

STABLE ROTAMERS ABOUT A SULFUR-TO-CARBON SINGLE BOND
 IN 1,4-DIMETHOXY-9-BENZYL SULFONYL TRIPYCENE:
 THEIR ISOLATION AND CHARACTERIZATION¹⁾

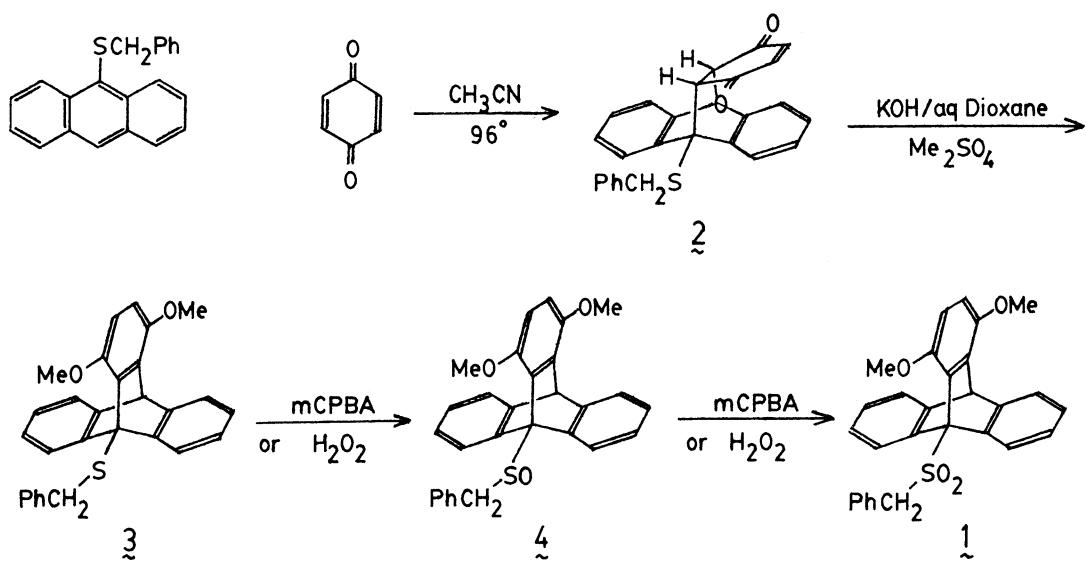
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Oxidation of 1,4-dimethoxy-9-benzylthiotriptycene with mCPBA or hydrogen peroxide to the corresponding sulfone and subsequent chromatography on silica gel yielded two stable rotamers about the S-C(9) single bond. Kinetic parameters for their interconversion as well as their spectroscopic data have been also presented.

Triptycene derivatives with a substituent in a bridgehead position have provided a number of stable rotamers about carbon-to-carbon, nitrogen-to-carbon, and silicon-to-carbon single bonds.²⁾ In a continuation to our previous reports on the stable conformers about heteroatom-to-carbon single bonds, we have further investigated the atropisomerism involving a sulfur-to-carbon single bond, whose length ranges between 1.76 Å and 1.82 Å depending on the oxidation states of the sulfur atom.³⁾ We now report the first isolation and characterization of stable rotational isomers about the single bond connecting the sulfonyl sulfur atom and the tetrahedral bridgehead carbon atom in 1,4-dimethoxy-9-benzylsulfonyl triptycene (1).

Preparation of the sulfone 1 was accomplished according to the following route (Scheme 1).⁴⁾

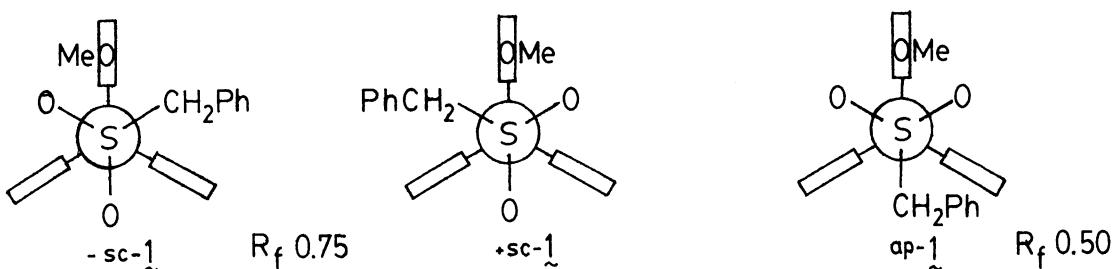


Scheme 1.

