Synthesis of *anti*-4,5,14,15-Tetramethyl[2_2](2,7)naphthalenophane-1,11-diene and Its Dianion. ESR and ENDOR Studies of Its Radical Anion and Other Related Radical Ions[1a]

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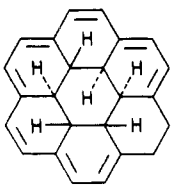
A synthesis of *anti*-4,5,14,15-tetramethyl[2_2](2,7)naphthalenophane-1,11-diene (**4**) has been achieved in ten steps from 1,8-naphthalic anhydride in an overall yield of 4%. The key step in the synthesis employed a double-barreled sulfur analogue of the Sommelet–Hauser rearrangement. Unexpectedly, formation of the dianion and radical anion of **4** occurred without intramolecular cyclization. The radical anions and the radical cations both of **4** and of *anti*-4,5,14,15-tetramethyl[2_2](2,7)naphthalenophane (**19**) have been characterized by ESR and ENDOR spectroscopy.

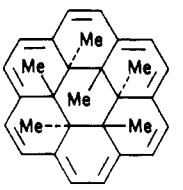
One of the unanswered questions regarding the aromaticity of (4*n* + 2)annulenes is whether there is an upper limit for the Hückel rule and, if so, at what ring size will the character of the annulene change from being aromatic to being polyolefinic. Various theoretical studies have predicted that this change will occur at a ring size in the range of 18 to 30 members.[2-5] In studies of the higher annulenes the commonly employed criterion for aromaticity has been the presence of a diatropic ring current. Haddon and Fukunaga have provided theoretical justification for this criterion.[6] Furthermore, Haddon has shown how NMR chemical shift values can be used in a quantitative fashion to correlate relative aromaticity of different annulenes.[7] The elegant studies of Nakagawa on dehydroannulenes containing acetylene and/or acetylene–cumulene bonds showed that all of the (4*n* + 2)annulenes containing from 14 to 30 members have a diatropic ring current, although the relative aromaticity of the [30]-annulene example was low.[8]

In a previous study on the degree of aromaticity exhibited by bridged [18]annulenes, we found that small deviations from the ideal annulene, such as nonequivalence of contributing Kekule structures, had a marked effect in lowering the observed diatropic ring current.[9] Thus, to test the upper limit for aromaticity in annulenes, it is important that all of the requirements for an ideal aromatic ring be met. These requirements include rigid planarity of the annulene ring, equivalence of the hybridization of ring members, and equivalence of the Kekule structures contributing to the resonance hybrid.

Even though 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**1**) shows a very high degree of aromaticity,[9] we undertook in the present study to prepare **2**, which with its all-trans arrangement of internal substituents would be a more nearly perfect example of a bridged [18]annulene. It was



1



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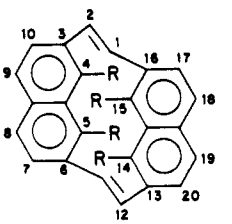
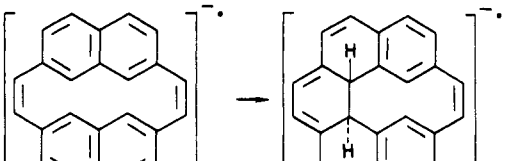


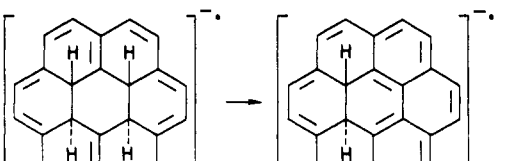
3, R = H
4, R = Me

anticipated that the internal methyl substitution present in **2** would prevent the easy oxidation that occurs with **1** and so allow a more extensive study of the properties of **2** than is possible with **1**.

In a previous study of *anti*-[2_2](2,7)naphthalenophane-1,11-diene (**3**), it was shown that the corresponding radical anion $3^{-}\cdot$ underwent intramolecular cyclization to give $5^{-}\cdot$, which, in turn, probably via $6^{-}\cdot$, led to the radical anion $7^{-}\cdot$.[10]



$3^{-}\cdot$ $5^{-}\cdot$



$6^{-}\cdot$ $7^{-}\cdot$

It seemed probable that, if the internal positions of the naphthalenophane were alkylated, as in **4**, the dehydrogenation–aromatization process ($6^{-}\cdot \rightarrow 7^{-}\cdot$) could be avoided. Chemical, or electrochemical, reduction of **4** might then be expected to give the dianion 8^{2-}, which, by treatment with dimethyl sulfate, could yield the desired annulene **2**.

An obvious difficulty in synthesizing **4** from a naphthalene precursor is the fact that the substitution patterns

(1) (a) The naming and numbering of the [2_n]cyclophanes in this paper follows an earlier suggestion on nomenclature. See: V. Boekelheide, *Top. Curr. Chem.* **113**, 89–143 (1983). (b) University of Oregon. (c) Universität Basel.

