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THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF CYCLOPROPANE DERIVATIVES

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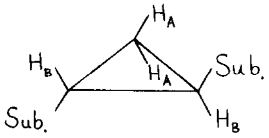
PROTON n.m.r. spectra of some substituted cyclopropane derivatives have recently been reported and interpreted for the elucidation of their structures (1).

In the present research, the chemical shifts and coupling constants of several trans-1,2-disubstituted cyclopropane derivatives have been determined. According to Jackman (2) the cis and trans coupling constants in trans-1,2-dibromocyclopropane are equal. However, Gutowsky (3) has shown that it is unlikely for each pair of AB coupling constants to be identical in the A_2B_2 spin system. The spectra obtained in the present research were first analyzed by assuming the J_{AB} coupling constants being equal, and found to be in fairly good agreement with the calculated spectra. However, detailed analyses showed that the cis and trans coupling constants were not equal. The n.m.r. spectrum of trans-1,2-dibenzoylcyclopropane was analyzed as AA'XX' system and other spectra as AA'BB' system.

The values obtained for the 60 Mc. spectra are given in Tables 1 and 2. We assumed that the cis coupling constants are larger than the trans constants.



Sub.= Substituent

FIG. 1

TABLE 1

Chemical Shifts Relative to TMS as Internal Standard

Substituents	Solvents	Chemical Shifts (c.p.s.)	
		H_A	H_B
$-COCl$	CCl_4	109.26	170.09
$-COC_6H_5$	"	98.73	195.31
$-COOCH_3$	"	79.71	121.80
$-COOCH_3$	CF_3COOH	99.70	143.22
$-COOH$	"	105.24	144.80
$-CONH_2$	"	107.61	151.13
$-CONHCOOCH_3$	"	106.03	163.00
$-CN$	$CHCl_3$	95.27	123.63
$-CH_2OH$	"	23.99	56.72
$-CH_2I$	CCl_4	47.56	72.07
$-NHCOOC_2H_5$	"	56.93	152.07

TABLE 2

Coupling Constants

Substituents	Solvents	Coupling Constants, J_{AB}(c.p.s.)	
		J_{cis}	J_{trans}
$-COC_6H_5$	CCl_4	8.7	5.3
$-COOCH_3$	"	8.8	6.6
-COCl	"	9.1	5.9
-CN	$CHCl_3$	10.2	5.5

The gem. coupling constant, J_{AA} and the vicinal constant, J_{BB} of dibenzoylcyclopropane are as follows:

J_{AA}= -4.0 c.p.s. J_{BB}=4.5 c.p.s.

It was not possible to fit the calculated spectrum to the observed if the gem. coupling constant was taken as positive. The n.m.r. spectra of trans-1,2-bismethylolcyclopropane and bisiodomethylcyclopropane indicated the hindered rotation of substituents. If the rotation of substituents were sufficiently fast, the two hydrogens would be equivalent and hence the spectra would be of the type A_2X. However, it seems that the observed spectra can be accounted for only on the basis of ABX spectra predicted for hindered rotation in which the two hydrogens are not equivalent (FIG. 2).

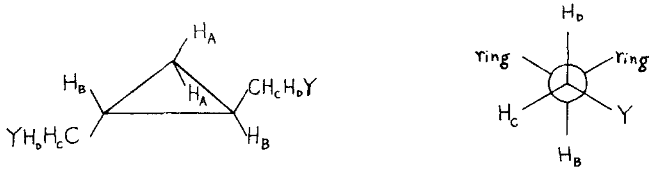


FIG. 2

The analysis of the spectrum of 1,2-bismethylolcyclopropane provided the three coupling constants, J_{CD}= 11.6 c.p.s., J_{BD}= 9.7 c.p.s. and J_{BC}= 4.9 c.p.s., where we assumed that the J_{trans} is larger than the J_{gauche}.

The analyses of the n.m.r. spectra of cis-1,2-disubstituted and other cyclopropane derivatives are now proceeding and they will be reported shortly. All the compounds, here examined, have been synthesized in our laboratory; detailes of the syntheses will be published elsewhere.

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REFERENCES

1. D. J. Patel, M. E. H. Howden and J. D. Roberts, J. Amer. Chem. Soc. 85, 3218 (1963).
   J. D. Graham and M. T. Rogers, J. Amer. Chem. Soc. 84, 2249 (1962).
   K. B. Wiberg and B. J. Nist, J. Amer. Chem. Soc. 85, 2788 (1963).
2. L. M. Jackman, Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry p.127. Tokyo Kagaku Dojin Press, Tokyo (1962).
3. D. M. Grant and H. S. Gutowsky, J. Chem. Phys. 34, 699 (1961).