On heating a mixture of 9-benzylthioanthracene (1.4 g) and p-benzoquinone (1.5 g) in acetonitrile (5.0 ml) in a sealed tube at 96 °C for 44 h, the Diels-Alder adduct χ , 9-benzylthio-9,10-dihydro-9,10-[4',5'](3',6'-dioxocyclohexeno)anthracene,⁵⁾ was obtained quantitatively based on the consumed starting sulfide. Base-catalyzed enolization of χ (820 mg) followed by methylation in situ with dimethyl sulfate (5 ml) in aqueous dioxane [dioxane (26 ml) and 1 mol·l⁻¹ aq KOH solution (150 ml)] yielded 1,4-dimethoxy-9-benzylthioptrycene (λ)⁶⁾ in 84% yield after chromatography on silica gel.

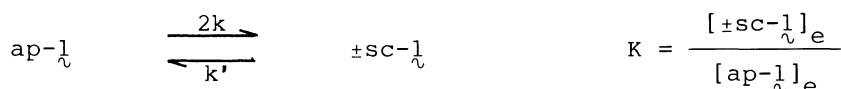
Oxidation of the 9-triptycyl sulfide λ into the desired 9-triptycyl sulfone λ was performed quantitatively either with 30% hydrogen peroxide in acetic acid or with m-chloroperoxybenzoic acid in dichloromethane or in acetic acid. The sulfone λ was obtained directly from λ with two or more equivalents of the oxidants, or stepwise via the corresponding sulfoxide, 1,4-dimethoxy-9-benzylsulfinyltriptycene (λ),⁷⁾ with just one equivalent each of the oxidant in these oxidation reactions ($\lambda \rightarrow \lambda$, $\lambda \rightarrow \lambda$). Inspection of the oxidation products by ¹H NMR revealed the sulfone λ to be a mixture of two isomeric conformers, the ratios of which were dependent on the oxidation reaction conditions, especially on the reaction solvents and the reaction temperatures employed.⁸⁾

Separation of the rotamers in question, \pm sc- λ and ap- λ , was achieved quite easily by column chromatography on silica gel or much more effectively by preparative TLC (Merck, #5717, CH₂Cl₂ as a developing solvent), as the R_f -value difference between these two conformers was unexpectedly large, the R_f -value for \pm sc- λ being 0.75 and that for ap- λ 0.50. Straightforward assignment of these rotamers as above is accessible by comparison of these NMR spectra as shown in the following Newman projections along the S-C(9) axis: The one isomer with a larger R_f -value shows an AB pattern spectrum (centered at δ 5.41, $\Delta\nu$ = 56 Hz, J = 14.4 Hz) for the benzylic protons, while the other isomer coming out later shows a singlet spectrum



(δ 4.82) for the benzylic protons. It is interesting to note that the chromatographic behaviors of these two conformers are strongly affected by the relative arrangement of the three proximate oxygen atoms within the molecules. The characteristic NMR data of the triptycenes in Scheme 1 are shown in Table 1.

