1965). The only direct evidence was the observation of uv maxima at 215–216 and 263–265 nm. If the claim is correct, then there must be a sizable substituent effect associated with the introduction of *tert*-butyl groups on the ring. However, the spectra of the alleged thiophene sulfoxide is in accord with what might be expected for the intermediate ii: M. Prochazka and M. Palecek, *ibid.*, 32, 3049 (1967). On the other hand, the *S*-methylthiophenium ion was observed to have absorptions in these regions: G. L. Brumlik, A. I. Kosak, and R. Pitcher, *J. Amer. Chem. Soc.*, 86, 5360 (1964); R. M. Acheson and D. R. Harrison, *J. Chem. Soc. C*, 1764 (1970).



(8) Other absorptions: $\delta_{TMS}^{CCl_4}$ 0.95 (s, 18), 1.4 (s, 12), 6.1 (s, 2).

(9) The approximation of R. J. Kurland, M. B. Rubin, and W. B. Wise (*J. Chem. Phys.*, 40, 2426 (1964)) for the AB system was used.

(10) The entropy of activation ($\Delta S^{\ddagger}$) is most likely near zero for a simple inversion process, as has been observed for other sulfoxides[11] and the related phosphole ring.[12] The errors inherent in line-shape analysis procedures have dissuaded us from attempting to obtain accurate experimental activation parameters for this simple two-spin system in which the resonances also show broadening from other sources.

(11) D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4854 (1968).

(12) W. Egan, R. Tang, G. Zon, and K. Mislow, *ibid.*, 92, 1442 (1970).

(13) E. W. Garbisch and R. F. Sprecher, *ibid.*, 91, 6785 (1969).

(14) Analysis of the various types of interactions originated with H. P. Koch and W. Moffit, *Trans. Faraday Soc.*, 47, 7 (1951).

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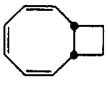
trans,cis,cis,trans-1,3,5,7-Cyclodecatetraene–*trans*-Bicyclo[6.2.0]deca-2,4,6-triene, a Rapidly Interconverting Möbius Tautomeric System

Sir:

Insights derived from "orbital symmetry" considerations[1] have brought about widespread acceptance of the idea that most low-energy thermal reactions occur *via* "aromatic" activated complexes.[2] One of the more intriguing aspects of the general problem of aromaticity is concerned with the consequences of delocalization through a "Möbius" array of orbitals.[1b,3,4] We now report the observation of a rapidly interconverting "Möbius"[1b] tautomeric pair of hydrocarbons.

When *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**1**)[5] (0.2% (v/v) in pentane) was irradiated in quartz with a low-pressure mercury lamp, a single component (**a**) was formed as the primary product. The uv spectrum of **a** showed $\lambda_{\max}^{\text{hexane}}$ 291 nm (ϵ 3480) and elemental analysis indicated a $C_{10}H_{12}$ composition.

Of particular interest is the nmr spectrum (60 MHz), which consists of two complex multiplets at τ 3.7–5.2 and 6.7–8.6 at −76°. As the temperature is raised both multiplets are broadened and portions of each move toward the center of the spectrum. The coalescence temperature (T_c) is 48 ± 2° in carbon disulfide and 50 ± 2° in carbon tetrachloride. At 76° the spectrum consists of three multiplets at τ 3.9–4.7, 5.8–6.5, and 7.5–8.4 in the ratio 6:2:4. It is important to note that only two protons undergo site exchange in this process.



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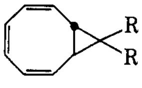
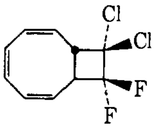
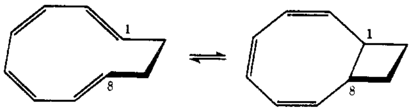


3a, R = H
b, R = CH_3

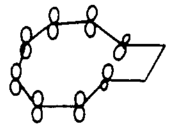


5

In view of the fact that *cis*-bicyclo[6.1.0]nona-2,4,6-triene[6] (**2a**) and its 9,9-dimethyl analog[7] **2b** and *cis*-9,9-dichloro-10,10-difluorobicyclo[6.2.0]deca-2,4,6-triene[8] (**4**) are initially converted to the corresponding trans isomers (**3a**, **3b**, and **5**) upon photolysis, we interpret the nmr temperature dependence of component **a** on the basis of a rapid and reversible valence tautomerism between the title compounds **6** and **7**. The coalesced two-proton peak at τ 6.18 in the 76° spectrum represents a weighted average of the signals for H-1 and H-8 in **6** (vinyl) and **7** (bridgehead).[9] Since the orbitals of the reacting bonds consitute a Möbius array and contain eight electrons, the activated complex **8** can be considered to be "aromatic."



