O_2 rather than benzvalene is reduced. The correspondence of quantum yields, intensity effects, and rates for aldehyde formation to those in the absence of O_2, however, suggests that two molecules of benzvalene are consumed in both cases. It appears that oxygen intercepts a precursor of the cyclohexadiene without diminishing the effectiveness of the chain-carrying process.

[10] Participant in the ACM Honor Semester Program, 1969.

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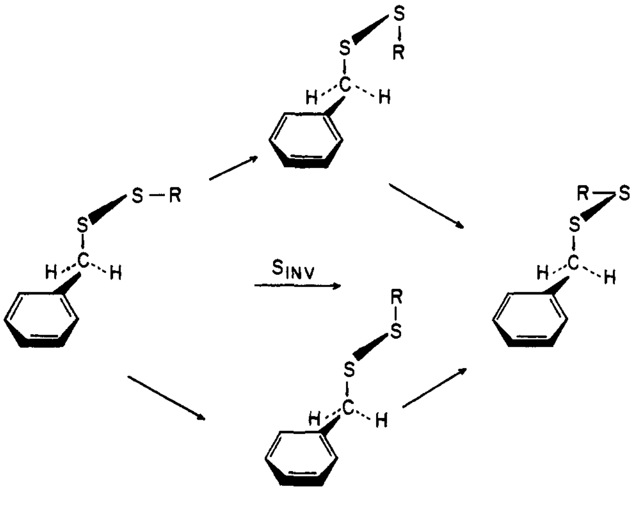
Barriers to Rotation about the Sulfur-Sulfur Bond in Acyclic Disulfides[1]

Sir:

Although the presence of a barrier to rotation about the S–S bond of a disulfide was established over 20 years ago, empirical estimates of its size have varied between 2 and 16 kcal/mol.[2] In addition, barriers to rotation in H_2S_2 have recently been calculated[3] to be 9.3 and 6.0 kcal/mol for the cis and trans transition states, each of which is produced by a 90° rotation about the S–S bond from the ground-state conformation[2a] (see Scheme I). These values agree well with the qualitative conclusions arrived at from a study of the rotational spectra of H_2S_2 and D_2S_2.[4] Of the existing data on this rotational process, the most interesting result is provided by Kessler and Rundel[2e] who found a barrier of 15.7 kcal/mol in bis(4-methyl-2,6-di-*tert*-butylphenyl)disulfide. This figure represents a minimal value for the S–S barrier since rotation about both the C–S and S–S bonds must be restricted for separation of the meta proton signals to be observed by nmr. Less hindered diaryl disulfides show hindrance to rotation about the C–S bonds only.[2e]

Scheme I



We wish to report a study of the low-temperature nmr spectra of a series of eight acyclic disulfides from which the barriers to rotation about the S–S bond can be *directly* and *unambiguously* determined. Assessment of the influence of structure on the height of the barrier in this series provides strong evidence that the cis transition state, previously assumed to be less stable,[2b,4,5] is actually of lower energy than the trans transition state.

The disulfides studied have the general structure $C_6H_5CH_2SSR$. Because of the asymmetry of a disulfide in its ground-state conformation, the methylene protons of the benzyl group are diastereotopic and may possess a nonequivalence of chemical shift when rotation about the S–S bond is slow on the nmr time scale. Scheme I shows a three-dimensional representation of the two enantiomeric forms of an alkyl benzyl disulfide and the possible pathways for their interconversion (racemization). At low temperature the 90- or 100-MHz nmr absorption of the benzylic protons appears as an AB quartet.[6,7] As the temperature is raised the strong central lines broaden and move toward each other. From the temperature at which the two lines coalesce, T_c, the rate constant for interconversion of enantiomers has been calculated using the expression[6] $k = \pi/\sqrt{2}(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{1/2}$. The rates determined by this method for the eight disulfides are presented in Table I in the form of free energies of activation. Problems of solubility and fortuitous shift equivalence required the use of several different solvents and mixed solvents for the series. As can be seen, the barriers measured for R = CCl_3 in four different solvents are constant within experimental error, which indicates the solvent effect on $\Delta G^{\ddagger}$ to be negligible. The effect of concentration on $\Delta G^{\ddagger}$ was also examined for the trichloromethyl derivative and found to be negligible in that the barrier remained at 9.4 kcal/mol for 0.03–0.4 *M* solutions of disulfide in vinyl chloride-toluene (3:1). In order to make reliable comparisons between the $\Delta G^{\ddagger}$'s in Table I, $\Delta G^{\ddagger}$ must be temperature independent, *i.e.*, $\Delta S^{\ddagger}$ must be near zero. We have therefore measured the rotation rates over the range of temperatures amenable to a complete line-shape (CLS) method of analysis[6] for three of the disulfides. The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in these cases also appear in Table I. The values of $\Delta S^{\ddagger}$ show a variation of 5 eu, which is within the limits of accuracy of the CLS method. This range of $\Delta S^{\ddagger}$ appears sufficiently small to allow a meaningful comparison of the $\Delta G^{\ddagger}$'s in Table I.

