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The Chemical Shifts of the Bridge Methylene Protons of 1,6-Methano[11]annulene Systems. Positive Evidence for the Assignments

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Synopsis. The assignments of the chemical shifts to the bridge methylene protons of 1,6-methano[11]annulen-9-one (**3**) were established on the basis of their lanthanoid-induced shifting. Those of the protonated cation of **3** were proven from the spectrum of a mixture of 12-d_1 derivatives of **3** in trifluoroacetic acid.

The ^{1}H-NMR chemical shifts of the bridge protons are key indices to know the tropicity of bridged annulenes. Thus, the assignments of the chemical shifts to the bridge protons are quite important, especially those of asymmetrical bridged-annulenes such as 1,6-methano[11]annulene systems.

During the course of our investigations of the condensed pi-electron systems containing the methano[11]annulene part (**1**) and its protonated species (**2**),[1] we noticed that the chemical shifts of the bridge methylene protons of methano[11]annulenes had been assigned without positive proof. This paper will deal with the evidence for the assignments to the bridge protons of 1,6-methano[11]annulen-9-one (**3**) and its protonated cation (**4**).[2]

Results and Discussion

The chemical shifts of the bridge methylene protons of 1,6-methano[11]annulenes (mainly bicyclo[5.4.1]dodeca-2,5,7,9,11(1)-pentaen-4-ylidenes), except those of **3**, were previoulsy assigned without any explanation.[3] The assignments to the bridge protons (H_s and H_a, the *syn* and *anti*-protons to the cycloheptatriene system respectively) of **3** by Vogel and his co-workers[2] were based on an assumption of long-range couplings (W-shape couplings) between H_2, (H_5), and H_a (δ=1.68, (dt), $J_{a,s}$=11.4 Hz, and $J_{a,2}$=$J_{a,5}$=1.5 Hz). The assignment may be reasonable because, in the spectrum most 1,6-methano[11]annulenes,[3] the center of the signals (a doublet) due to the other bridge proton (H_s) appears in the δ=0.2—0.0 range; the chemical shifts of H_s may not be affected greatly by substituents on the C_5-bridge. However, one can point out that the long-range couplings might be replaced by allylic couplings between H_2, (H_5), and H_s, since the allylic angles of H_a (θ=0°, from a molecular model) indicate J_{allylic}=0 Hz, while those of H_s (θ=60°) indicate J_{allylic}=1.5 Hz. Thus, we can not apply the assignments of the bridge methylene protons of **3** to those of more complicated systems such as **1** without any positive evidence for the W-shape coupling. In order to distinguish the signals for H_a and those for H_3 of **3**, we used lanthanoid-shift reagents (Eu(fod)$_3$ and Pr(fod)$_3$). The lanthanoid-induced shifting (given in Table 1) of the peripheral protons is normal pseudocontact shifting. Now, the signals appearing as the doublet of triplets at δ=1.68 and as the doublet at δ=0.04 are for H_a and H_s respectively, since the former are shifted more than the latter. *The long-range couplings are exactly due to the W-shape coupling between H_2, (H_5), and H_a.*

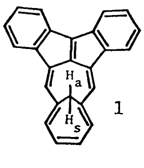
Table 1. Chemical shifts (δ) and lanthanoid-induced shifts ($\Delta\delta$, ppm) of 1,6-methano[11]annulen-9-one (**3**)

Proton	δ[a]	$\Delta\delta$				
		Concn of Eu(fod)$_3$[b]			Concn of Pr(fod)$_3$[b]	
		0.047	0.063	0.104	0.019	0.06
$H_{8,10}$	6.02	c)	−2.01	−2.92	+1.08	+2.78
$H_{7,11}$	7.18	c)	−0.55	−0.78	+0.26	+0.73
$H_{2,5}$	6.90	c)	−0.37	−0.51	+0.12	+0.39
$H_{3,4}$	7.21	c)	−0.37	−0.47	+0.03	+0.14
H_a-(dt)	1.68	−0.68	−0.96	−1.34	+0.57	+1.55
H_s-(d)	0.04	−0.26	−0.36	−0.53	+0.17	+0.59

a) Ref. 2. b) Mole ratios to the substrate. c) Overlapping each other.

