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 <±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.

Acknowledgments. The authors thank the National Research Council of Canada for generous financial support and receipt of a Postdoctoral Fellowship by one of us (J. K. S.). The authors are also grateful to the National Science Foundation for financial support and for a traineeship for C. E. M.

Robert R. Fraser,* Guy Boussard, John K. Saunders
Department of Chemistry, University of Ottawa
Ottawa, Canada

Joseph B. Lambert, Craig E. Mixan
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received April 19, 1971

(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

(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).

Table I. Results of Hückel and McLachlan Calculations for the Dibenzopentalenosemiquinone Radical Anion

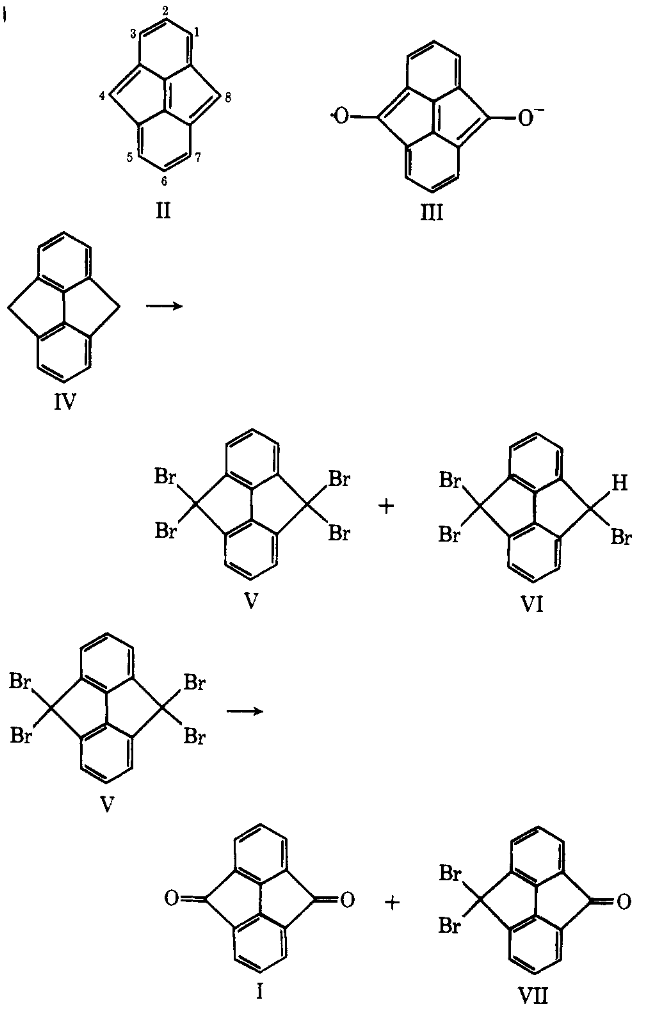
			Spin density[b]			Hückel energy	
h	k	k_α[a]	ρ_1	ρ_4	ρ_0	E_9	E_{10}
1.0	0.9	1.0	0.2067	0.1728	0.0578	−0.0542	0.2152
0.8	0.8	1.0	0.2024	0.1706	0.0667	−0.0538	0.2059
0.8	1.6	1.0	0.1796	0.0766	0.1107	−0.3222	0.5192
1.2	1.6	1.0	0.1936	0.1063	0.0836	−0.2291	0.4453
1.6	1.6	1.0	0.2043	0.1296	0.0630	0.1480	0.3852
1.6	0.8	1.0	0.2218	0.2012	0.0210	−0.2226	0.1226
1.0	1.0	1.0	0.2030	0.1611	0.0681	0.0000	0.2541
1.0	1.0	0.8	0.1693	0.2093	0.0835	0.1126	0.3143
1.6	1.2	0.8	0.1791	0.2226	0.0579	0.0930	0.3115
Experimental			0.1780		0.0791		

[a] k_α is the k for the bonds α to the carbonyls. [b] Negative spin densities are predicted for all other atoms.

extent of the perturbation from the planar [12]annulene may be estimated by comparison to the corresponding pyracylene series.[2]

