2,7-Methanothia[9]annulene: Synthesis and Equilibrium with Its Norcaradiene Valence Isomer

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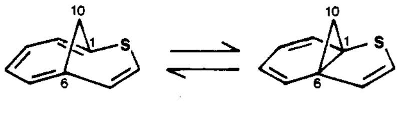
Abstract: 2,7-Methanothia[9]annulene (**1**) was synthesized from 1,6-diiodo-1,3,5-cycloheptatriene in 13 steps. Variable-temperature ^{13}C NMR and electronic spectra indicated that **1** is in equilibrium with its valence isomer, 9-thiatricyclo-[4.3.1.0^{1,6}]deca-2,4,7-triene (**2**). From the ^{13}C NMR spectra, the equilibrium ratio **1**/**2** was estimated as 16/84 in $CDCl_3$–CS_2 (1:1) at 30 °C. Comparison of the temperature dependence of ^{13}C chemical shifts of **1** with that of other related systems suggested the presence of some stabilization in **1**, which was attributed to the aromaticity of **1** as a 10π-electron system although direct evidence for the presence of diatropicity in **1** could not be obtained from ^1H NMR spectroscopy due to a fast equilibrium even at low temperatures.

The chemistry of bridged annulenes has been extensively studied by Vogel and his co-workers and has made a great contribution to our understanding of aromaticity.[1] As for bridged heteroannulenes, however, only a few examples have been reported[1g,2-4] although a wide variety of compounds is possible in principle. This is probably due to the limited availability of useful synthetic methods for the preparation of such heterocycles. We have previously reported the photochemical synthesis of 1,6-disubstituted cycloheptatrienes which are very useful precursors for bridged heterocycles.[5-7]

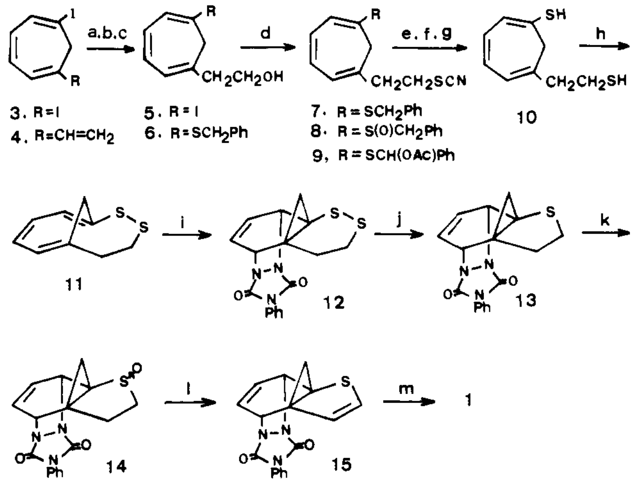
We now report here the synthesis of 2,7-metanothia[9]annulene (**1**)[8] and the existence of an equilibrium between **1** and its valence isomer **2**.[9]



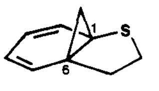
1 **2**

Annulene **1** was synthesized by a route depicted in Scheme I starting from 1,6-diiodo-1,3,5-cycloheptatriene (**3**).[5] One of the iodine groups was converted to a 2-hydroxyethyl group by selective monovinylation[5] followed by hydroboration to give alcohol **5**. After introduction of a benzylthio group by palladium-catalyzed substitution,[10] the resulting alcohol **6** was converted into thiocyanate **7** with $Ph_3P(SCN)_2$.[11] Oxidation of **7** to **8** followed by treatment with trifluoroacetic anhydride–acetic anhydride–2,6-lutidine (Pummerer rearrangement)[12] gave **9**, which was reduced with lithium aluminum hydride to dithiol **10**, a key intermediate in this synthetic scheme. Oxidation of **10** with iodine under high dilution conditions afforded disulfide **11**. Since all attempts of desulfurization of **11** to **16** using trivalent phosphorus compounds were unsuccessful,[13] **11** was converted into **12**, having a bond between bridgehead carbons, by cycloaddition with 4-phenyl-1,2,4-tria-