(2) H. C. Longuet-Higgins and L. Salem, *Proc. R. Soc., Ser. A*, **251**, 172–185 (1959).

(3) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215–228 (1962).

(4) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685–692 (1965).

(5) M. J. S. Dewar, R. C. Haddon, and P. J. Student, *J. Chem. Soc., Chem. Commun.* 569–570 (1974).

(6) R. C. Haddon and T. Fukunaga, *Tetrahedron Lett.*, **21**, 1191–1192 (1980).

(7) R. C. Haddon, *Tetrahedron*, **28**, 3613–3635 and 3635–3655 (1972).

(8) M. Nakagawa, *Pure Appl. Chem.*, **44**, 885–924 (1975).

(9) T. Otsubo, R. Gray, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2449–2456 (1978).

(10) Ch. Elschenbroich, F. Gerson, and J. A. Reiss, *J. Am. Chem. Soc.*, **99**, 60–64 (1977).

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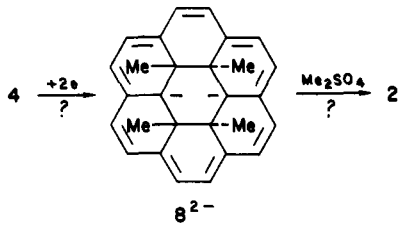


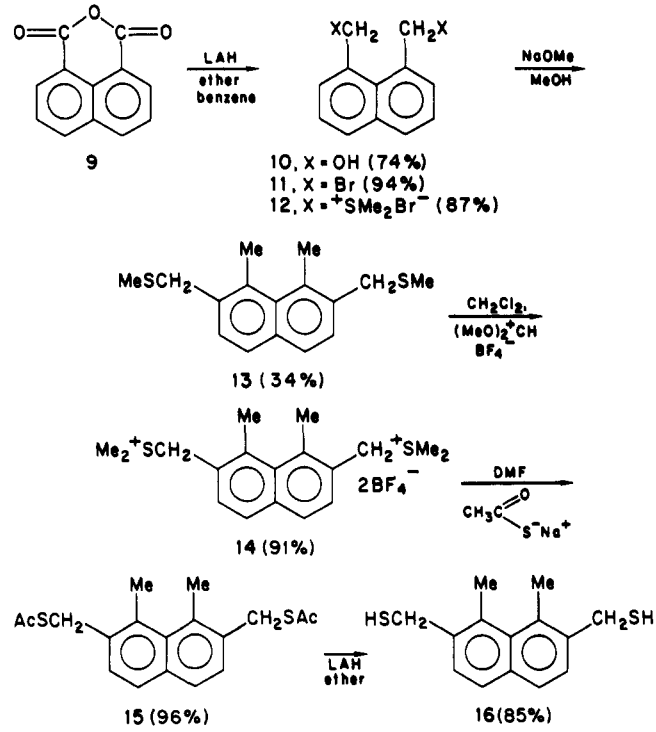
for naphthalene are not conducive for providing 1,2,7,8-tetrasubstituted naphthalene derivatives. However, we were able to circumvent this difficulty by employing the sulfur analogue of the Sommelet–Hauser rearrangement.[11,12] As shown in Scheme I, lithium aluminum hydride reduction of the commercially available 1,8-naphthalic anhydride (9) readily gave 1,8-bis(hydroxymethyl)naphthalene (10), and this in turn was converted by standard procedures to the corresponding dibromide 11 and the bis(sulfonium) derivative 12. When run on a 30.0-g scale, the Sommelet–Hauser rearrangement of 12 proceeded in 34% yield to give the bis(sulfide) 13. Treatment of 13 with dimethoxycarbonium tetrafluoroborate[13] led to the bis(sulfonium) salt 14. Conversion of 14 to the bis(thioacetate) 15 proceeded smoothly and reduction of 15 with lithium aluminum hydride then led to the bis(mercaptan) 16.

The coupling of 14 and 16 to give the corresponding dithiacyclophane 17 proceeded smoothly in 78% yield as shown in Scheme II. A Wittig rearrangement of 17 followed by methylation then gave the bis(methylthio)[2₂](2,7)naphthalenophane 18. This, in turn, was converted to the corresponding bis(sulfonium) salt followed directly by a Hofmann elimination using sodium hydride in tetrahydrofuran to give the desired *anti*-4,5,14,15-tetramethyl[2₂](2,7)naphthalenophane-1,11-diene (4) in 32% yield. To provide additional evidence for the correctness of the structural assignments, 4 was hydrogenated over platinum to give *anti*-4,5,14,15-tetramethyl[2₂](2,7)-naphthalenophane (19).

