

THE NUCLEAR MAGNETIC RESONANCE SPECTRUM AND AROMATIC CHARACTER OF
1,6;8,13-PROPANO-[14]ANNULENE (1a)

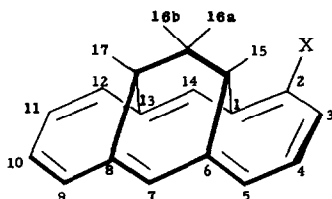
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To corroborate the postulated aromaticity of [14]annulenes (2) we have analysed the pmr spectra of the recently synthesized 1,6;8,13-propano-[14]annulene (3) (I) and its 2-nitro derivative (II).



- I, X = H
II, X = NO₂

The hydrocarbon I has two planes of symmetry and its fourteen protons appear as three types of spin systems: AA'BB' (H₂, H₃, H₄, H₅, and H₉, H₁₀, H₁₁, H₁₂), and A₂ (H₇, H₁₄) for the ring protons, and A₂B₂ (H₁₅, H₁₇, H_{16a}, H_{16b}) for the bridge protons. At 220 MHz, the AA'BB' system becomes essentially AA'MM' (Fig. 1a) but spinning sidebands overlapped to some extent with the lines of low intensity, making the analysis less certain. However, the 60-MHz spectrum (Fig. 1b) as calculated from the results of the computer analysis of the 220-MHz spectrum was in good agreement with experiment which indicates the general correctness of the coupling constant assignments.

In the nitro derivative II, there is no symmetry and the resulting nine-spin system for the ring protons could only be partly interpreted. The low-field doublet of H₃ and singlet of H₁₄ are well separated from the resonances of the other protons. In the upfield portion of the spectrum, the doublet of H₅ and the singlet of H₇ partially overlap, while H₄ appears as a doublet of doublets at the high-field end of the multiplet for the highly coupled four-spin system of the residual ring protons (H₉ to H₁₂). Furthermore, spinning sidebands increased the difficulty of interpretation of line intensities. No attempt was made to assign the lines in this complex pattern in detail. The shift and coupling parameters which have been derived for I and II are summarized in Table I.

The comparison of the chemical shifts of the protons in several related compounds as shown in Table II indicates that the resonance frequencies of the peripheral protons in I are in general accord with those of other bridged annulenes. The downfield shift resulting from the ring current is slightly greater in the [14]annulenes than in the [10]annulenes, as predicted from simple theoretical models (6). The aromatic character of I is further confirmed by the resonance frequency of the bridged protons 15 and 17, which corresponds to a shielding of 3.1 ppm relative

to ~~1,6~~-1,6;8,13-bismethano-[14]annulene (7). The similarity of the vicinal coupling constants $J_{3,4}$ and $J_{4,5}$ indicates that the π -electrons are largely delocalized and that the C-C bonds should be about of equal length (8). The coupling constant $J_{15,17}$, which can only be observed in the nitro compound, is a good example of a long-range coupling resulting from the perfect W-configuration (9).

The substituent effects ΔW and ΔJ associated with the nitro group (see Table I) may not be directly comparable to the corresponding effects of nitro on the bridged [10]annulenes (5) because the nitro derivative had low solubility in chloroform and had to be measured in methylene chloride, which provides a potential solvent effect. On top of this, the perturbing influence of bromine on a 10 π -electron system appears to differ from its perturbation on a 14 π -electron system (5). Nevertheless, the results are in rather good agreement with the substituent effects reported previously (5, 10), which provides additional evidence that the π -electron system of I is similar to the aromatic systems of naphthalene and the bridged [10]annulenes (11). (See Table II).

The spectra were recorded on Varian HR-220 and A-56/60A spectrometers. The line positions were determined using audio sideband calibration and are statistical averages obtained from several scans in both field directions. The starting parameters were refined by the iterative computer program LAOCOON (12). The standard deviation of the calculated from the experimental line positions was in all cases less than 0.1 Hz. On this basis, the errors in chemical shifts and coupling constants are estimated to be less than 0.002 ppm and 0.1 Hz, respectively.