Scheme I



^{a} CH_2=CHMgBr-cat.·Li_2CuCl_4; 87%. ^{b} 9-BBN, NaOH–H_2O_2; 82%. ^{c} $PhCH_2SNa$-cat.·$Pd(Ph_3P)_4$; 91%. ^{d} $Ph_3P(SCN)_2$; 81%. ^{e} MCPBA; 95%. ^{f} $(CF_3CO)_2O$–$(CH_3CO)_2O$, 2,6-lutidine; 91%. ^{g} $LiAlH_4$; 100%. ^{h} I_2, Et_3N; 86%. ^{i} PTAD; 32%. ^{j} $P(NMe_2)_3$; 88%. ^{k} MCPBA; 100%. ^{l} $CF_3SO_3SiMe_3$, i-Pr_2EtN: 58%. ^{m} Na, EtOH; 49%.



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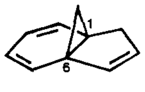

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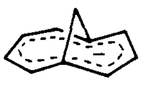

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(8) Numbering in the formula **1** is not made as an annulenyl system but as a bicyclo[4.3.1]decane system for ready comparison with other related compounds.

(9) Presented in part at the 9th International Congress of Heterocycllic Chemistry, August 1983, Tokyo. Abstracts G-22.

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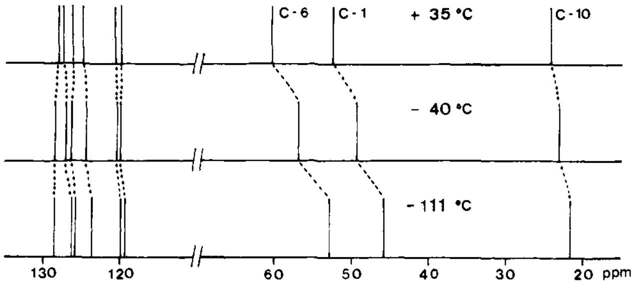

Figure 1. Schematic representation of the variable-temperature ^{13}C NMR spectra of the fluxional system **1** ⇄ **2** (100.40 MHz, 1:1 CD_2Cl_2–CS_2, Me_4Si as internal standard).

zoline-3,5-dione (PTAD). In contrast to **11**, the tetracyclic disulfide **12** was smoothly desulfurized to **13**, which in turn was oxidized to give sulfoxide **14**. A pummerer-type reaction of **14** with trimethylsilyl triflate and base[14] directly afforded **15**. The final step of this synthetic scheme, deprotection of PTAD, was accomplished by using sodium in ethanol[15] to give an oil of a molecular formula C_9H_8S [m/e 148.0336 (calcd 148.0346)]: ^1H NMR ($CDCl_3$ at 30 °C) δ 0.39 (d, 1 H, J = 4.9 Hz), 1.55 (d, 1 H, J = 4.9 Hz), 5.94–6.35 (m, 6 H) and ^{13}C NMR (1:1 $CDCl_3$–CS_2 at 30 °C) δ 24.0 (dd), 52.3 (s), 60.2 (s), 119.6 (d), 120.4 (d), 124.8 (d), 126.1 (d), 127.2 (d), 127.9 (d).

Although the coupling constant of the bridge methylene protons (J = 4.9 Hz) and the presence of six sp^2 and two quaternary sp^3 carbon signals seem to suggest that the product has a tricyclic structure **2**,[16] variable-temperature ^{13}C (Figure 1) and ^1H NMR and electronic spectra (Figure 2) clearly show the presence of an equilibrium mixture of **1** and **2**. The ^{13}C NMR signals of C-1, C-6, and C-10, especially those of the former two, show regular and substantial upfield shifts with decreasing temperatures whereas those of the sp^2 carbons show only slight temperature dependence. This fact is explicable only in terms of a rapid equilibrium (in the NMR time scale) between **1** and **2** with the latter being the major and thermodynamically more stable component.[17]

