

In conclusion, "mirror-image catalysis" provides a method for deducing the absolute stereochemical course of the GX I reaction. The establishment of a single stereochemical outcome at both carbon positions strongly suggests that the recently observed nonstereospecific thiohemiacetal utilization¹² by GX I is not a property of the initial proton abstraction but is most likely due to an enzyme-catalyzed epimerization of the wrong isomer by an addition-elimination mechanism prior to abstraction. Finally, the results highlight the utility of high-field NMR in distinguishing marginally nonequivalent protons.

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(12) Griffis, C. E. F.; Ong, L. H.; Buettner, L.; Creighton, D. J. *Biochemistry* 1983, 22, 2945.

Synthesis and Characterization of [7]Circulene¹

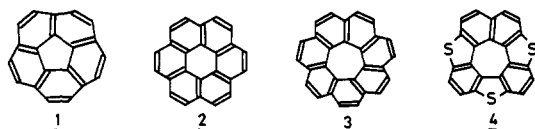
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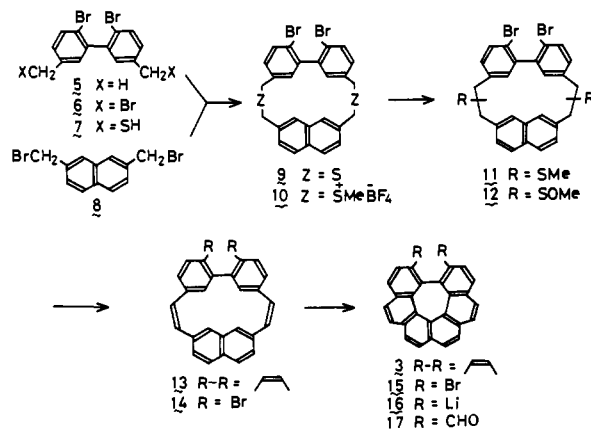
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Lawton's papers describing his elegant synthetic approach² to the bowl-shaped³ [5]circulene (1) ("corannulene", the next lower



homologue of [6]circulene (coronene) (2) have provoked considerable interest in the preparation of [7]circulene (3), the next higher homologue of [6]circulene.⁴

In this communication, we report our successful synthesis of [7]circulene (3) and an X-ray analysis, which has revealed its



(1) Presented in part at the 47th Annual Meeting of the Chemical Society of Japan, April 1983, Kyoto.

(2) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* 1966, 88, 380-381.

(3) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* 1971, 93, 1730-1745.

(4) A heterocyclic [7]circulene analogue 4 incorporating three thiophene rings has been reported: Dopfer, J. H.; Wynberg, H. *Tetrahedron Lett.* 1979, 763-766; *J. Org. Chem.* 1975, 40, 1957-1966.

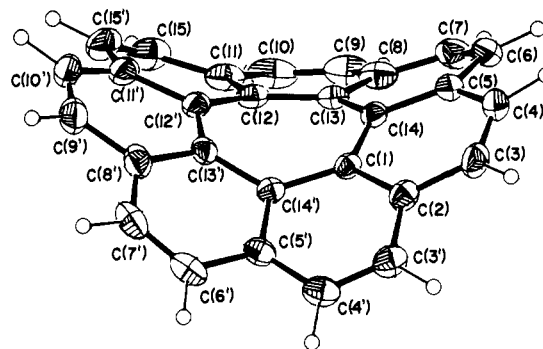


Figure 1. Molecular structure of 3. Non-hydrogen atoms are drawn by the thermal ellipsoids at the 30% probability level. Hydrogen atoms are shown by the spheres corresponding to the artificial isotropic temperature factor of 1.0 Å⁻².

saddle-shaped structure as expected from the examination of the molecular model.

We reasoned that Reiss's attempted photocyclization⁵ of the cyclophane intermediate 13 directly into 3 failed because of the inherent rigid structure of 13, incorporating both naphthalene and phenanthrene moieties. We directed our efforts to a two-stage synthetic approach that involves (1) photocyclization of the more flexible biphenylnaphthalene cyclophane 14 to the 1,16-dehydrohexahelicene 15 and (2) modification of the side chains to secure the missing benzene ring to complete the synthesis.