Examination of the barriers to rotation throughout the series reveals the presence of two structural effects on barrier height. With the exception of R = CCl_3 and CF_3 all compounds show an increase in $\Delta G^{\ddagger}$ as the size of R increases.[8] The additional enhancement

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[1] This work was presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Mar 28–April 2, 1971, Abstract ORGN-082.

[2] (a) O. Foss, *Advan. Inorg. Chem. Radiochem.*, **2**, 237 (1960); (b) D. W. Scott, H. L. Fink, M. E. Gross, G. B. Guthrie, and H. M. Huffman, *J. Amer. Chem. Soc.*, 72, 2424 (1950); (c) D. W. Scott, H. L. Fink, J. P. McCullough, M. E. Gross, R. E. Pennington, and G. Waddington, *ibid.*, **74**, 2478 (1952); (d) G. Claeson, G. Androes, and M. Calvin, *ibid.*, **83**, 4357 (1961); (e) H. Kessler and W. Rundel, *Chem. Ber.*, **101**, 3350 (1968).

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[5] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954).

[6] For a review of the measurement of rate processes by nmr, see G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

[7] The nature of this spectral pattern at low temperature is consistent only with a "freezing out" of the S–S rotational process. Retardation of rotation about the C–S bond would be expected to produce an AB pattern for the gauche rotamer and a singlet for the trans rotamer. The exclusive presence of this gauche rotamer is extremely unlikely.

Table I. Rotational Barriers and Spectral Data for Disulfides of Formula $C_6H_5CH_2SSR^a$

R	Solvent[b]	T_c, °C	$\Delta\nu_{AB}$,[c] Hz	J_{AB},[c] Hz	$\Delta G^{\ddagger}$,[d] kcal/mol	$\Delta H^{\ddagger}$,[d] kcal/mol	$\Delta S^{\ddagger}$,[d] eu
CCl_3	A-B	−83	16	12.2	9.4		
	C	−87	4[e]	12.1	9.2[e]		
	C-B	−80	25	12.3	9.4		
	A	−87	17	12.3	9.1		
	A-B	(by CLS)			9.4	9.1	−1.6
$C(C_6H_5)_3$	C-B	−95	19	12.0	8.8		
	C	−97	26	12.5	8.6		
	D-E	−92	40	12.5	8.7		
CF_3	A-B	−104	4.5	12.7	8.3		
C_6Cl_5	C-B	−108	30[f]	12.5	8.0		
C_6F_5	C-B	−109	40[f]	12.5	7.9		
C_6H_5	A	−115	15	12.5	7.7		
$C(CH_3)_3$	A	−113	15	12.1	7.9		
	A	(by CLS)			7.8	6.8	−6.7
$CH_2C_6H_5$	A-F[g]	−128	15[h]	13	7.2		
	A-F[g]	(by CLS)			7.0	6.6	−2.6

[a] The dibenzyl disulfide spectra were measured on a Bruker HFX-10 spectrometer. All other spectra were run on a Varian HA-100 spectrometer. The concentrations of disulfide varied between 0.05 and 0.1 *M*. The temperatures were determined immediately after each spectral measurement using a thermocouple in a dummy tube. The accuracy of the temperature obtained should be $< \pm 1°$. The disulfides were prepared by standard methods and satisfactory analyses were obtained for all the new disulfides. [b] A = vinyl chloride, B = toluene or toluene-d_8, C = CS_2, D = CF_2Br_2, E = acetone-d_6, F = $CHCl_2F$. Unless otherwise noted, all mixed solvents contained a 3:1 volume ratio of components in the order given. [c] $\Delta\nu_{AB}$ and J_{AB} represent the chemical-shift nonequivalence at T_c and the geminal coupling constant, respectively, for the benzylic protons in units of hertz. The values for $\Delta\nu_{AB}$ were obtained by extrapolation of values observed at lower temperatures to T_c. [d] The estimates of random error are as follows: $\Delta G^{\ddagger} = \pm 0.3$ kcal/mol, $\Delta H^{\ddagger} = \pm 0.7$ kcal/mol, and $\Delta S^{\ddagger} = \pm 3.5$ eu. [e] The very small nonequivalence gives $\Delta G^{\ddagger}$ a larger probable error (± 0.5 kcal/mol) in this case. [f] This value is only approximate as the solution froze at −120°. [g] This solvent was 50:50 by volume. [h] The nonequivalence observed at 90 MHz (13.6 Hz) has been adjusted to the 100-MHz scale.