The relative ratio **1**/**2** can be estimated if one assumes appropriate chemical shifts for C-1 and C-6. Since the chemical shifts (in 1:1 $CDCl_3$–CS_2 at 30 °C) of C-1 and C-6 of **16**[18] (δ 40.4 and 40.7) and C-1 of **17** (40.6) (cf. C-6: 48.3) are very similar to each other, those of C-1 and C-6 of **2** can be reasonably assumed to be approximately the same as those of **17**, the mean value of C-1 and C-6 thus being about 45 ppm. As for the chemical shifts of C-1 and C-6 of **1**, it seems reasonable to use the value of 115 ppm as their average since the corresponding values of 1,6-methano[10]annulene[19] and annulenyl ion **18**[20] are 114.6 and 113.7 ppm, respectively. With use of these values and the observed average of 56 ppm for **1**/**2** the relative ratio of **1** to **2** can be roughly estimated to be 16:84 at 30 °C (in 1:1 $CDCl_3$–CS_2).[21,22]

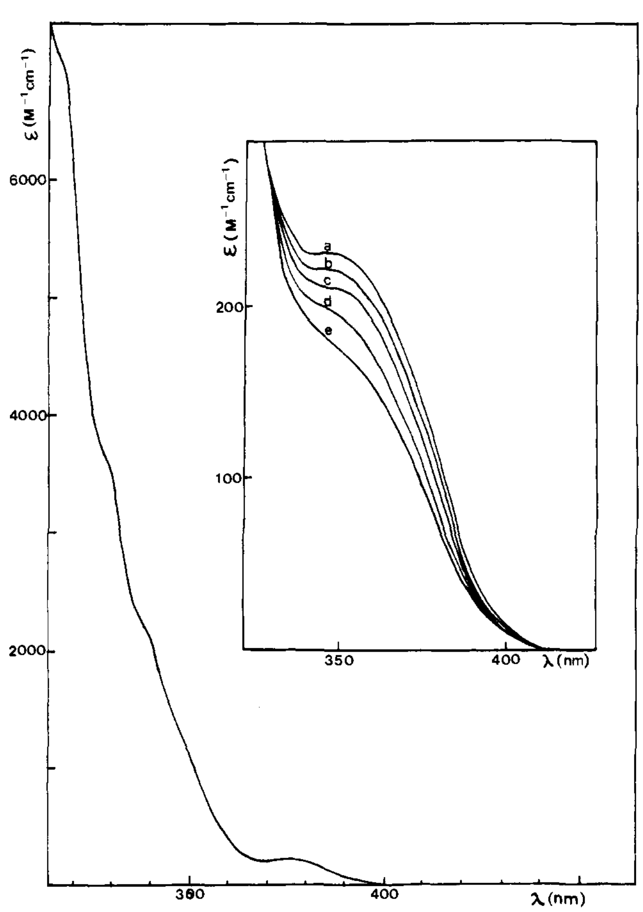

Figure 2. Electronic spectra of the fluxional system **1** ⇄ **2** in cyclohexane. Insert shows variable-temperature spectra of the system in heptane: (a) 48 °C; (b) 26 °C; (c) 0 °C; (d) -24 °C; (e) -55 °C.

Table I. Electronic Spectra of the Fluxional System **1** ⇄ **2** and Some Other Related Compounds

compd	solvent[a]	λ_{max}, nm	ϵ, cm^{-1} M^{-1}	ref
1 ⇄ **2**	C	236 (sh)	6900	present work
		260 (sh)	3700	
		280 (sh)	2200	
		350 (sh)	220	
16	C	270	2600	present work
17	C	270	3100	24
$(CH_2{=}CH)_2S$	H	255	6300	25
		275	5000	
benzo[*b*]-thiophen[b]	C	298	3680	26

[a] C and H denote cyclohexane and hexane, respectively. [b] Only the longest wavelength absorption is listed.

It is well established that the ^1H-vicinal coupling constant of the bridge protons of a bicyclo[4.*n*.1] system like **1** is 9–12 Hz whereas that for tricyclo[4.*n*.1.0] systems like **2** is 4–6 Hz.[23] The relevant coupling constant of the fluxional system **1** ⇄ **2** decreases slightly but regularly with decreasing temperature (4.9 Hz at 35 °C vs. 4.0 Hz at -111 °C in 1:1 CD_2Cl_2–CS_2). This indicates that **1**, having a higher expected value, is more favorable at higher temperatures. This is consistent with the above-mentioned temperature dependence observed in ^{13}C NMR spectra.