N-Bromosuccinimide bromination of 2,2'-dibromo-5,5'-dimethylbiphenyl (5)⁶ afforded the bis(bromomethyl) derivative 6, which was converted into the bis(mercaptomethyl)biphenyl 7 by routine procedures. The coupling of 7 and 2,7-bis(bromomethyl)naphthalene (8) was carried out in dimethylformamide with cesium carbonate⁸ to give the dithiacyclophane 9,⁹ mp 173-174 °C (56% yield). Reaction of 9 with dimethoxycarbonium fluoroborate in dichloromethane yielded the disulfonium salt 10 whose Stevens rearrangement mediated by sodium hydride provided a 67% yield of the bis(sulfide) 11, an oil. Oxidation of 11 with *m*-chloroperbenzoic acid gave the bis(sulfoxide) 12 whose pyrolysis at 300 °C (0.001 mm) produced the unsaturated cyclophane 14, pale orange needles, mp 213-215 °C (63% yield from 11). A cyclohexane solution of 14 containing a trace amount of iodine was irradiated with a high-pressure mercury lamp¹⁰ for 1 h to afford 1,16-dehydro-2,15-dibromohexahelicene (15):¹¹ mp 299-301 °C (47% yield); mass spectrum, *m/e* 484, M⁺; ¹H NMR (CDCl₃) δ 7.82-8.66 (multiplet); UV (cyclohexane) λ_{max} (log ε), 245 (4.80), 270 (sh, 4.72), 277 (4.73), 312 (4.48), 326 (4.40). Lithiation of the dibromide 15 with *n*-BuLi in tetrahydrofuran and formylation of the resulting dilithio derivative 16 with dimethylformamide gave the dialdehyde 17: pale yellow prisms, mp 303-305 °C (54% yield); mass spectrum, *m/e* 382, M⁺; ¹H NMR (CDCl₃) δ 2.02 (s, 2 H), 7.78-8.45 (m, 12 H). Intramolecular reductive coupling¹³ of the dialdehyde 17 with LiAlH₄ and titanium trichloride in dimethoxyethane completed the outer perimeter of [7]circulene (3): yellow plates, mp 295-296 °C (35% yield); mass spectrum, *m/e* 350 M⁺; ¹H NMR is characteristic in its single sharp peak at δ 7.45, and the ¹³C NMR exhibiting

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(6) 2,2'-Dibromo-5,5'-dimethylbiphenyl (5), mp 109-110 °C, was prepared from 5,5'-dimethyl-2,2'-dinitrobiphenyl¹ via 2,2'-diamino-5,5'-dimethylbiphenyl.

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(9) Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

(10) Halos, EH-300, Eikosha Co., Osaka, Japan.

(11) Optical resolution of the dibromide 15 by means of HPLC employing (+)-poly(triphenylmethyl methacrylate)¹² gave (-)-15, [α]_D²⁵ -505° (c 1.36 × 10⁻³, MeOH).

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three peaks at δ 136.0, 132.1, and 127.5 corresponds to the molecular symmetry; UV(cyclohexane) λ_{\max} (log ϵ) 236 (sh, 4.44), 266 (sh, 4.86), 275 (5.14), 296 (4.46), 331 (3.91), 388 (sh, 290), 403 (2.83).

The molecular structure of **3** has been determined by X-ray crystallography,¹⁴ and Figure 1 is an ORTEP drawing¹⁷ of **3**. The crystallographic 2-fold axis coincident with the C(1)–C(2) bond passes through the midpoints of C(12)–C(12') and C(15)–C(15') bonds, and this makes only half of the molecule independent. The central 7-membered ring assumes a boat conformation, and the whole molecular shape closely approximates a saddle form. The C–C bonds can be classified into four groups: (1) the central core bonds (e.g., C(1)–C(14)) with bond distances of 1.447–1.466 Å, av 1.457 Å, (2) the spoke bonds (e.g., C(1)–C(2)) with bond distances of 1.433–1.435 Å, av 1.434 Å, (3) the next outer bonds (e.g., C(2)–C(3)) with bond distances of 1.407–1.423 Å, av 1.414 Å and (4) the outermost bonds (e.g., C(3)–C(4)) with bond distances of 1.327–1.344 Å, av 1.338 Å. The average esd for each C–C bond is 0.005 Å.

