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RING-CURRENT EFFECTS ON CARBON-13 CHEMICAL SHIFTS OF SP-HYBRIDIZED CARBONS IN CYCLOPHADIYNES(1)

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Ring-current effects have been important, familiar phenomena in the ^1H NMR spectroscopy. However, there have been rather a few studies of ring-current effects on ^{13}C-chemical shifts.2) Model compounds needed for such studies should be selected with adequate prudence because the ^{13}C resonance shift caused by a ring-current effect is generally too small as compared with the ^{13}C-chemical shift variation due to other factors. Recently, marked ring-current effects on ^{13}C-chemical shifts were observed in some bridged annulenes.2a,b) For benzenoid system, weak effects were observed on ^{13}C NMR study of [12]paracyclophane. though the methylene-carbon signals in problem were not clearly assigned.2c)

We have studied ^{13}C NMR spectra of cyclophadiynes3) from the following advantage: in each pair of rigid compounds A_3 and B_3, and strainless ones A_4 and B_4, the diacetylene sp-carbons should be closely fixed with the same spatial arrangements on the aromatic ring as seen from X-ray analysis of B_3,3b) and were considered to be appropriate ones for examining ring-current effects on ^{13}C-chemical shifts. Thus, we have found clear evidence for the presence of these effects on their ^{13}C NMR spectra. The ^{13}C shifts obtained are shown in the Figure.4)

Both middle and propargylic methylene-carbons in A_3 show almost equal chemical shifts to those of the corresponding carbons in B_3. On the other hand, both inner and outer sp-carbons in A_3 are shielded by 1.2ppm relative to the corresponding carbons in B_3. This upfield shifts of 1.2ppm should be mainly caused by the difference in ring-current effects between the two aromatic rings, which was theoretically estimated earlier.6)Similar but slight upfield shifts of sp-carbons (inner -0.4; outer -0.6ppm) are also observed in the tetramethylene-bridged pair,

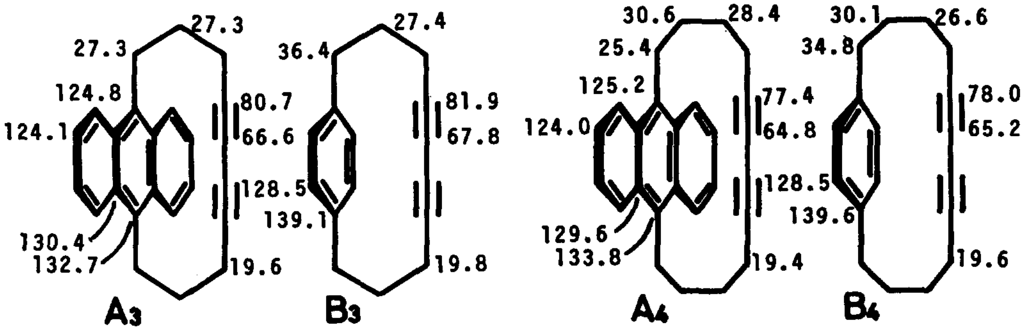

Figure. Carbon-13 chemical shifts, δ

A_4 and B_4. The larger upfield shifts seen in the trimethylene-bridged pair than those observed in the tetramethylene-bridged one are easily explained by the shorter non-bonded interatomic distances between the sp-carbons and the aromatic rings in the former pair.

In comparison of the chemical shifts of strained B_3 with those of strainless B_4, downfield shifts of sp-carbons (inner +2.6; outer +3.9ppm) and an upfield shift of the bridgehead sp^2-carbons (-0.5ppm) are found. These shifts would be caused by rehybridization of normal sp- or sp^2-hybridized carbons due to transannular π-electron interactions containing repulsion. Similar shifts of sp-carbon signals and the bridgehead sp^2-ones are also found in the anthracenophadiyne pair, A_3 and A_4.

References and Footnote

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4) Measurement conditions: Varian XL-100-15 FT NMR spectrometer (25.2 MHz), ^{1}H noise decoupling, 0.12M CDCl$_3$ solution, TMS as internal standard, δ ±0.1ppm. The assignments of signals were based on molecular symmetry, NOE, and ^{13}C-chemical shifts of various diacetylenes reported in Ref. 5.
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