of $\Delta G^{\ddagger}$ for the trifluoromethyl and trichloromethyl disulfides can be attributed to the strong inductive effects of these substituents[9] which should increase the barriers. Analogous inductive effects on barriers to rotation have been reported for sulfenamides,[10] peroxides,[11] and in diethoxy disulfide.[12] Interpretation of our results in terms of steric retardation of rotation is also supported by the results of Kessler and Rundel.[2e]

If the presence of a steric effect is acknowledged, then two conclusions may be made regarding the rotational process. First of all, the magnitude of the barrier in the absence of a steric effect will be 7.0 kcal or less for acyclic disulfides. Furthermore, in order for steric retardation to be present, rotation most likely occurs *via* the cis transition state since the trans pathway would be expected to show steric acceleration.[13] The preference for rotation *via* the cis transition state would appear to be very large in view of the magnitude of the barrier found in bis(4-methyl-2,6-di-*tert*-butylphenyl) disulfide.

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(8) It should be recognized that no parameters exist for estimating the bulk of R in this particular situation. Nevertheless, the order of decreasing size will likely be $(C_6H_5)_3C > CCl_3 > C(CH_3)_3 > C_6Cl_5 > C_6F_5 > C_6H_5 > C_6H_5CH_2 > CF_3$ as estimated from the available E_s values reported by R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 598.

(9) In comparison with the inductive effects of the CF_3 and CCl_3 groups it is apparent that the smaller inductive effects of C_6F_5 and C_6Cl_5 do not increase $\Delta G^{\ddagger}$ relative to C_6H_5.

(10) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969).

(11) R. N. Jackson, *J. Chem. Soc.*, 4585 (1962).

(12) F. Seel, W. Gombler, and R. Budenz, *Justus Liebigs Ann. Chem.*, **735**, 1 (1970).

(13) As pointed out by a referee, this argument neglects consideration of a destabilizing steric effect on the trans transition state. An examination of Courtauld models indicates this effect to be smaller than the steric effect in the ground state. An alternate pathway involving inversion at sulfur was rejected by Kessler and Rundel[2e] on the basis of their earlier observations (H. Kessler, A. Riecker, and W. Rundel, *Chem. Commun.*, 475 (1968)) that this barrier is greater than 15 kcal/mol in diaryl sulfides. For the same reason a rotation–inversion pathway similar to that described for the inversion of sterically hindered amines (C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 542 (1971)) appears improbable.

Dibenzo[*cd,gh*]pentaleno-4,8-quinone and Its Semiquinone Radical Anion. Model Planar [12]Annulene Derivatives

Sir:

Dibenzo[*cd,gh*]pentaleno-4,8-quinone (I) is the first neutral, fully unsaturated derivative of the theoretically important dibenzo[*cd,gh*]pentalene (II).[1] Considerable interest in such species derives from calculations and previous investigations[1,2] which indicate that II and dibenzopentalenosemiquinone radical anion III should be excellent examples of derivatives of planar perturbed [12]annulenes. Thus, III should shed insight into the question of whether electronic destabilization (antiaromaticity) is associated with a planar monocyclic array of 12 electrons. Furthermore, the

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(1) (a) For the structure of dihydrodibenzopentalene see B. M. Trost, P. L. Kinson, C. A. Maier, and I. C. Paul, *J. Amer. Chem. Soc.*, in press. (b) For the synthesis and properties of dilithium dibenzopentalenide see B. M. Trost and P. L. Kinson, *ibid.*, **92**, 2591 (1970). (c) For the dibenzopentalenyl radical cation and dication see P. Kinson and B. M. Trost, *Tetrahedron Lett.*, 1075 (1969).

(2) B. M. Trost, G. M. Bright, C. Freihart, and D. Brittelli, *J. Amer. Chem. Soc.*, **93**, 737 (1971).