When a solution of *anti*-4,5,14,15-tetramethyl[2₂](2,7)-naphthalenophane-1,11-diene (4) in perdeuteriotetrahydrofuran was exposed to a potassium mirror at −78 °C, it slowly gave a deep green, almost black, solution of a diamagnetic dianion. The ^1H and ^{13}C NMR spectra clearly showed that this dianion corresponded to structure 4^{2-} and not to the desired structure 8^{2-}. There was no evidence from these spectra for a diatropic ring current or the formation of sp^3-hybridized carbons at the 4-, 5-, 14-, and 15-positions. Specifically, the ^{13}C NMR spectra exhibited seven lines in the sp^2 carbon region as expected for 4^{2-}, whereas structure 8^{2-} should exhibit only six lines in this region. It is somewhat surprising that the intramolecular cyclization observed for 3 is absent in the case of 4. Presumably, the intramolecular cyclization is a reversible equilibrium. It may be that this equilibrium is likewise unfavorable in the case of the radical anion of 3, but the dehydrogenation step drives the reaction to give the cyclized product.

Formation of the dianion 4^{2-} is reversible and, on oxidation followed by workup, 4 is recovered in high yield. The nature of the dianion 4^{2-} is also of some interest. Minsky et al. have recently presented data to show that dianions of benzenoid polycycles, although singlets, frequently have a thermally accessible excited triplet state.[14]

Scheme I



Scheme II

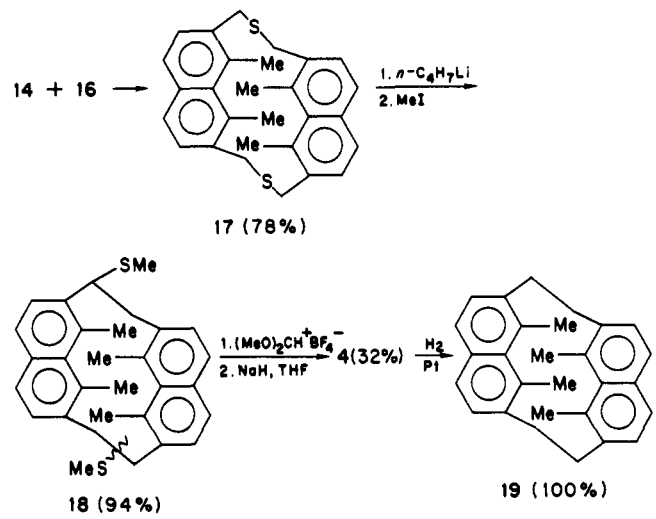


Table I. Proton Coupling Constants, in mT,[a] for the Radical Ions of *anti*-4,5,14,15-Tetramethyl[2₂](2,7)naphthalenophane-1,11-diene (4) and for the Radical Anion of the Unsubstituted [2₂](2,7)Naphthalenophane-1,11-diene (3)

position	$3^{-\cdot}$ [b]	$4^{-\cdot}$	$4^{+\cdot}$
1, 2, 11, 12	0.087 (4 H)	0.097 (4 H)	0.054 (4 H)
7, 10, 17, 20	0.032 (4 H)	0.039 (4 H)	<0.01 (4 H)
8, 9, 18, 19	0.108 (4 H)	0.097 (4 H)	0.225 (4 H)
4, 5, 14, 15	0.307 (4 H)	0.222 (12 H)	0.316 (12 H)

[a] Experimental error: ±1%. [b] Taken from ref 10.

This was found to be true for 4^{2-}. At −52 °C the purple, almost black, solutions of 4^{2-} provide clean NMR spectra. When warmed to 0 °C, the solution becomes deep green and the NMR signals are no longer observable. Upon cooling the solution once again to −52 °C, the original color and NMR signals return. Thus 4^{2-} provides another ex-

(11) G. E. Hilbert and L. A. Pinck, *J. Am. Chem. Soc.*, **60**, 494–495 (1938).

(12) We thank Dr. Manfred Müller for helpful discussions regarding the sulfur analogue of the Sommelet–Hauser rearrangement.

(13) R. F. Borch, *J. Org. Chem.*, **34**, 627–629 (1969).

(14) A. Minsky, A. Y. Meyer, R. Poupko, and M. Rabinovitz, *J. Am. Chem. Soc.*, **105**, 2164–2172 (1983).

