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 utilization[12] 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.

Acknowledgment. We thank the National Institutes of Health (GM 29204 and GM 31879) for support of this research. The Brüker WM 500-MHz NMR spectrometer is supported in part by a grant from the National Science Foundation (CHE-791620). We express our gratitude to Peter Demou for his expert technical assistance and Professor John Gerlt for valuable discussions. R.V.J.C. is a Yale-Celanese Fellow.

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Synthesis and Characterization of [7]Circulene[1]

Koji Yamamoto,* Tadashi Harada, and Masao Nakazaki*

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

Takuo Naka, Yasushi Kai, Shigeharu Harada, and Nobutami Kasai

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

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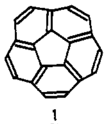
Lawton's papers describing his elegant synthetic approach[2] to the bowl-shaped[3] [5]circuene (**1**) ("corannulene", the next lower homologue of [6]circulene (coronene) (**2**)) have provoked considerable interest in the preparation of [7]circulene (**3**), the next higher homologue of [6]circulene.[4]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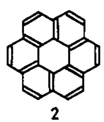
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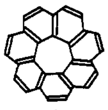
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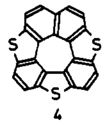

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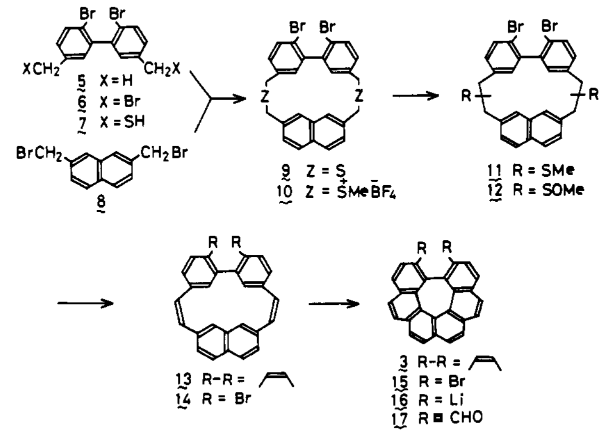
In this communication, we report our successful synthesis of [7]circulene (**3**) and an X-ray analysis, which has revealed its saddle-shaped structure as expected from the examination of the molecular model.



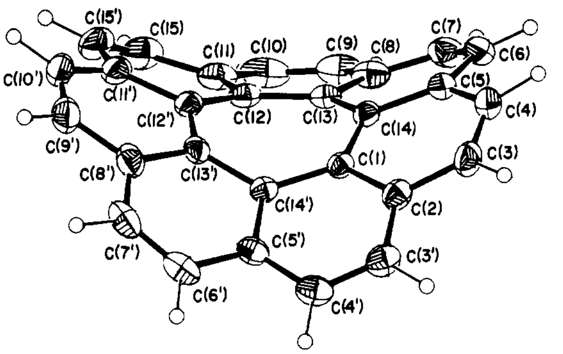


Figure 1. Molecular structure of **3**. Non-hydrogen atoms are drawn by the thermal ellipsoids at the 30% probability level. Hydrogen atoms are shown by the spheres corresponding to the artifical isotropic temperature factor of 1.0 Å^{-2}.

We reasoned that Reiss's attempted photocyclization[5] 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 carbonate[8] 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 lamp[10] 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$^+$; ^{1}H NMR ($CDCl_3$) 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$^+$; ^{1}H NMR ($CDCl_3$) δ 2.02 (s, 2 H), 7.78–8.45 (m, 12 H). Intramolecular reductive coupling[13] of the dialdehyde **17** with $LiAlH_4$ 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$^+$; ^{1}H NMR is characteristic in its single sharp peak at δ 7.45, and the ^{13}C NMR exhibiting

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

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(11) Optical resolution of the dibromide **15** by means of HPLC employing (+)-poly(triphenylmethyl methacrylate)[12] gave (−)-**15**, $[\alpha]^{22}_{D}$ −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 drawing[17] 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 distanes 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.

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(14) Crystal data of **3**: $C_{28}H_{14}$, M_r 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) Å^3, Z = 4, D_x = 1.390 g cm^{-3}. Diffraction intensities were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo Kα 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 (HBLS-V)[16] to the R index of 0.094 for nonzero reflections (non-hydrogen atoms anisotropically, hydrogen atoms isotropically).

(15) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN-78: A System Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and Louvain, Belgium, 1978.

(16) Ashida, T. "HBLS-V: The Universal Crystallographic Computing System-Osaka"; The Computation 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 Characterization[1]

Nobuo Nakamura

Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Tokyo 113, Japan

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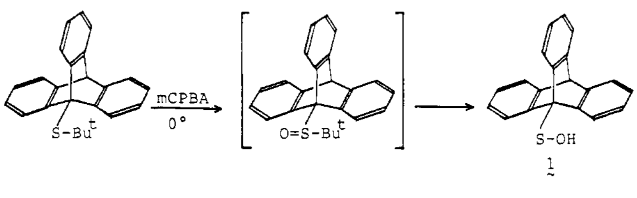
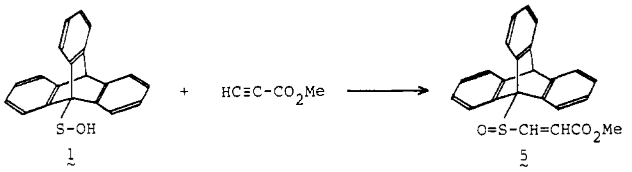
Although sulfenic acids are well recognized as important intermediates in organosulfur chemistry,[2] their high reactivity and the difficulty in generating them under mild conditions have precluded their isolation. Gas-phase conditions were sometimes employed for isolation and study of unstabilized sulfenic acid of short lifetimes.[2b] A few special examples known hitherto have been stabilized by their electronic properties and hydrogen bonding,[2a,c] while 2-methyl-2-propanesulfenic acid has been reported to be stable in solution[3] 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]

Scheme I



Scheme II



A solution of 9-(*tert*-butylthio)triptycene[11] (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 ^{1}H 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 ^{13}C 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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(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.

(3) Davis, K. E.; Shelton, J. R. *Int. J. Sulfur Chem.* **1973**, *8*, 197.

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(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*. ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 34.25 (Me C's of *t*-Bu), 47.07 (quanternary 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**: ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR (CD_2Cl_2) 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 (atomatic 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 $C_{20}H_{14}OS\cdot0.4H_2O$: C, 77.59; H, 4.82; S, 10.35. Found: C, 77.71; H, 4.80; S, 10.29. (d) Molecular weight. Calcd for $C_{20}H_{14}OS$: 302. Found (osmometry in benzene): 302.

0002-7863/83/1505-7172$01.50/0