that reported by Albert and Phillips[16] and Wang,[17] indicating that the boron atom was originally substituted at the 5-position of the pyrimidine ring system.

(16) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956).
(17) S. Y. Wang, *J. Am. Chem. Soc.*, **81**, 3786 (1959).

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C^{13} and H^1 Nuclear Magnetic Resonance Spectra of Cycloalkanes

Sir:

We have measured C^{13} and H^1 n.m.r. spectra of the cycloalkanes from cyclopropane to cycloheptadecane, as well as those of several n-alkanes from hexadecane to dotriacontane. The results are presented in Table I along with data on some of the same compounds reported elsewhere. The C^{13} spectra were measured as previously reported.[1] Solid samples were dissolved
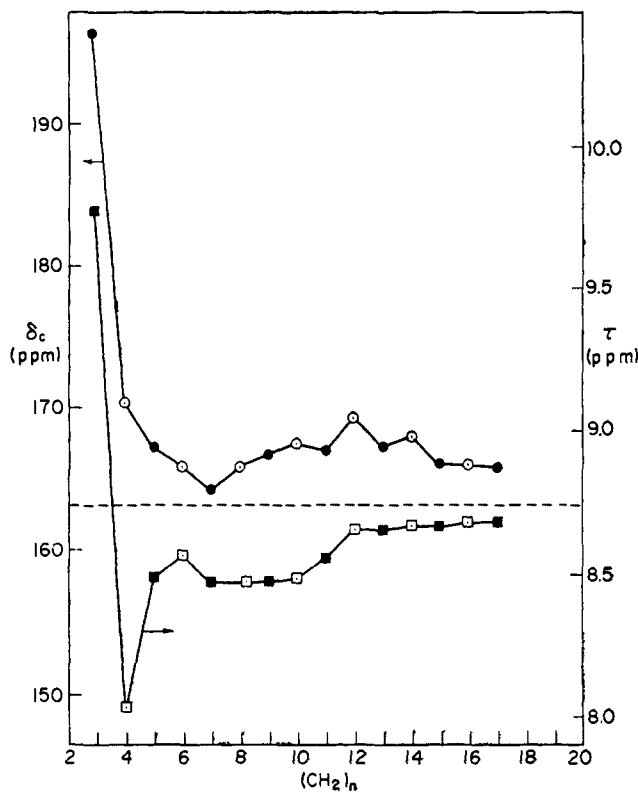

Fig. 1.—Nuclear magnetic shieldings in cycloalkanes: carbon (○,●); hydrogen (□,■); central CH_2 groups in long-chain n-alkanes for both carbon and hydrogen (- - - -).

in CS_2 and their shieldings corrected to neat liquid values. All measurements were referred to external CS_2. The H^1 spectra were obtained with a Varian A-60 spectrometer and referred to internal tetramethylsilane.[2] Corrections to infinite dilution were made for the cycloalkanes and n-alkanes in carbon tetrachloride.

The hydrogen and carbon shieldings are plotted against ring size in Fig. 1. The latter values display

(1) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).
(2) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

TABLE I

Alkane	δ_c,[e] p.p.m.	J_{C-H}, c.p.s. This work	J_{C-H}, c.p.s. Other work[a]	τ, p.p.m. This work[g]	τ, p.p.m. Other work
C_3H_6	196.3	162 ± 2	161		9.778,[b] 9.78[c]
C_4H_8	170.4	136 ± 1	134		8.02,[d] 8.04[c]
C_5H_{10}	167.2	131 ± 2	128	8.494[h]	8.492,[b] 8.49[d] 8.49[c]
C_6H_{12}	165.9	127 ± 2	124	8.566	8.564,[b] 8.56[c]
C_7H_{14}	164.3	126 ± 2	123	8.474	8.470,[b] 8.46[c]
C_8H_{16}	165.9	127 ± 2	122	8.470	8.46[c]
C_9H_{18}	166.7	125 ± 2		8.473	
$C_{10}H_{20}$	167.5	126 ± 2	118	8.486	
$C_{11}H_{22}$	167.1	126 ± 2		8.555	
$C_{12}H_{24}$	169.3[f]	123 ± 3	123	8.658	
$C_{13}H_{26}$	167.3[f]	127 ± 2		8.652	
$C_{14}H_{28}$	167.9[f]	126 ± 2		8.670	
$C_{15}H_{30}$	166.1[f]	126 ± 2		8.666	
$C_{16}H_{32}$	166.0[f]	126 ± 3		8.681	
$C_{17}H_{34}$	165.8[f]	126 ± 2		8.684	
$n-C_{16}H_{34}$	163.1			8.743	
$n-C_{20}H_{42}$	163.7[f]	128 ± 3		8.745	
$n-C_{22}H_{46}$	163.3[f]	127 ± 2		8.744	
$n-C_{28}H_{58}$	163.9[f]	128 ± 2		8.745	
$n-C_{32}H_{66}$	163.0[f]	124 ± 4		8.747	