The crucial difference between the multiplicities of H_a and H_s should be generally found in the specta of other 1,6-methano[11]annulenes containing the cycloheptatriene system, such as **1** and the hydrocarbon (**5**).[4]

The spectrum of cation **2** shows a broad-doublet at δ=−0.21 (J=11.4 Hz, $W_{1/2}$=5 Hz) and a doublet at δ=0.45 (J=11.4 Hz, $W_{1/2}$=1 Hz) for the bridge protons.[1] Similarly, the signals for those of **4**[2] and the cation (**6**)[5] are seen as broad-doublets in the higher-field and doublets in the lower-field: **4**: δ=−0.6 (bd) and δ=−0.4 (d); **6**: δ=−1.8 (bd) and δ=−0.3 (d). For those, the high-field- and low-field protons were assigned tentatively to H_a and H_s respectively.[2,6)]



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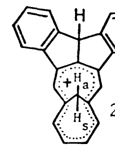

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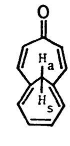

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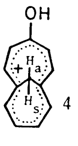
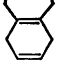


4

In order to establish the assignments, we chose the 12-monodeuterated derivatives of **4** as the models. A mixture of the ketones (**7** and **8**) was prepared from the acetal (**9**) based on a modification of the method of Vogel.[2] The ^{1}H-NMR spectra of the mixture in CCl_4 and in trifluoroacetic acid (TFA) are shown in Fig. 1. The spectrum in CCl_4 indicates that **7** and **8** are formed in a ratio of 3 to 1. In TFA, the cations (**12** and **13**) should be formed in a 3-to-1 ratio respectively.



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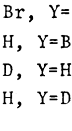

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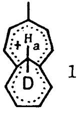

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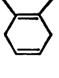

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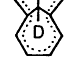
10a X=Br, Y=H
10b X=H, Y=Br
11a X=D, Y=H
11b X=H, Y=D



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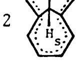

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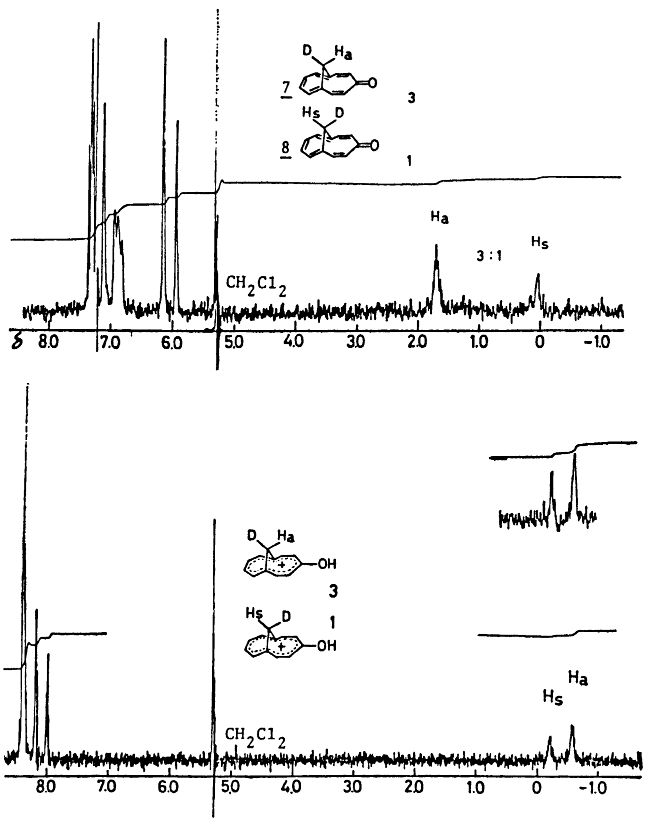

Fig. 1. ^{1}H-NMR spectra of 1,6-methano[11]annulen-9-one-12-d_1 (**7** and **8**) in CCl_4 (upper) and in TFA (lower).

Now, the high-field bridge proton of **4** is H_a, and the other is H_s. Thus, it is true that the line-broadening of the signals for H_a of **4** is due to the W-shape coupling between H_2, (H_5), and H_a. This assignment can aslo be applied to each bridge proton of **2** and **6**.

Experimental

General. Melting points were determined on a Thomas Hoover MP apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi Model 215 spectrometer. NMR spectra were obtained on Varian A-60 or JEOL JNM-PMX 60 spectrometers, using tetramethylsilane and/or dichloromethane as internal standards. Mass spectral studies were conducted using a Hitachi M-52 spectrometer.

*12,12-Dibromotricyclo$[5.4.1.0^{1,7}]$dodeca-9-en-4-one Ethylene Acetal (**9a**).* To a mixture of the acetal (**9**, 2.0 g) and *t*-BuOK (1.41 g) in dry ether (25 ml) was added a solution of bromoform (1.3 ml) in ether (1.3 ml) at 0 °C under a nitrogen atmosphere over a period of 1 h. After 19 h stirring at 0 °C, the mixture was diluted with water (60 ml) and extracted with CH_2Cl_2 (3×40 ml). The extracts were combined, dried ($MgSO_4$), concentrated, and subjected to chromatography on alumina. The adduct, **9a**, was isolated in a 28.3% yield (1.04 g). **9a**: colorless prisms, mp 95—122 °C; NMR ($CDCl_3$) δ=1.62—1.93 (m, 8H), 2.28 (bd, 4H), 3.88 (s, 4H), and 5.58 (bt, 2H). Found: C, 44.23; H, 4.86%; M^+, 380 (1.24%), 378 (2.49%), and 376 (1.58%). Calcd for $C_{14}H_{18}Br_2O_2$: C, 44.47; H, 4.80%.