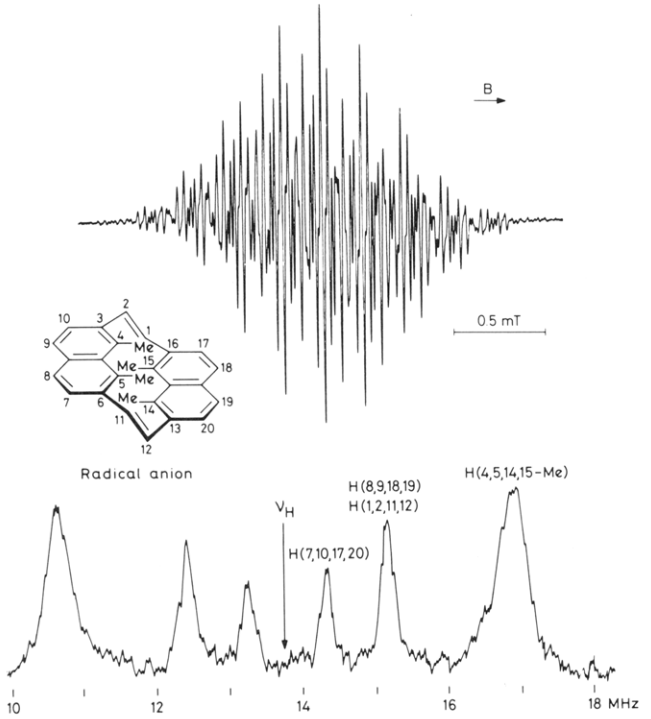
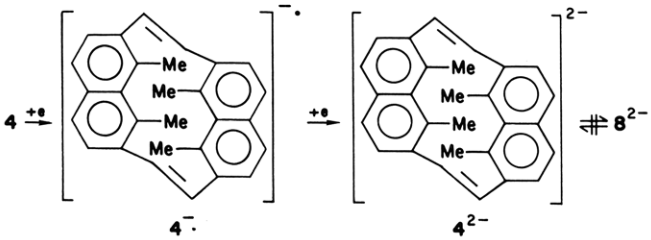


Figure 1. ESR (top) and proton ENDOR (bottom) spectra of the radical anion of *anti*-4,5,14,15-tetramethyl[2_2](2,7)-naphthalenophane-1,11-diene (**4**). Solvent, DME; counterion, K^+; temperature, 193 K. ν_H = frequency of the free proton.

ample of a dianion having a thermally accessible excited triplet state.



Formation of the dianion 4^{2-} occurs in a two-step process involving formation first of the radical anion $4^{-\cdot}$. When a solution of **4** in 1,2-dimethoxyethane (DME) at 193 K was reduced either electrolytically (n-$Bu_4N^+ClO_4^-$ as the supporting electrolyte) or by reaction with solvated electrons (formed on dissolving potassium metal), the radical anion $4^{-\cdot}$ was obtained. The ESR spectrum of $4^{-\cdot}$ is shown in Figure 1, together with the corresponding proton ENDOR signals. In Table I, the pertinent hyperfine data for $4^{-\cdot}$ are compared with the analogous values for the radical anion of the unsubstituted *anti*-[2_2](2,7)-naphthalenophane-1,11-diene (**3**).[10] This comparison leaves no doubt that the observed ESR and ENDOR spectra are those of the unrearranged radical anion $4^{-\cdot}$. Paramagnetic species that might have resulted from cyclization of $4^{-\cdot}$ were not detected, in contrast to the behavior of the radical anion of **3** under the same conditions.

Oxidation of *anti*-4,5,14,15-tetramethyl[2_2](2,7)-naphthalenophane-1,11-diene (**4**) with aluminum trichloride in methylene chloride led to formation of the radical cation $4^{+\cdot}$. Figure 2 displays the ESR and proton ENDOR spectra of $4^{+\cdot}$; the hyperfine data derived therefrom are included in Table I.

The radical anion and the radical cation were likewise generated from *anti*-4,5,14,15-tetramethyl[2_2](2,7)-naphthalenophane (**19**) by reduction with solvated electrons in DME and by oxidation with aluminum trichloride in methylene chloride, respectively. Analysis of the ESR and proton ENDOR spectra of $19^{-\cdot}$ and $19^{+\cdot}$ yielded the hyperfine data listed in Table II, which also gives the corresponding values obtained previously for the radical anion of the unsubstituted *anti*-[2_2](2,7)naphthalenophane (**20**).[10]