The stable rotamers, both \pm sc- λ and ap- λ , were subjected to thermal equilibration experiments. Starting from the pure conformers, the interconversion of



ap- λ and \pm sc- λ in dimethyl sulfoxide-d₆ was studied at 101.0, 126.7, and 139.0 °C

and monitored by integration of the methoxyl signals and by that of the benzylic proton signals in the ^1H NMR spectrum.⁹⁾ The results are summarized in Table 2.¹⁰⁾

Table 1. Characteristic ^1H NMR Data of the Triptycenes (3 , 4 , and 1)^{a)}

CH ₂			--- OCH ₃ ---			10-H	2-H, 3-H	8-H	13-H
H _A	H _B	J _{AB}							
3	3.93	-	3.72	3.75	5.85	6.43(s) ^{b)}	8.03	8.03	
$\text{4a}^{\text{c)}$	4.72	5.22	13.5	3.38	3.82	5.83	6.55(q) ^{b)}	8.03	8.68
$\text{4b}^{\text{c)}$	4.65	4.94	13.5	3.72	3.84	5.83	6.53(q)	8.03	8.88
$\pm\text{sc-1}$	5.10	5.72	14.4		3.85	5.90	6.72(s)	8.17	8.40
ap- 1	4.82	-		3.80		5.89	6.59(s)	8.41	8.41

a) ^1H NMR spectra were recorded on a Varian EM-390 (90 MHz) with CDCl_3 solutions. The chemical shifts are expressed in δ unit, and the coupling constants (J's) in Hz. b) "s" and "q" denote singlet and quartet, respectively. c) 4a is a major isomer and 4b is a minor one.¹¹⁾ The 2-H and 3-H protons of the both isomers exhibit AB quartets centered at δ 6.55 ($\Delta\nu$ = 13.0 Hz, J = 9.0 Hz) and δ 6.53 ($\Delta\nu$ = 9.8 Hz, J = 9.0 Hz), respectively.

Table 2. Kinetic Parameters for the Interconversion of $\pm\text{sc-1}$ and ap- 1 in Dimethyl Sulfoxide-d₆

Tem- perature °C	K ($\pm\text{sc}/\text{ap}$)	$k \times 10^6$	$k' \times 10^6$	$\Delta G^\ddagger / \text{kcal} \cdot \text{mol}^{-1}$	
		s^{-1}	s^{-1}	$\text{ap} \rightarrow \pm\text{sc}$	$\pm\text{sc} \rightarrow \text{ap}$
101.0	2.54	1.40	1.09	32.0	32.2
126.7	2.74	20.0	14.5	32.1	32.8
139.0	3.04	67.2	44.1	32.1	32.5

The equilibrium constant, K ($\pm\text{sc-1}/\text{ap-1}$) = 2.74 at 126.7 °C, is larger than a statistical ratio, suggesting that the ground state of the $\pm\text{sc}$ -isomer is favored over that of the ap-isomer by ca. 0.8 $\text{kcal} \cdot \text{mol}^{-1}$ in dimethyl sulfoxide-d₆ at 126.7 °C. The rotational barrier (ΔG^\ddagger) of ca. 32 $\text{kcal} \cdot \text{mol}^{-1}$ is somewhat higher than expected, if the longer S-C bond length (ca. 1.77 Å) than the normal C-C bond (1.54 Å) is taken into account. When the Newman projections presented above are inspected, it becomes evident that, in the transition state of these conformational changes, one of the two sulfonyl oxygen atoms eclipses the peri-methoxyl group, and that the other oxygen atom and the benzyl group also eclipse the two peri-hydrogen atoms on the triptycene skeleton. Since the rotational transition state either from $\pm\text{sc-1}$ to ap- 1 or that from ap- 1 to $\pm\text{sc-1}$ is the same, the difference of the rotational barriers between the forward and the backward processes may be reflected by the ground state stabilities of these two rotamers. One possible explanation for this trend may be deduced from the molecular model examination. If the group dipole directions of the methoxyl and the sulfonyl moieties were considered with the model, the $\pm\text{sc}$ -conformer would be apparently more polar than the ap-conformer and hence the former would be much better solvated in dimethyl sulfoxide-d₆ than the latter. This would be one of the reasons why the

\pm sc-isomer was more stabilized in this solvent.