*12-Bromotricyclo$[5.4.1.0^{1,7}]$dodeca-9-en-4-one Ethylene Acetal (**10a** and **10b**).* A mixture of **9a** (2.63 g), tributyltin hydride (2.22 g), AIBN (13 mg), and dry cyclohexane (18 ml) was heated at 60 °C for 2.5 h and then at 80 °C for 1.5 h while being stirred under an argon atmosphere. Carbon tetrachloride (5 ml) was then added to the solution, and the mixture was concentrated *in vacuo*. The resulting oil was chromatographed on alumina, and eluted with hexane–benzene. A colorless, amorphous powder (1.61 g) was thus obtained. A mixture of **10a** and **10b**: NMR (CCl_4) δ= 1.53—1.83 (m, 8H), 2.16 and 2.23 (bs each, 4H), 2.88 (s, 0.6H), 3.18 (s, 0.4H), 3.80 and 3.85 (s each, 4H), and 5.48 (bs, 2H). Found: M^+, 300 (10.2%) and 298 (11.7%).

*Tricyclo$[5.4.1.0^{1,7}]$dodeca-9-en-4-one-12-d_1 Ethylene Acetal (**11a** and **11b**).* To a solution of a mixture of **10a** and **10b** (1.0 g) in THF (dry, oxygen free) was added *n*-BuLi (1.56 M in hexane, 2.9 ml) at −78 °C under argon. After 1.5 h stirring, the solution was allowed to warm to room temperature. After having 0.5 ml of methanol-d_4 syringed in, stirred for 10 min, poured onto brine, and extracted with ether (3×50 ml), the combined organic solutions were dried ($MgSO_4$) and evaporated, yielding a pale yellow oil (728 mg, 98.6%). NMR (CCl_4) δ=0.13 (bs, 0.75H), 0.66 (bs, 0.25H), 1.38—1.78 (m, 8H), 2.20 (bs, 4H), 3.84 (s, 4H), and 5.45 (bs, 2H). The crude **11a** and **11b** thus obtained were used without further purification.

*Bicyclo[5.4.1]dodeca-2,5,7,9,11(1)-pentaen-4-one-12-d_1 (**7** and **8**).* A solution of bromine (527 mg) in CH_2Cl_2 (7 ml) was added to a mixture of **11a** and **11b** (728 mg) in CH_2Cl_2 (20 ml) at −78 °C over a period of 20 min. The subsequent evaporation of the solvent gave a pale yellow solid, which was then heated under reflux with 15% KOH in methanol (20 ml) for 2 h. After the solvent had then been removed and the mixture had been diluted with water (50 ml) and extracted with ether (3×40 ml), the extracts were combined, dried ($MgSO_4$), and concentrated, yielding a colorless oil (714 mg). To a solution of the crude products in THF (20 ml) were added perchloric acid (60%, 0.4 ml) and water (4 ml), after which the mixture was heated at 50 °C for 5 h. After most of the THF had been removed *in vacuo*, and the mixture had been diluted with water (50 ml), and extracted with ether (3×25 ml), the combined organic solutions were washed with aqueous $NaHCO_3$, water, and brine, dried ($MgSO_4$), and evaporated, thus yielding a pale yellow oil (580 mg). It was chromatographed on silica gel (30 g) and eluted with hexane–benzene, thus yielding bicyclo[5.4.1]-dodeca-7,9,11(1)-trien-4-one-12-d_1 as a pale yellow oil (320 mg, 52%). IR (film) 1716 cm^{-1}; NMR (CCl_4) δ=1.57 (bs, 0.3H), 2.85—3.10 (m, 8.7H), 5.98 (m, 2H), and 6.46 (m, 2H). The dehydrogenation of the ketones (90 mg) with DDQ (418 mg) in benzene (4.5 ml) at 115 °C for 12 h in a sealed tube gave a mixture of **7** and **8** (26 mg, 30%, mp 69.5—71.8 °C) after repeated chromatography on alumina (15 g). IR (CCl_4) 1624 cm^{-1}; MS *m/e* (%) 171(29.7), 170 (4.5), 143 (53.2), and 142 (100).

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