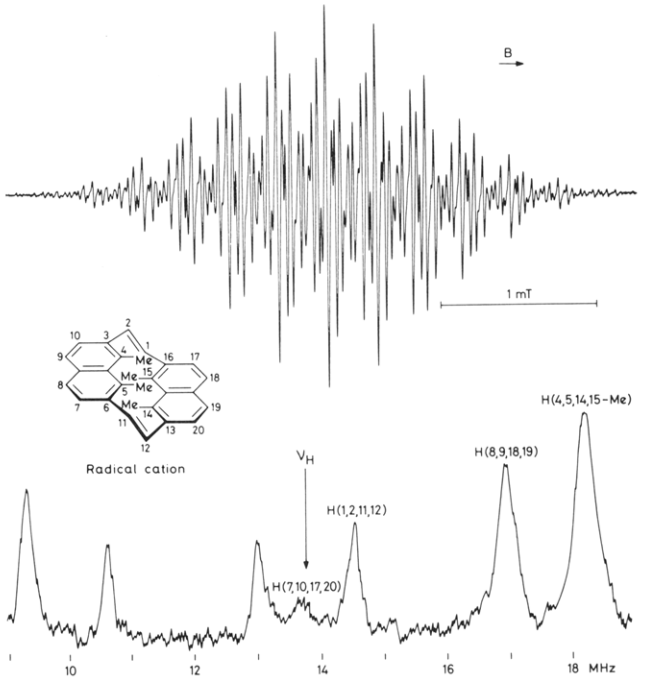


Figure 2. ESR (top) and proton ENDOR (bottom) spectra of the radical cation of *anti*-4,5,14,15-tetramethyl[2_2](2,7)-naphthalenophane-1,11-diene (**4**). Solvent, CH_2Cl_2; temperature, 273 K. ν_H = frequency of the free proton.

Assignments of the coupling constants to sets of four equivalent protons in the radical ions of **4** and **19** are based on arguments similar to those used in the paper on the radical anions of **3** and **20**.[10] Comparison of the data for $19^{-\cdot}$ and $20^{-\cdot}$ (Table II) suggests that the assignments made in that paper for the protons in the positions 4, 5, 14, 15 and 8, 9, 18, 19, of $20^{-\cdot}$ should be reversed.

The radical ions of **19** were less persistent than those of its 1,11-diene **4**. The g value of all four radical ions is 2.0027, within the limits of the experimental error (±0.0001).

Experimental Section[15]

1,8-Bis(hydroxymethyl)naphthalene (10). This was prepared by a modification of the procedure of Mitchell et al.[16] To a stirred slurry of 12.5 g (0.33 mol) of lithium aluminum hydride in 250 mL of dry ether and 115 mL of dry benzene was added 25 g (0.13 mol) of 1,8-naphthalic anhydride as a solid over a 1-h period. Upon completion of the addition, the reaction mixture was boiled under reflux for 3 h and then concentrated to remove the ether. Ethyl acetate was slowly added, followed by a 5% solution of aqueous hydrochloric acid to dissolve the aluminum salts. The crude product was collected by filtration and recrystallized from 95% ethanol to provide 17.55 g (74%) of **10** as

(15) The ^1H NMR spectra were determined with either Varian XL-100 (100 MHz) of Nicolet NT-360 (360 MHz) spectrometers. The ^{13}C NMR spectra were determined with a Nicolet NT-360 (90.7 MHz) spectrometer. Mass spectra were obtained with a CEC-21B-110 instrument set at 70 eV. Ultraviolet and visible spectra were measured with a Cary 15 spectrometer. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Elemental analyses are by Dr. R. Wielesek of the University of Oregon microanalytical laboratories. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Other solvents were reagent grade.

(16) W. J. Mitchell, R. D. Topson, and J. Vaughan, *J. Chem. Soc.*, 2526 (1962).

Table II. Proton Coupling Constants, in mT,[a] for the Radical Ions of *anti*-4,5,14,15-Tetramethyl[2₂](2,7)-naphthalenophane (19) and the Radical Anion of the Unsubstituted [2₂](2,7)Naphthalenophane (20)

position	$20^{-\cdot}$ [b]	$19^{-\cdot}$	$19^{+\cdot}$
1, 2, 11, 12	0.104 (4 H)	0.077 (4 H)	0.061 (4 H)
7, 10, 17, 20	0.083 (4 H)	0.055 (4 H)	<0.03 (4 H)
	0.043 (4 H)	0.030 (4 H)	<0.03 (4 H)
8, 9, 18, 19	0.194 (4 H)[c]	0.199 (4 H)	0.304 (4 H)
4, 5, 14, 15	0.268 (4 H)[c]	0.293 (12 H)	0.365 (12 H)

[a] Experimental error: ±2%. [b] Taken from ref 10. [c] Assignments reversed relative to those made previously.[10]

white needles, mp 160–161 °C (lit.[15] mp 158 °C).

1,8-Bis(bromomethyl)naphthalene (11). This was prepared by following a procedure devised from the report of Mitchell et al.[17] To a stirred mixture of 17.55 g (93.3 mmol) of 1,8-bis(hydroxymethyl)naphthalene and 5 g (57.7 mmol) of lithium bromide in 400 mL of ether was slowly added 20 mL (0.213 mol) of phosphorus tribromide at room temperature. After 17 h the reaction mixture was poured into a separatory funnel that was partially filled with ice. Chloroform (500 mL) was added to the organic layer, which was then separated, washed with a saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. Evaporation of the organic layer gave 27.62 g (94%) of 1,8-bis(bromomethyl)naphthalene as white crystals, mp 133–134 °C (lit.[18] mp 130–131.5 °C).