Scheme I shows the preparation of dibenzopentalenoquinone from 4,8-dihydrodibenzo[*cd,gh*]pentalene (IV), whose synthesis and properties we have previously described.[1] Treatment of a carbon tetrachloride solution of dihydrodibenzopentalene with 4.2 mol equiv of molecular bromine, while irradiating the solution with a tungsten lamp, afforded a 53% yield of 4,4,8,8-tetrabromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (V),[3] mp 258° dec, and a 25% yield of 4,4,8-tribromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (VI), mp 148–155°. The materials were separated by multiple elution preparative thick-layer chromatography (silica gel, PF-254 Skelly B (hexanes)). Treatment of tetrabromodihydrodibenzopentalene with a 20-fold excess of silver acetate in acetic acid for 93 hr at room temperature in the dark, followed by aqueous hydrochloric acid hydrolysis for 23 hr at room temperature, affords a 37% yield of dibenzo[*cd,gh*]pentaleno-4,8-quinone (I), mp 254–258°, and a 30% yield of 4-keto-8,8-dibromo-4,8-dihydrodibenzo[*cd,gh*]pentalene (VII), mp 163–168°. The materials were separated by multiple elution preparative thick-layer chromatography (unactivated silica gel G, 6% dichloromethane–pentane). Dibenzopentalenoquinone shows infrared absorption bands at 1751 and 1709 cm^{-1} (intensity ratio 1.75:1). Its protons appear in the nmr as an A_2B pattern (δ 7.47, 7.20, J_{ab} = 7.3 Hz). Its mass spectrum shows the molecular ion and base peak at *m/e* 206, and peaks for successive loss of CO at *m/e* 178 (16) and 150 (84) to afford the biphenylene radical cation. Ultraviolet maxima (nm (log ϵ)) appear at 254 sh (4.10), 261 (4.23), 268 (4.23), 278 sh (3.85), 312 sh (3.10), and 357 (2.95). The absence of ring cleavage concomitant with hydrolysis is truly remarkable considering the tremendous strain of the hydrocarbon framework.[1a]

Scheme I. Preparation of Dibenzopentalenoquinone



Electrolytic reduction of a deaerated solution of 4,8-dibenzopentalenoquinone (5.34 × $10^{-4}M$) in DMSO[4] containing 0.100 *M* tetra-*n*-butylammonium perchlorate as a supporting electrolyte generated two polarographic waves. The first is a reversible one-electron wave at −0.895 V *vs.* sce and the second irreversible at −1.630 *V vs.* sce. Controlled potential reduction in an esr cavity demonstrated the species formed at potentials corresponding to the first wave to be the desired radical anion III. The esr spectrum of III exhibits splitting constants of 4.540 (4 H) and 0.918 G (2 H). Reference to the McConnell relationship with Q = 25.5 ± 1.5 G/e indicates that the spin density on C_1 is 0.178 ± 0.010 and that the spin density on C_2 is 0.036 ± 0.002. These results are in agreement with the predictions of Hückel and McLachlan calculations[5] for the system.

Table I shows the results of the Hückel and McLachlan calculations for a number of values of h and k. A modification wherein the bonds α to the carbonyl are

---

[3] All new compounds have been fully characterized.

[4] Freshly distilled at reduced pressure from calcium hydride.

[5] Examination of Hückel and McLachlan calculations indicates that the odd electron in the radical anion is in the orbital designated ψ_{10} in the Hückel calculations (as opposed to ψ_9). ψ_{10} stays higher in energy than ψ_9 in spite of large variations in h and k. In cognizance of this fact, the odd electron was "placed" in ψ_{10} for the McLachlan calculations.

assigned a lower value of k (0.8) to take into account the unusual length of these bonds[6] is seen to improve the agreement between the calculations and experiment. It is important to note that the spin density of 0.178 on C_1 indicates that 70% of the total odd electron density resides at these four positions.[7]

Further information concerning the spin distribution of the odd electron in III can be obtained from the g factor. Semiquinone radical anions containing no halogen usually have g factors in the narrow range 2.0044 ± 0.0004, while hydrocarbon radical anions have g values in the range 2.0026 ± 0.0001.[8,9] The g factor of dibenzopentalenosemiquinone radical anion (2.0035) is unusually low, suggesting that the spin density on the oxygen atoms is unusually low. Reference to the previously derived relationship among half-wave potential, g factor, and oxygen spin density[10] suggests each oxygen atom in dibenzopentalenosemiquinone radical anion bears a spin density of only 0.0791, in good agreement with McLachlan calculations. Calculations indicate that the remaining 14% of the odd electron density should mainly be distributed between the two carbonyl carbons. Thus, little, if any, excess spin density may reside on the vinyl cross-link. These results strongly support the view that dibenzopentalenosemiquinone radical anion closely resembles a [12]-annulene semiquinone radical anion.[11]

The polarographic characteristics of the quinone and the esr spectral properties of the semiquinone anion radical support the description of this perturbed planar [12]annulene as an antiaromatic. Thus, the unusually high spin density in the hydrocarbon framework suggests a strong electronic demand by the [12]annulene system. Furthermore, the substantially more negative reduction potential compared to pyracyloquinone and anthraquinone reflects a thermodynamic instability in the dibenzopentalene system compared to the pyracylene or anthracene system. The magnitude of the differences (0.157 and 0.111, respectively) provides support for the contention that electronic destabilization accompanies a planar [12]annulene.

Acknowledgment. We wish to express our appreciation to the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of our program.