References

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- 3) G. Valle, V. Bussetti, M. Mammi, and G. Carazzolo, *Acta Crystallogr., Sect. B*, 25, 1432 (1969); D. E. Sands, *Z. Krist.*, 119, 245 (1963); S. C. Abrahams, *Acta Crystallogr.*, 10, 417 (1957).
- 4) New compounds in the present communication gave satisfactory elemental analyses and spectroscopic data. Mp's are uncorrected.
- 5) χ : Mp 155-157 °C (decomp); ^1H NMR (CDCl_3 , δ) AB centered at 3.20 ($\Delta\nu = 6$ Hz, $J = 8.5$ Hz, 4',5'-H's), AB centered at 4.24 ($\Delta\nu = 40.5$ Hz, $J = 12.0$ Hz, CH_2), 4.70 (1H, brs, 10-H), AB centered at 6.08 ($\Delta\nu = 16.0$ Hz, $J = 10.5$ Hz, 1',2'-H's), 7.03-7.73 (12H, m, aromatic H's), 7.98 (1H, m, 4- or 5-H); ^{13}C NMR (CDCl_3 , δ) 34.34 (benzylic C), 49.73 (10-C), 51.42, 52.85 (4',5'-C's), 58.95 (9-C), 123.88, 124.08, 124.33, 124.72, 126.74, 127.00, 127.26, 128.69, 129.14 (aromatic C's with H), 136.41, 136.80, 138.69, 139.27, 141.35 (aromatic ipso-C's), 138.43, 141.35 (olefinic C's), 195.57 (3'-C), 197.90 (6'-C).
- 6) χ : Mp 234-235 °C; ^{13}C NMR (CDCl_3 , δ) 36.64 (benzylic C), 46.91 (10-C), 56.24, 58.03 (OMe's), 63.75 (9-C), 109.81, 112.53 (2',3'-C's), 123.73, 124.94, 125.55, 126.97, 128.56, 128.92 (aromatic C's with H), 134.56, 137.36, 138.41, 144.58, 145.32, 148.80, 149.62 (aromatic ipso-C's).
- 7) Major isomer χ_a : ^{13}C NMR (CDCl_3 , δ) 47.31 (10-C), 56.44, 57.98 (OMe's), 58.31 (benzylic C), 71.99 (9-C), 110.94, 112.33 (2,3-C's), 122.99, 123.85, 124.45, 124.70, 125.06, 125.19, 126.00, 127.79, 128.68, 129.69 (aromatic C's with H), 132.49, 134.68, 137.08, 140.73, 144.14, 145.64, 146.94, 147.95, 149.45 (aromatic ipso-C's). For minor isomer χ_b , only ^1H NMR spectrum could be taken.
- 8) Oxidation of the sulfide χ with mCPBA in dichloromethane gave the \pm sc to ap ratios ranging from 0.17 to 0.25 within the temperature range from 20 to 45 °C, the ap-isomer favorably formed. On the other hand, oxidation of χ with mCPBA in acetic acid resulted in formation of both isomers in the ratio of 0.53-0.83 at temperatures 20-80 °C. These facts imply that the methoxyl group in the peri-position may play an important role in the peroxy-acid oxidation reaction of the present sulfide. \pm sc- χ : mp 282 °C (decomp); IR (Nujol) 1300, 1140 cm^{-1} . ap- χ : mp 284-285 °C (decomp); IR (Nujol) 1330, 1310, 1140 cm^{-1} .
- 9) In DMSO-d_6 solvent, \pm sc- χ shows its methoxyl signals at 3.81 and 3.84, and its benzylic protons at 5.20 and 5.31 (AB quartet, $J = 14.0$ Hz). In the same solvent, ap- χ shows its methoxyl signals at 3.60 and 3.77 and its benzylic protons at 4.86 (singlet).
- 10) Poor solubilities of the sulfone χ in other solvents of high boiling points have only allowed the kinetic experiments in DMSO-d_6 .
- 11) χ_a and χ_b could not be separated by chromatographic techniques. The ratio of χ_a to χ_b was about 10:1 as determined by 400 MHz NMR spectra, and the ratio did not change on heating.

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