1,8-Bis[(dimethylsulfonio)methyl]naphthalene Dibromide (12). A solution of 27.62 g (87.1 mmol) of 1,8-bis(bromomethyl)naphthalene in 250 mL of dimethyl sulfide was stirred at room temperature for 24 h. Ether (500 mL) was added to complete the precipitation of the salt, which was collected by filtration to provide 33.63 g (87%) of a white powder; mp 120–121 °C dec; IR (KBr) ν_{max} 2960, 1430, 1210, 770 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.03 (3 H, s, SCH_3), 2.90 (3 H, br s, SCH_3), 5.37–5.56 (2 H, m, $ArCH_2$), 7.44–8.29 (3 H, m, Ar H).

Anal. Calcd. for $C_{16}H_{22}S_2Br_2$: C, 43.85; H, 5.06. Found: C, 44.29; H, 5.06.

1,8-Dimethyl-2,7-bis[(methylthio)methyl]naphthalene (13). To a stirred 25% solution of sodium methoxide in methanol (1350 mL) held at 0 °C was added 30 g (68.3 mmol) of **12** over a 5-min period. The mixture was stirred at 0 °C for 1.5 h, allowed to warm to room temperature, and finally boiled under reflux for 24 h. After the mixture had been neutralized with concentrated hydrochloric acid, it was concentrated followed by addition of water and dichloromethane. The organic layer was separated, dried, and concentrated to give an oily, orange solid. After passage of the crude product over a short column of silica gel using a 1:1 mixture of benzene–hexane for elution, the yellow solid, isolated from the main fraction of eluate, was recrystallized from absolute ethanol to give 6.3 g (34%) of yellow plates. Sublimation of a small sample gave a white powder: mp 108–109 °C; IR (KBr) ν_{max} 2900, 1435, 1380, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (3 H, s, SCH_3), 2.80 (3 H, s, $ArCH_3$), 3.87 (2 H, s, $ArCH_2$), 7.27 (1 H, AB-d, J = 8 Hz, Ar H), 7.54 (1 H, AB-d, J = 8 Hz); UV ($CHCl_3$) λ_{max} 337 sh (ϵ 772), 304 (8532), and 241 nm (90 210); mass spectrum, m/e 276 (M^+), 229 ($M^+ - SCH_3$).

Anal. Calcd for $C_{16}H_{20}S_2$: C, 69.51; H, 7.29. Found: C, 69.47; H, 7.08.

Hayashi and Oda have repported that potassium *tert*-butoxide in *t*-butyl alcohol is a superior base for effecting the sulfur analogue of the Sommelet–Hauser rearrangement.[19] However, for the preparation of **13** the use of sodium methoxide in methanol proved to be equally as good and is more convenient.

1,8-Dimethyl-2,7-bis[(dimethylsulfonio)methyl]naphthalene Bis(tetrafluoroborate) (14). To a suspension of 4.5 g (27.7 mmol) of dimethoxycarbonium tetrafluoroborate[13] in 10 mL of dichloromethane held at 0 °C was added dropwise with stirring a solution of 1.22 g (4.42 mmol) of **13** in 15 mL of dichloromethane. After a mixture had been stirred at 0 °C for 1 h, it was allowed to warm to room temperature and was stirred for an additional 2 h. Then the mixture was concentrated and cold methyl formate was added. The resulting precipitate was collected, giving 1.93 g (91%) of a white powder: mp 220 °C dec; IR (KBr) ν_{max} 3030, 1435, 860 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.87 (3 H, s, $ArCH_3$), 2.92 (6 H, S, SCH_3), 4.91 (2 H, s, $ArCH_2$), 7.53 (1 H, AB-d, J = 8 Hz, Ar H), 7.85 (1 H, AB-d, Ar H).

Anal. Calcd for $C_{18}H_{26}S_2B_2F_8$: C, 45.03; H, 5.46. Found: C, 44.80; H, 5.24.

1,8-Dimethyl-2,7-bis[(acetylthio)methyl]naphthalene (15). To a solution of 3.1 g (31.6 mmol) of sodium thioacetate in 50 mL of dimethylformamide was added 2.5 g (5.21 mmol) of **14**. The resulting solution was stirred at room temperature for 24 h and then was diluted with water. The aqueous mixture was extracted with ether, which was then washed with water, dried, and concentrated to give 1.66 g (96%) of a yellow crystalline solid. A small sample was recrystallized from hexane, yielding tan plates: mp 104–105 °C; IR (KBr) ν_{max} 1690, 1130, 1100, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (3 H, s, $COCH_3$), 2.74 (3 H, s, $ArCH_3$), 4.32 (2 H, s, $ArCH_2$), 7.32 (1 H, AB-d, J = 8 Hz, Ar H), 7.56 (1 H, AB-d, Ar H); mass spectrum, m/e 332 (M^+), 257 ($M^+ - SCOCH_3$).