Registry No. **3**, 76276-09-0; **5**, 13688-64-7; **6**, 87586-74-1; **7**, 87586-75-2; **8**, 38309-89-6; **9**, 87586-76-3; **10**, 87586-78-5; **11**, 87597-03-3; **12**, 87597-04-4; **14**, 87586-79-6; **15**, 87586-80-9; **16**, 87586-81-0; **17**, 87586-82-1; dimethoxycarbonium fluoroborate, 18346-68-4.

Supplementary Material Available: Table SI of fractional atomic coordinates of [7]circulene (**1** page). Ordering information is given on any current masthead page.

(14) Crystal data of **3**: C₂₈H₁₄, *M*, 350.4, monoclinic, space group *C2/c*, *a* = 13.106 (2) Å, *b* = 11.664 (2) Å, *c* = 11.015 (3) Å, β = 95.67 (1)°, *U* = 1675.5 (5) Å³, *Z* = 4, *D_x* = 1.390 g cm⁻³. Diffraction intensities were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo K α radiation. A total of 2449 reflections was collected up to 2θ = 60°, among which 1535 were nonzero reflections. The structure was solved by the direct method (MULTAN-78)¹⁵ and refined by the block-diagonal least squares (HBLV-16) to the *R* index of 0.094 for nonzero reflections (non-hydrogen atoms anisotropically, hydrogen atoms isotropically).

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(16) Ashida, T. "HBLV-16: The Universal Crystallographic Computing System-Osaka"; The Computer Center, Osaka University, 1979.

(17) Johnson, C. K. "ORTEP-II"; Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

A Stable Sulfenic Acid, 9-Triptycenesulfenic Acid: Its Isolation and Characterization¹

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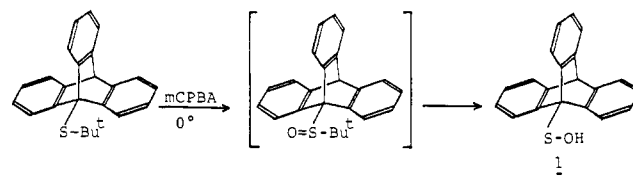
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Although sulfenic acids are well recognized as important intermediates in organosulfur chemistry,² their high reactivity and the difficulty in generating them under mild conditions have precluded their isolation. Gas-phase conditions were sometimes employed for isolation and study of unstabilized sulfenic acid of short lifetimes.^{2b} A few special examples known hitherto have been stabilized by their electronic properties and hydrogen

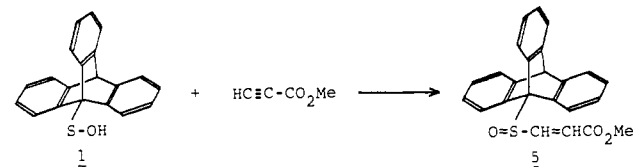
(1) Chemical Abstracts numbering for triptycene (9,10-dihydro-9,10-[1',2']benzenoanthracene) is adopted in this paper. (a) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1438. (b) Kawada, Y.; Iwamura, H. *Ibid.* **1983**, *105*, 1449.

(2) (a) Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467 and references cited therein. (b) One of referees kindly notified us that methanesulfenic acid had been generated in gas phase and studied by means of microwave spectroscopy: Penn, R. E.; Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 3622. (c) Sandler, S. R.; Karo, W. "Organic Functional Group Preparations"; Academic Press: New York, 1972; Vol. III, Chapter 4.

