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NMR SPECTRA OF THREE-MEMBERED RING COMPOUNDS. II.
BROMO- AND IODOCYCLOPROPANE

Gerd Schrumpf and Wolfgang Lüttke

Organisch-Chemisches Institut
der Universität Göttingen

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Although a great deal of nmr information about three-membered ring compounds has accumulated in the past, only few precise data on monosubstituted cyclopropanes have appeared in the literature (1-3). In view of our investigations in the vinylcyclopropane and biscyclopropyl series (4,5) it appeared highly desirable to obtain chemical shift and coupling data of monohalogen- and monoalkylcyclopropanes. Besides, the very rigid geometry of the cyclopropane ring allows substituent effects being studied with a minimum geometrical distortion of the hydrocarbon framework. In this study we want to report the analysis of the nmr spectra of bromo- and iodocyclopropane together with their ^{13}C satellite spectra.

Both compounds were measured at 100 MHz as neat liquids with 6% benzene added for internal referencing. Experimental lines were assigned to theoretical transitions with the aid of spin tickling techniques, and the nmr parameters were obtained using the LAOCOON computer program (6). Final data for those species of the two compounds containing only ^{12}C nuclei are summarized in the table. ^{13}C satellite spectra were recorded at two different radio power levels, one at a stronger rf amplitude in order to optimize the signal-to-noise ratio, and one at a lower power level to minimize saturation effects. In the latter case spectra accumulation was employed. Analysis of the spectra proceeded by the effective Larmor frequency method. The H-H coupling constants thus obtained agreed with those obtained from the normal spectrum to within 0.1 Hz. One-bond ^{13}C-H couplings as shown in the table are taken as twice the difference between the effective chemical shift of the satellite spectra and the corresponding chemical shift obtained from the main spectra. After consideration of all possible sources of error we cannot claim the precision of the ^{13}C-H couplings to better than 0.25 Hz. All other data are accurate to 0.1 Hz.

Table

Chemical shifts and coupling constants in bromo- and iodocyclopropane[a)]

	C_3H_5Br	C_3H_5J
ν_1	-636.02	-626.57
ν_3	-648.00	-653.31
ν_5	-448.11	-499.60
J_{12}	10.61	9.78
J_{13}	- 6.14	- 5.93
J_{14}	6.99	6.65
J_{15}	7.11	7.51
J_{34}	10.23	9.98
J_{35}	3.82	4.37
$J(^{13}C_1-H_1)$	163.0	162.4
$J(^{13}C_1-H_3)$	164.7	165.2
$J(^{13}C_3-H_5)$	193.4	187.9

a) All data are given in Hz; the chemical shifts are measured relative to internal benzene; the numbering follows fig. 1.

Protons cis to the substituent are more strongly shielded than those on the opposite side of the ring plane, the shift difference between cis and trans protons in bromocyclopropane being about only one half that in iodocyclopropane.

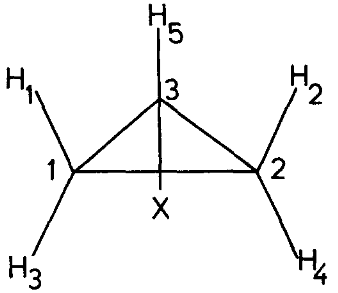

Fig. 1 Numbering of atoms in monosubstituted cyclopropanes

A close analogy exists to vinyl bromide and vinyl iodide, where the protons trans to the substituent are more strongly shielded than the cis protons the shielding difference for the bromide, again, being about half that of the iodide (7). As in the vinyl series, transfer of charge and anisotropy effects might account for the relative shielding in the substituted cyclopropanes.

Coupling constants are considered to be insensitive to anisotropy effects. Therefore, they may be interpreted only in terms of substituent electronegativity. Recently the coupling constants of cyclopropane became available (8) (J_{gem}=-4.34 Hz; J_{cis}=8.97 Hz; J_{trans}=5.58 Hz; $J(^{13}C-H)$=160.45 Hz). In accord with the suggestions made by Schaefer et al. (9) the vicinal couplings J^1_{vic} decrease, while J^2_{vic} increase with increasing substituent electronegativity. It should be noted that in both compounds the vicinal cis-couplings J_{12} and J_{34} are different.

The ^{13}C-H couplings through the bond adjacent to the carbon-halogen bond is approximately 30 Hz larger than the cyclopropane value bromine substitution leading to stronger coupling than iodine substitution by about 5 Hz. Corresponding differences found in methyl (10) and ethyl (11) halides are about 1 to 2 Hz, while the ^{13}C-H couplings to the geminal proton in vinyl bromide and iodide differ by about 6 Hz (7).

The unequal $J(^{13}C-H)$ values for the protons in cis and trans position to the substituent reveal the chemical non-equivalence of both protons. The differences are small, but well beyond the experimental error. This finding agrees well with the reported nonequivalence of the methylene protons of vinyl bromide and iodide, where the ^{13}C-H coupling to the trans proton is smaller than that to the cis proton by 3 and 5 Hz, respectively (7). There are a few further data available for comparison. While in vinyl chloride (7) and tetravinylsilane (12) the cis proton is also slightly more coupled to the adjacent carbon nucleus, the trans proton has the larger ^{13}C-H coupling constant in vinyl fluoride (7) and vinyl cyanide (12,13).

The analogies between cyclopropyl and vinyl bromide and iodide, respectively, are obvious; but we feel that the range of data for monosubstituted cyclopropanes has to be enlarged before any conclusions as to common coupling mechanisms in the two series can be drawn. Thus, the spectra of cyclopropyl fluoride, chloride, and cyanide are analyzed and compared to the data of the corresponding vinylic compounds (14).

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