The electronic spectrum of this fluxional system shows a shoulder at 350 nm along with additional shoulders below 300 nm (Figure 2 and Table I). Considering the electronic spectra of **16**, **17**, and divinyl sulfide of a similar structure (Table I), the 350-nm absorption cannot be ascribed to **2** but must be due to

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(14) After we developed this new, general synthetic route to vinyl sulfides, similar reactions using trimethyliodosilane were reported. Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1983**, *24*, 2619.

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(16) That no skeletal rearrangement occurred during this deprotection procedure was demonstrated by formation of **15** from the reaction of **1** with PTAD.

(17) No line broadening could be observed even at -111 °C for C-1 and C-6 in ^{13}C NMR spectra (100.40 MHz) and for the bridge methylene protons in ^1H NMR (399.65 MHz). Since the change in the resonance frequencies for C-1 and C-6 due to the valence isomerization **1** ⇄ **2** is ca. 7000 Hz (at 100.40 MHz), $\Delta G^{\neq}$ for this system is calculated to be less than 6.2 kcal/mol.

(18) Compound **16** was synthesized by the reaction of **13** with sodium and ethanol.

(19) (a) Günther, H.; Schmickler, H.; Bremser, W.; Straube, F. A.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 570. (b) Günther, H.; Schmickler, H.; Königshofen, H.; Recker, K.; Vogel. E. *Ibid.* **1973**, *12*, 243.

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(21) Although we believe that the estimation of these chemical shifts for C-1 and C-6 (115 ppm for **1** and 45 ppm for **2**) is rather reliable, small changes in these values do not exert any substantial effect on the following discussion. For example, the combinations 120–45 and 115–43 lead to the ratios 15:85 and 18:82, respectively.

(22) $\Delta G°_{30\,°C}(\mathbf{2} \rightleftarrows \mathbf{1})$ = 1.0 kcal/mol.

(23) Vogel, E.; Wiedemann, W.; Roth, H. D.; Eimer, J.; Günther, H. *Justus Liebigs Ann. Chem.* **1972**, *759*, 1. Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237.

Table II. ^{13}C Shift Temperature Gradients (Δ)[a] for Bridgehead Carbons of the Fluxional System **1** ⇄ **2** and Related Tricyclo[4.3.1.$0^{1,6}$]decane Systems

compd	Δ	compd	Δ
1 ⇄ **2**	5.37[b]	 19	1.11
16	1.87[b]	 20	0.52[b]
17	1.75[b]		
adamantane	0.58[c]	 21	0.57

[a] In 10^{-2} ppm/K units. Calculated from chemical shifts in $CDCl_3$–CS_2 (1:1) (22.49 MHz; internal standard: Me_4Si) at −60, −30, 0, and +30 °C. For detailed data, see the supplementary material. [b] For unsymmetrical compounds the averages of the two chemical shifts are used. [c] The average of the tertiary (0.62) and secondary carbons (0.53). Reference 29.

the extended conjugated system of **1**. Furthermore, the intensity of the absorption shows reversible temperature dependence (Figure 2): it diminishes with decreasing temperatures indicating the decrease of the concentration of **1** and the spectrum reverts to its original one on raising temperatures. This observation is in good accordance with the temperature dependence of the ^{13}C chemical shifts described above, confirming our conclusion that the equilibrium between **1** and **2** is established in solution. Moreover, the decrease in concentration of **1**, due to the temperature change, estimated from ^{13}C NMR spectra (between −60 and +30 °C) and that from the electronic spectra (between −55 and +48 °C) are similar to each other, i.e., about 50%, supporting the validity of the aforementioned evaluation of the equilibrium ratio from ^{13}C NMR spectra.