Anal. Calcd for $C_{18}H_{20}S_2O_2$: C, 65.03; H, 6.06. Found: C, 64.79; H, 6.06.

1,8-Dimethyl-2,7-bis(mercaptomethyl)naphthalene (16). To a solution of 500 mg (13.1 mmol) of lithium aluminum hydride in 50 mL of dry ether was added dropwise a solution of 1.63 g (4.91 mmol) of **15** in 100 mL of dry ether over a period of 1 h at room temperature. The mixture was then boiled under reflux an additional 2 h before the slow addition of water followed by a 5% aqueous solution of hydrochloric acid. The ether layer was then separated and dried over anhydrous magnesium sulfate. The crude yellow solid obtained upon concentration was sublimed at 100 °C and 0.01 torr to give 1.04 g (85%) of a white powder. A small sample of this was recrystallized from absolute ethanol, yielding white needles: mp 99–100 °C; IR (KBr) ν_{max} 2920, 1440, 1385, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (1 H, t, J = 7 Hz, SH), 2.93 (3 H, s, $ArCH_3$), 3.91 (2 H, d, $ArCH_2$), 7.30 (1 H, AB-d, J = 8 Hz, Ar H), 7.58 (1 H, AB-d, Ar H); mass spectrum, m/e 248 (M^+), 215 ($M^+ - SH$).

Anal. Calcd for $C_{14}H_{16}S_2$: C, 67.69; H, 6.49. Found: C, 67.48; H, 6.49.

***anti*-5,6,16,17-Tetramethyl-2,13-dithia[3.3](2,7)naphthalenophane (17).** A solution of 2.15 g (4.48 mmol) of the bis(sulfonium salt) **14** and 1.11 g (4.48 mmol) of the dithiol **16** in 300 mL of dimethylformamide was added dropwise via a Hershberg funnel over a 15-h period to a vigorously stirred, room-temperature solution of 3.1 g (57.3 mmol) of 85% KOH in 38 mL of water and 700 mL of methanol contained in a Morton flask. After an additional 2 h of stirring, the reaction mixture was concentrated and then mixed with water and chloroform. The organic layer was separated and dried over anhydrous magnesium sulfate. The organic layer was filtered, silica gel was added, and the crude product was preadsorbed upon concentration. Column chromatography over silica gel with chloroform as the eluant then gave 1.49 g (78%) of a white powder. A small sample was recrystallized from chloroform to give a white amorphous powder: mp 268–271 °C; IR (KBr) ν_{max} 2915, 1470, 1440, 1385, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (3 H, s, $ArCH_3$), 3.90 (2 H, s, $ArCH_2$), 7.40 (1 H, AB-d, J = 9 Hz, Ar H), 7.52 (1 H, AB-d, Ar H); UV ($CHCl_3$) λ_{max} 298 (sh) (ϵ 24 500); mass spectrum, m/e 428 (M^+), 382 ($M^+ - CH_2S$).

Anal. M_r calcd for $C_{28}H_{28}S_2$ 428.163, found 428.165 (high resolution mass spectrum).

***anti*-4,5,14,15-Tetramethylbis(methylthio)[2₂](2,7)naphthalenophane (18).** To a stirred suspension of 300 mg (0.7 mmol) of dithiacyclophane **17** in 20 mL of dry tetrahydrofuran at room temperature was injected 1.6 mL (2.56 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The mixture was stirred for 5 min, at which time no starting material remained. The colored solution was quenched by the injection of 0.25 mL (4.0 mmol) of iodomethane and then concentrated. Chloroform and water were added and the organic layer was separated and dried

(17) D. Mitchell, J. H. Eilert, and N. L. Bauld, *Tetrahedron Lett.*, 2865–2866 (1979).
(18) E. D. Bergmann and J. Szmuszkovic, *J. Am. Chem. Soc.*, **75**, 2760–2761 (1953).
(19) Y. Hayashi and R. Oda, *Tetrahedron Lett.*, 5381–5384 (1968).

over anhydrous magnesium sulfate. Concentration of the organic layer gave 300 mg (94%) of a yellow powder suitable for use in the next step. An analytical sample was provided by silica gel chromatography using chloroform as the eluant. The main eluant fraction was concentrated until a solid precipitated, which was removed by filtration to give an amorphous white powder; mp 334–340 °C; IR (KBr) ν_{max} 2900, 1430, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67–1.42 (6 H, m, $ArCH_3$), 2.19 (3 H, s, SCH_3), 3.4–3.0 (2 H, m, $ArCH_2$), 3.8–3.4 (1 H, m, Ar*CH*–SCH_3), 8.0–7.1 (4 H, m, Ar H); UV ($CHCl_3$) λ_{max} 281 nm (ϵ 24300); mass spectrum, m/e 456 (M^+), 418 ($M^+ - CH_2S$).