[a] Ref. 10. [b] Tables of τ values for a variety of organic compounds, G. V. D. Tiers, Minnesota Mining and Mfg. Co., 1958. [c] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961). [d] E. Lippert and H. Prigge, *Ber. Bunsenges. Physik. Chem.*, **67**, 415 (1963). [e] Standard deviation ±0.3 p.p.m. for cyclics; standard deviation ±0.5 p.p.m. for n-alkanes. [f] Measured in CS_2 and corrected as described in text. [g] Standard deviation ±0.001 p.p.m. for cyclics; standard deviation ±0.002 p.p.m. for n-alkanes; all measurements made in carbon tetrachloride and corrected as described in text. [h] Standard deviation ±0.003 p.p.m.

an oscillatory behavior for medium rings, but smooth curves can be drawn through the points for odd- and even-membered rings separately. This oscillatory phenomenon, which is also observed for other properties such as heats of combustion[3a] and refractions,[3b] suggests that the ease with which conformational changes occur is reflected in the carbon shieldings. There appears to be no corresponding effect on the hydrogen shieldings, which parallel those of carbon only in the extremely high shieldings observed in cyclopropane. In an attempt to account for the cyclopropane spectra, we have turned to the ring-current model previously used to explain hydrogen shieldings in molecules containing three-membered rings.[4,5] The hydrogen and carbon shieldings, relative to those in central methylene groups in long-chain n-alkanes, are 1.0 and 33 p.p.m., respectively. As the assumed current radius is increased from 0.88 Å.,[4,5] the calculated carbon shielding[6] decreases and that for the protons increases until their *ratio* becomes 33 for a radius of 1.10 Å. The *values* of the shieldings are reproduced by assuming that a current corresponding to 3.5 electrons flows in the 1.10-Å. ring. The equivalent dipole of this current is about 20% larger than that of the 4.5-electron, 0.88-Å., current assumed by Winstein, Boikess, and Brauman[5]; the difference would not markedly affect their correlations for distant protons. The magnetic susceptibility of cyclopropane can be similarly calculated by assuming

(3) (a) Sj. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952); (b) L. Ruzicka, V. Prelog, *et al.*, *Helv. Chim. Acta*, **32**, 256 (1949).
(4) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).
(5) S. Winstein, R. S. Boikess, and J. I. Brauman, private communication.
(6) The calculations were performed by J. I. Brauman.

that it consists of three normal methylene groups with the addition of a ring current. The experimental molar susceptibility[7] is -39.9×10^{-6}, and the methylene group susceptibility is given[8] as -11.3 to -11.9×10^{-6}, indicating an anomalous enhancement of -4 to -6×10^{-6}. The value calculated from our assumptions is -6.0×10^{-6}. Thus, the simple form of a ring-current model accounts satisfactorily for the hydrogen and carbon magnetic shieldings and the magnetic susceptibility of cyclopropane, as well as for the long-range shielding effects of three-membered rings in polycyclic compounds. There seem to be at present no empirical grounds for further refinement of the model. No quantitative theoretical justification for the assumption of a ring current has been found, nor have any other explanations for these data been proposed.