The equilibrium between **1** and **2** is the first experimental demonstration of cycloheptatriene–norcaradiene equilibrium in bicyclo[4.3.1]decane derivatives, although there are some precedents in bicyclo[4.4.1]undecane derivatives.[19a,27,28] In order to shed light on the detailed nature of this equilibrium, we studied the temperature dependence of ^{13}C chemical shifts of some related tricyclo[4.3.1.$0^{1,6}$]decane derivatives between −60 and +30 °C. Results obtained for the bridgehead carbons are summarized in Table II. For all the compounds studied the signals shift upfield linearly with decreasing temperatures. Inspection of Table II, where the temperature gradients are expressed in terms of Δ values (ppm/K), reveals the following interesting features. First, Δ values for compounds **20** and **21**, which are incapable of undergoing norcaradiene–cycloheptatriene valence isomerization, are very small and almost the same as that of adamantane having similar skeletal rigidity, suggesting that these values are due to intrinsic temperature dependence. Second, Δ values for compounds **16**, **17**, and **19** having a norcaradiene structure are slightly larger than those for **20** and **21**. This is probably accounted for in terms of an equilibrium with the corresponding cycloheptatriene structure to a very minor extent. Third and most important, the Δ value for the fluxional system **1** ⇄ **2** is much larger than those for **16**, **17**, and **19** and almost ten times as large as those for **20** and **21**. This clearly shows that in the case of the system **1** ⇄ **2** there must be some factor which stabilizes the corresponding cycloheptatriene structure **1** compared with **16**, **17**, and **19**. We think that the most straightforward explanation for the stabilization is provided by invoking the aromaticity of **1**, although direct evidence for the diatropicity cannot be obtained from ^1H NMR spectra because of the rapid equilibrium even at low temperatures.[17] It appears that **1** can enjoy the aromatic stabilization to some extent, but it is not large enough to prevent the kinetically favorable pericyclization to **2** from taking place. This is in contrast to the corresponding bridged 10π-carbanionic system **18** which is reported to exist as a delocalized aromatic compound[24,30] and seems to reflect the difference in resonance energy between **18** and **1**.[31]

Finally, it should be noted that the longest wavelength absorption of **1** (λ_{max} 350 nm, ϵ 1400[32]) is about 50 nm higher than that of benzo[*b*]thiophene (Table I). 2,7-Methanoaza[10]annulene and 3,8-methano-10-methoxyaza[10]annulene, both of which are reported to be aromatic, also have the longest wavelength absorptions [364 nm, ϵ 2200 (cyclohexane) for the former[2a] and 385 nm, ϵ 2000 (methanol) for the latter[2c]], about 50 nm higher than those of quinoline [314 nm, ϵ 2900 (cyclohexane)][33] and 3-methoxyisoquinoline [336 nm, ϵ 3470 (methanol)].[34] This seems to support, though does not prove, our conclusion that **1** has an aromatic character although the coincidence of the value of 50 nm itself is fortuitous.

Acknowledgment. We are grateful to Prof. E. Vogel of the University of Köln for helpful discussions. We are indebted to Prof. Iwamura and Dr. Tsukada of the Institute for Molecular Science and of Prof. Kinoshita and Dr. Sugano of The Institute for Solid State Physics, The University of Tokyo, for their assistance in measuring variable-temperature NMR (JOEL GX 400) and electronic spectra, respectively. R.O. thanks the Kurata Foundation (the Kurata Research Grant) for financial support. The generous supply of the silyl halides from Shin-etsu Chemical Co. Ltd. is also gratefully acknowledged.

Registry No. **1**, 73173-00-9; **2**, 90970-08-4; **3**, 4642-24-4; **4**, 73172-90-4; **5**, 73172-95-9; **6**, 73172-96-0; **7**, 90970-09-5; **8**, 90970-10-8; **9**, 90970-11-9; **10**, 90970-12-0; **11**, 90970-13-1; **12**, 90970-14-2; **13**, 90970-15-3; **14**, 90970-16-4; **15**, 90970-17-5; CH_2=CHMgBr, 1826-67-1; $PhCH_2SNa$, 3492-64-6; $Ph_3P(SCN)_2$, 66365-41-1.

Supplementary Material Available: ^1H and ^{13}C NMR, infrared, mass spectral, and elemental analytical data for the compounds **5**–**16** and variable-temperature ^{13}C NMR data for the compounds **1**, **16**, **17**, and **19**–**21** (6 pages). Ordering information is given on any current masthead page.

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(32) Calculated by using the values of molar fraction 0.16 and ϵ 220.

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