---

(6) The corresponding bonds in dihydrodibenzopentalene are found to be exceptionally long.[1a] This large deviation from normal bond lengths is associated with the high degree of stain in the molecule. Dibenzopentalenoquinone should be even more highly strained as a result of the sp^2–sp^2 hybridization of the bonds α to the carbonyl *vs.* sp^2–sp^3 hybridization of the corresponding bonds in dihydrodibenzopentalene.

(7) Calculations indicate that the spin density at C_2 is negative.

(8) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(9) A. J. Stone, *Mol. Phys.*, 3, 233 (1960).

(10) S. F. Nelsen, B. M. Trost, and D. H. Evans, *J. Amer. Chem. Soc.*, **89**, 3034 (1967).

(11) For the semiquinone anion of 1,7-[12]annulenoquinone, the spin density corresponding to C_1 of I and oxygen is 0.137 and 0.083, respectively.

(12) National Institutes of Health Predoctoral Fellow, 1968–1970.

(13) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Recipient.

Philip S. Kinson,[12] Barry M. Trost*[13]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received April 12, 1971

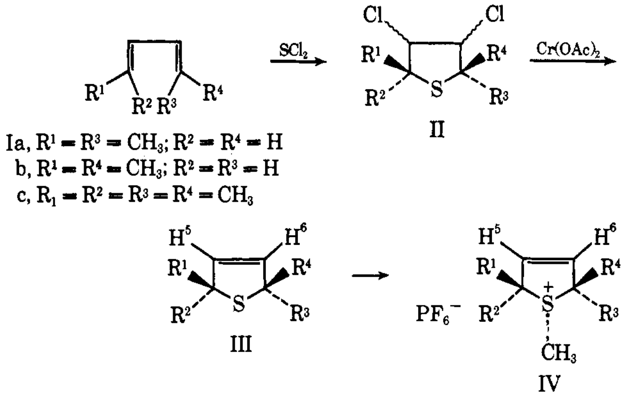
Stereochemistry of *n*-Butyllithium-Induced Fragmentation of Dihydrothiophenium Hexafluorophosphates. A Novel Sulfurane Reaction

Sir:

The question of sulfurane intermediates has led us to explore the reactions of cyclic sulfur compounds with organolithiums.[1] In this communication, we wish to report that the stereochemistry of organolithium-induced fragmentations of dihydrothiophenium salts provides strong evidence for the existence of such species.[2]

Dihydrothiophenes are generated by the two-step procedure outlined in Scheme I. Admixture of dilute hexane solutions of a diene (Ia,b,c) with sulfur dichloride generates an isomeric mixture of dichlorides II.[3] The crude dichlorides are directly reduced with the ethylenediamine complex of chromous acetate[4] to produce the desired dihydrothiophenes. Starting from *cis,trans*-2,4-hexadiene (Ia), a 9:1 mixture of *trans*-(IIIa) and *cis*-2,5-dimethyl-2,5-dihydrothiophenes (IIIb) was obtained. Alternatively, the *trans,trans*-2,4-hexadiene (Ib) produced a 3:2 mixture of the dihydrothiophenes IIIa and IIIb.[5] The overall yield for the two-step process is 12–13%. Utilizing 2,5-dimethyl-2,4-hexadiene (Ic) this sequence generated 2,2,5,5-tetramethyl-2,5-dihydrothiophene (IIIc) in 8% yield.

Scheme I. Preparation of Dihydrothiophenes and Their Salts



Alkylation of each pure dihydrothiophene with trimethyloxonium tetrafluoroborate in methylene chloride at −40° produced the corresponding sulfonium salt in 90% yields. Due to the hygroscopicity of the fluoroborates, metathesis to the hexafluorophosphate was performed.[6,7] The structures of the sulfonium salts were fully confirmed by their nmr spectral data (see Table I) which also provided the stereochemical assign-

---

(1) (a) B. M. Trost, W. L. Schinski, I. B. Mantz, and F. Chen, *J. Amer. Chem. Soc.*, **93**, 680 (1971), and references therein; (b) B. M. Trost, W. L. Schinski, and I. B. Mantz, *ibid.*, 91, 4320 (1969); (c) B. M. Trost and S. D. Ziman, *Chem. Commun.*, 181 (1969).

(2) For a related case see J. Bornstein, J. E. Shields, and J. H. Supple, *J. Org. Chem.*, 32, 1499 (1967).

(3) H. J. Baker and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 154, 52 (1935); F. Lautenschlaeger, *J. Org. Chem.*, 31, 1669 (1966).

(4) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

(5) In the analogous reaction, methyl phosphorous dichloride has been shown to add stereospecifically to the *trans,trans*-2,4-hexadiene: A. Bond, M. Green, and S. C. Pearson, *J. Chem. Soc. B*, 929 (1968).

(6) G. C. Brumlik, A. I. Kosak, and R. Pitcher, *J. Amer. Chem. Soc.*, 85, 5360 (1964).

(7) All new compounds gave satisfactory elemental analyses and were further characterized by infrared and nmr spectroscopy. Spectral data were consistent with the structure.