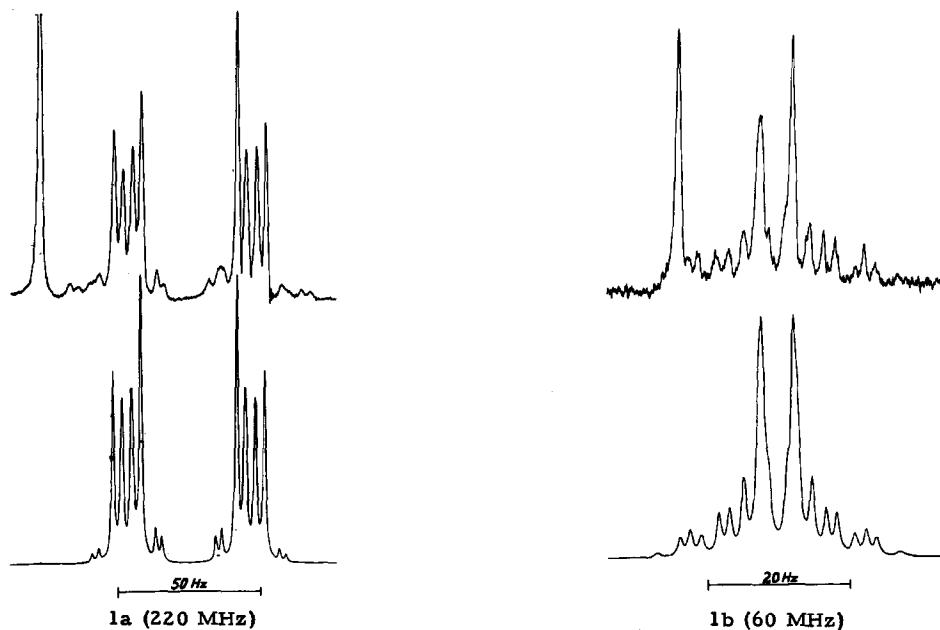


Figure 1. The AA'BB' spectra (above) of the peripheral protons in 1,6;8,13-propano-[14]annulene (I) at 220 MHz and 60 MHz including the computer-simulated spectra (below). The long-range coupling constants in the low-field part and the singlet of the protons 7 and 14 are not reproduced in the theoretical spectra.

Table I

Chemical Shifts W (σ -scale) and Coupling Constants J of 1,6;8,13-Propano-[14]annulene (I) in CDCl_3 and of 2-Nitro-1,6;8,13-propano-[14]annulene (II) in CH_2Cl_2

W or J	X = H (I)	X = NO_2 (II)	Δ
$W(2)$	7.736 ppm	-	-
(3)	7.554	8.721 ppm	1.167 ppm
(4)	7.554	7.633	0.079
(5)	7.736	7.979	0.243
(7)	7.885	7.956	0.071
(14)	7.885	8.548	0.663
(15)	-1.157	-1.266 ^a	-0.109
(16a)	-0.611	-0.447	0.164
(16b)	-0.611	-0.546	0.065
(17)	-1.157	-1.068 ^a	0.089
$J(2,5)$	1.37 Hz	-	-
(3,4)	9.50	10.27 Hz	0.77 Hz
(3,5)	0.41	-	-
(4,5)	9.15	9.03	-0.12
(15,17)	-	2.64	-
(15,16a)	2.84	2.87 ^b	-
(15,16b)	2.84	2.76 ^b	-
(16a,16b)	-	12.47	-

^a Assigned in accord with the spectrum of 2-nitro-1,6-methano-[10]annulene (5). ^b These couplings could be interchanged and are not as certain as the others.

Table II

Chemical Shifts in ppm on the σ -scale of the Peripheral Protons in Bridged Annulenes

Annulene	σ_2	σ_3	σ_{14}	Lit.
1,6-Methano-[10]annulene	7.27	6.95	-	13
1,6-Oxido-[10]annulene	7.46	7.26	-	13
1,6-Imino-[10]annulene	7.41	7.11	-	14
1,6;8,13-Bisoxido-[14]annulene	7.75	7.60	7.94	15
1,6-Methano-8,13-oxido-[14]-annulene	7.65 ^a	7.34 ^a	7.75	5
annulene	7.64 ^b	7.43 ^b	7.75	
1,6;8,13-Propano-[14]annulene	7.74	7.55	7.88	This work

^a Protons on methano side of the ring. ^b Protons on the oxido side of the ring.

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