The possibility of similar effects in larger rings cannot be entirely discounted, but we have found no satisfactory way to test such a hypothesis. The differences between the carbon shieldings in cyclic hydrocarbons, including cyclopropane, and those in linear ones may be crudely fitted by a model of the form proposed for n-alkanes.[9] The effects must have a different origin, however, despite the similarity in form, because it is easy to show that reasonable bond anisotropies cannot account for the large effects found in the carbon spectra. Furthermore, the differences between the effects on carbon and hydrogen shieldings cannot be explained by an expression with the radial and angular form of that which has been proposed. Whatever the source of the effects, the existence of these differences among rings and between even large rings and straight-chain hydrocarbons demonstrates the importance of conformational factors to the shieldings.

Significant differences between the one-bond carbon–hydrogen coupling constants measured in C^{13} spectra and those measured in H^1 spectra[10] appear in Table I. A possible source of this discrepancy is the asymmetric broadening of the multiplet components in the presence of couplings among the protons. A calculation[11] was carried out on the seven-spin system $-CH_2C^{13}H_2CH_2-$, using reasonable values for carbon–hydrogen and hydrogen–hydrogen long-range coupling constants. To simulate the subjective location of the centers of unresolved slightly asymmetric bands, the first moments of the satellite multiplets were calculated. With an assumed one-bond coupling of 124.0 c.p.s., the hydrogen spectrum gave an apparent coupling of 122.7 c.p.s. and the carbon spectrum, one of 125.7 c.p.s. The difference is in the same direction as that observed and is of about the same size.

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Aliphatic Dienyl Cations

Sir:

The dienylic cations I and II are stable in 96% H_2SO_4 and can be directly observed by the standard spectroscopic techniques. In contrast, cation IV has a half-life of less than 10 sec. at 25°. Addition of the dienylic alcohol III to 96% H_2SO_4 leads immediately and quantitatively to the cyclopentenyl cation V. This latter rearrangement is proving to be general and has been successful with homologs of III in which ethyl and isobutyl replaced the methyl at C-1. The cation V was identified by its characteristic n.m.r. spectrum.[1]
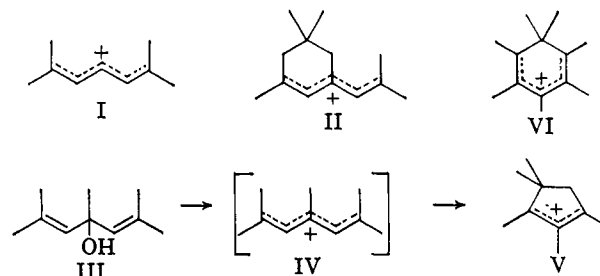
Previously there has been one isolated example of the direct observation of a dienylic cation of the type which is in equilibrium with an aliphatic triene. Doering, Saunders, and the group at Humble Oil Company discovered the heptamethylcyclohexadienyl cation (VI) as a product of exhaustive methylation of benzene.[2] Cation VI is half-formed at approximately a pH of zero. Cations I and II are probably of similar stability although chemical instability in the more dilute acids prevented accurate evaluation. It is certain that the half-formation point is below 50% H_2SO_4.

A number of cyclohexadienyl cations which were formed by protonation of benzene derivatives have been directly observed. The classic paper of MacLean and Mackor[3] reports the n.m.r. spectra of a number of such ions, including those formed by protonation of toluene, mesitylene, and hexamethylbenzene. The stability of the benzene ring necessitates high levels of acidity in order to produce these cations. MacLean and Mackor used $HF-BF_3$, and Olah and co-workers[4] have observed similar spectra in $HF-SbF_5$. The most basic of these alkyl benzenes is hexamethylbenzene and this is half-protonated in 92% H_2SO_4.[5]

(7) J. R. Lacher, J. W. Pollock, and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).

(8) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 94.

(9) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1701 (1963).

(10) C. S. Foote, *Tetrahedron Letters*, **9**, 579 (1963).

(11) The Frequint IV program, written by Dr. A. A. Bothner-By of Mellon Institute, was employed.

(1) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

(2) W. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(3) C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

(4) G. Olah and co-workers, unpublished results of the Dow Chemical Company.

(5) N. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).