Scheme I



Scheme II



bonding,^{2a,c} while 2-methyl-2-propanesulfenic acid has been reported to be stable in solution³ probably due to steric effects. Bulky groups have been used effectively to stabilize transient species such as [4]annulenes,⁴ disilenes,⁵ digermene,⁶ and diphosphenes.⁷ The steric properties of the triptycene skeleton have previously been applied to isolation of a variety of rotational^{8,9} and phase isomers.¹ We now report the first isolation and characterization of a stable sulfenic acid, 9-triptycenesulfenic acid (**1**), whose stability may be attributed mainly to the steric nature of a triptycene skeleton.¹⁰

A solution of 9-(*tert*-butylthio)triptycene¹¹ (0.86 mmol) in dichloromethane (20 mL) was treated with 1 equiv of mCPBA in dichloromethane (10 mL) at 0 °C. The mixture was stirred 12 h (0–25 °C) and washed with an aqueous bicarbonate solution. The usual workup including preparative TLC (Merck, Art. 5717), using a 1:2 mixture of hexane and dichloromethane, provided single major product **A** (*R_f* 0.30) in addition to the recovered 9-(*tert*-butylthio)triptycene (*R_f* 0.85). Compound **A**, mp 204–205 °C dec, obtained in 77.5% yield, carries no *tert*-butyl group as readily confirmable by ¹H NMR and exhibits spectral properties^{12a} completely consistent with the sulfenic acid **1** (Scheme I): (i) The conservation of the triptycene–sulfur linkage in the compound **A** is confirmed not only by the ¹³C NMR signal at 65.11 ppm, which is characteristic of a triptycene bridgehead carbon bearing a divalent sulfur functionality,¹³ but also by the IR band at 635 cm⁻¹,

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(5) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *218*. (b) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(6) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(7) (a) Yoshifuji, M.; Shima, I.; Inamoto, N. *J. Am. Chem. Soc.* **1981**, *103*, 4587. (b) Cowley, A. H.; Kilduff, J. E.; Pakulski, M.; Stewart, C. A. *Ibid.* **1983**, *105*, 1655 and references cited therein. (c) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Matsushita, T.; Nishimoto, K. *Ibid.* **1983**, *105*, 2495.

(8) Ōki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87 and references cited therein.

(9) (a) Nakamura, N. *Chem. Lett.* **1982**, 1611; (b) *Ibid.* **1982**, 1809.

(10) All new compounds gave satisfactory elemental analyses and/or spectral data.

(11) Obtained by the addition reaction of benzyne (generated from anthranilic acid and isopentyl nitrite in 1,2-dimethoxyethane) to 9-(*tert*-butylthio)anthracene. The detailed procedure has been submitted for publication in *Chemistry Letters*. ¹H NMR (CDCl₃) δ 1.72 (s, 9 H, *t*-Bu), 5.72 (s, 1 H, 10-H), 6.83–7.10 (m, 6 H, aromatic), 7.20–7.45 (m, 3 H, aromatic), 7.69–7.95 (m, 3 H, aromatic); ¹³C NMR (CDCl₃) δ 34.25 (Me C's of *t*-Bu), 47.07 (quaternary C of *t*-Bu), 54.13 (10-C), 65.61 (9-C), 122.99, 123.85, 124.42, 125.27 (aromatic C's with H), 145.23, 146.13 (aromatic ipso-C's).

(12) (a) **1**: ¹H NMR (CDCl₃) δ 3.20 (brs, 1 H, OH), 5.37 (s, 1 H, 10-H), 6.85–7.17 (m, 6 H, aromatic), 7.27–7.57 (m, 6 H, aromatic); ¹³C NMR (CD₂Cl₂) δ 53.42 (10-C), 65.11 (9-C), 121.80, 123.38, 124.88, 125.37 (aromatic C's with H), 143.02, 145.50 (aromatic ipso-C's); IR (Nujol) 3340, 1295, 1225, 1170, 780, 635 cm⁻¹. (b) The chemical shift of the hydroxyl proton is dependent on the sample concentration, and the signal moves to a higher field in a more dilute solution. (c) The analytical sample was dried in vacuo at room temperature to avoid possible decomposition at an elevated temperature: Anal. Calcd for C₂₀H₁₄OS·0.4H₂O: C, 77.59; H, 4.82; S, 10.35. Found: C, 77.71; H, 4.80; S, 10.29. (d) Molecular weight. Calcd for C₂₀H₁₄OS: 302. Found (osmometry in benzene): 302.