6 **7**



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Strong support for the above interpretation is provided by the 220-MHz nmr spectrum[10] of **a** (in carbon disulfide) at *ca.* −25° which displays a "deceptively simple" triplet at τ 3.97 (H-4 and H-5 of **6**, line separation = 9 Hz), a complex multiplet at 4.2–4.5 (H(2)–H(7) of **7** and H-3 and H-6 of **6**), a doublet of doublets at 4.60 (H-2 and H-7 of **6**, J_{21} = 16.5 Hz, J_{23} = 8 Hz), a broadened doublet at 4.83 (H-1 and H-8 of **6**, J_{12} = 16.5 Hz), and multiplets at 7.16 (H-1 and H-8 of **7**), 7.46 (H-9 and H-10 of **6**), 7.93 (H-9 and H-10 of **6** and H-9 and H-10 of **7**), and 8.23 (H-9 and H-10 of **7**). The integrated area of each signal is consistent with the ratio of combined vinyl to combined nonvinyl protons (*vide infra*). In double resonance experiments we have shown that irradiation of the multiplet at τ 7.46 alters the signal at 4.83 and that irradiation of the latter causes collapse of the former into a broadened doublet (line separation = 7 Hz).

Chemical evidence for the above equilibrium is provided by the observation that component **a** was catalytically hydrogenated (in ethanol) to produce a mixture which contained 36% cyclodecane, 29% *cis*-cyclodecene, and 7% *trans*-bicyclo[6.2.0]decane. Each of these products was identified by comparison of its infrared spectrum with that of an authentic sample.[11] That cyclodecene and cyclodecane did not arise prin-

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(1) Reviews: (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970; (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, 8, 1 (1969); (c) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, Chapter 8.

(2) For an initial application of this idea to the Diels–Alder and related reactions see M. G. Evans, *Trans. Faraday Soc.*, **35**, 824 (1939).

(3) (a) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964); (b) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

(4) (a) J. B. Grutzner and S. Winstein, *ibid.*, **90**, 6562 (1968); (b) S. W. Staley and D. W. Reichard, *ibid.*, **91**, 3998 (1969).

(5) This was prepared in 52% yield and >99.5% purity by the dropwise addition of 0.1 mol of 1,2-dibromoethane in 20 ml of ether to the tan suspension generated by addition of 0.1 mol of freshly distilled cyclooctatetraene to 0.2 g-atom of lithium in 250 ml of liquid ammonia, followed by 4-hr stirring at *ca.* −33°, work-up, and distillation: bp 55° (4.6 mm); uv $\lambda_{\max}^{\text{hexane}}$ 250 nm (ϵ 2090); nmr (CCl_4) slightly broadened singlet at τ 4.25 (6 H, vinyl) and complex multiplets at 6.7–7.1 (2 H, bridgehead) and 7.5–8.4 (4 H, cyclobutyl).

(6) (a) E. Vogel, W. Grimme, and E. Dinnė, *Tetrahedron Lett.*, 391 (1965); (b) G. Moshuk, G. Petrowski, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 2179 (1968); (c) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

(7) S. W. Staley and T. J. Henry, unpublished results.

(8) T. Martini, Ph.D. Thesis, University of Karlsruhe, 1968 (in collaboration with G. Schröder).

(9) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, Chapter VII.

(10) We are most grateful to Dr. Lloyd Kaplan, Mr. A. Geigley, Dr. J. E. Hennessey, and Mrs. Valerie Robinson for assistance in obtaining 100- and 220-MHz nmr spectra.

(11) (a) *cis*-Cyclodecene and cyclodecane: A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Amer. Chem. Soc.*, 74, 3636 (1952). (b) Authentic *trans*-bicyclo[6.2.0]decane was prepared from *cis*-9,10-dicarbomethoxy-*trans*-bicyclo[6.2.0]decane by saponification, electrolytic decarboxylation, and catalytic hydrogenation. We thank Dr. Jordan Bloomfield for a sample of the starting material.