Anal. Calcd for $C_{30}H_{32}S_2$: C, 78.90; H, 7.06. Found: C, 79.20; H, 7.12.

***anti*-4,5,14,15-Tetramethyl[2$_2$](2,7)naphthalenophane-1,11-diene (4). A.** A solution of 243 mg (0.53) mmol) of **18** in 10 mL of methylene chloride and 10 mL of chloroform was added dropwise over 0.5 h to a suspension of 950 mg (5.9 mmol) of dimethoxycarbonium tetrafluoroborate in 5 mL of methylene chloride at 0 °C. The ice bath was removed after 0.5 h and stirring was continued for an additional 3 h at room temperature. The solution was concentrated and cold methyl formate was added to precipitate the salt. The product was collected by filtration to provide 286 mg (85%) of a light green powder, mp >330 °C. The salt, which smelled of dimethyl sulfide, was used directly in the next step.

B. To a suspension of 50 mg (2.2 mmol) of sodium hydride in 20 mL of tetrahydrofuran was added 156 mg (0.25 mmol) of the disulfonium salt from A. The mixture was boiled under reflux for 6 h before an additional 35 mg of sodium hydride was added. The solution was heated at reflux for a further 18 h and then the excess sodium hydride was destroyed by the dropwise addition of water. The resulting mixture was concentrated, and mixed with methylene chloride and water, and the organic layer was separated and dried over anhydrous magnesium sulfate. The crude yellow residue obtained upon concentration was chromatographed over silica gel using carbon tetrachloride as the eluant. The eluant fractions containing a yellow band were concentrated to give 28.1 mg (32%) of yellow crystals. A sample was recrystallized from a 1:1 cyclohexane–methylcyclohexane mixture to yield yellow prisms; mp 345–346 °C; IR (KBr) ν_{max} 1590, 1545, 1460, 1430, 1384, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (3 H, s, $ArCH_3$), 6.72 (1 H, s, ArCH), 7.01 (1 H, AB-d, J = 8 Hz, Ar H), 7.52 (1 H, AB-d, Ar H); UV ($CHCl_3$) λ_{max} 375 nm (ϵ 2260), 280 (sh) (19200), 246 (92000); mass spectrum, m/e (relative intensity), 360 (100, M^+), 346 (11, $M^+ - CH_2$), 330 (7, $M^+ - 2CH_3$), 315 (22, $M^+ - 3CH_3$), 300 (39, $M^+ - 4CH_3$).

Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.09; H, 6.87.

***anti*-4,5,14,15-Tetramethyl[2$_2$](2,7)naphthalenophane (19).** A solution of 30 mg (0.083 mmol) of **4** in 125 mL of ethyl acetate containing a small amount of platinum dioxide was shaken under 25 psi of hydrogen for 2 h. The catalyst was removed by filtration and the solution was concentrated to give 30 mg (100%) of a white solid. Recrystallization of this from cyclohexane gave white prisms: mp 309–311 °C; ^1H NMR ($CDCl_3$) δ 1.41 (3 H, s, $ArCH_3$), 3.24–2.94 (2 H, m, $ArCH_2$), 7.21 (1 H, AB-d, J = 8 Hz, Ar H), 7.40 (1 H, AB-d, Ar H); UV (cyclohexane) λ_{max} 307 nm (ϵ = 5900), 225 (127000).

Anal. M_r calcd for $C_{28}H_{28}$, 364.219, found 364.217 (high resolution mass spectrum).

***anti*-4,5,14,15-Tetramethyl[2$_2$](2,7)naphthalenophane-1,11-diene Dianion (4^{2-}).** Potassium metal was repeatedly sublimed under high vacuum in a horizontal glass manifold to which an NMR tube (5 mm or 12 mm) had been vertically attached. A mirror of potassium was then formed in the top 1–2 cm of the NMR tube which had previously been charged with a sample (1 or 14 mg) of **4**. Tetrahydrofuran-d_8 (0.5 or 7 mL), which had been dried over lithium aluminum hydride for 3 days at room temperature and then over a potassium mirror at room temperature for 12 h, was distilled into the NMR tube. The NMR tube was sealed and the sample was completely dissolved before the tube was inverted at −78 °C to allow contact with the mirror. The tube was held at −78 °C with periodic agitation for 44 h before spectra were measured. Its ^1H NMR spectrum was recorded at −80 °C at 360 MHz, and its ^{13}C NMR spectrum was measured at −52 °C at 90.7 MHz. ^1H NMR: δ −0.21 (3 H, s, $ArCH_3$), 6.05 (1 H, d, J = 7.6 Hz, Ar H), 6.18 (1 H, s, Ar*CH*), 6.83 (1 H, d, Ar H). ^{13}C NMR: δ 20.9 (q), 109.8 (s), 111.8 (d), 115.2 (d), 116.8 (d), 134.2 (s), 134.6 (s), 139.2 (s).

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