

HETERA-p-CARBOPHANES. VII. MINOR IMPORTANCE OF THE RING CURRENT EFFECT ON CARBON-13 CHEMICAL SHIFTS OF THE ANSA CARBONS IN DIOXADIOXO[n]PARACYCLOPHANES¹⁾

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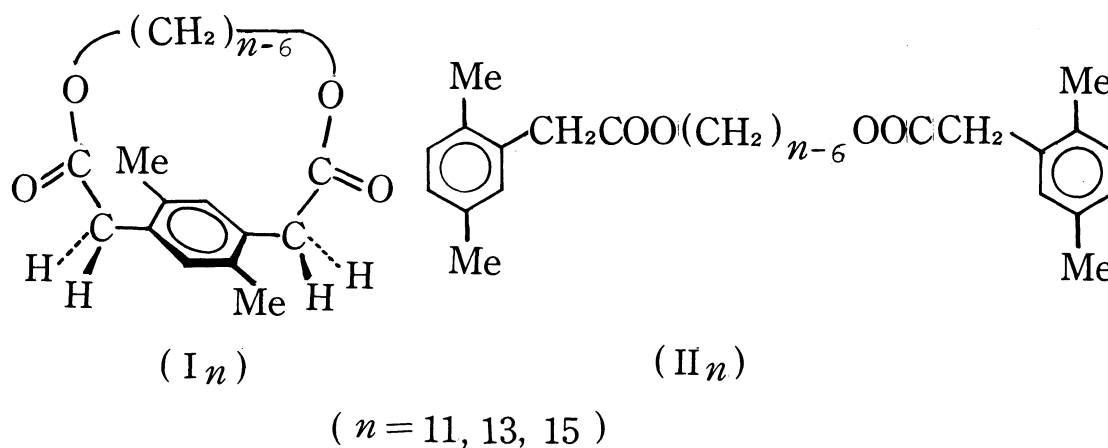
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¹³C NMR spectra of a series of dioxadioxo[n]paracyclophanes are observed to compare with those of open-chain analogs. The ring current effect of the benzene ring is found to be of minor importance in determining the chemical shifts of the carbons in the ansa chain.

¹H NMR spectra of [n]paracyclophanes are well documented and the abnormal shielding of methylene protons, which are remote from the benzene ring in a sense of the intervening bonds, is attributed to the ring current effect arising from the π -electron system of the benzene ring.²⁾ In contrast, there have been a few studies on ¹³C NMR spectra which possibly involve the ring current effect. Levin and Roberts reported ¹³C NMR spectrum of [12]paracyclophane and postulated the presence of the ring current effect to explain the high-field shift of 0.7 ppm of a signal due to an ansa-chain carbon.³⁾ However, there remain some ambiguities in the assignment. Kaneda, Misumi et al. compared the ¹³C NMR data of [n](9,10)-anthracenophanes and derivatives with those of the corresponding [n]paracyclophanes and derivatives to conclude that the ring current effect is operative, at least in anthracene derivatives, although the signal due to the central carbon of the ansa chain is not necessarily at the highest magnetic field.⁴⁾ They had to use deuterated compounds for assignment of the spectra.

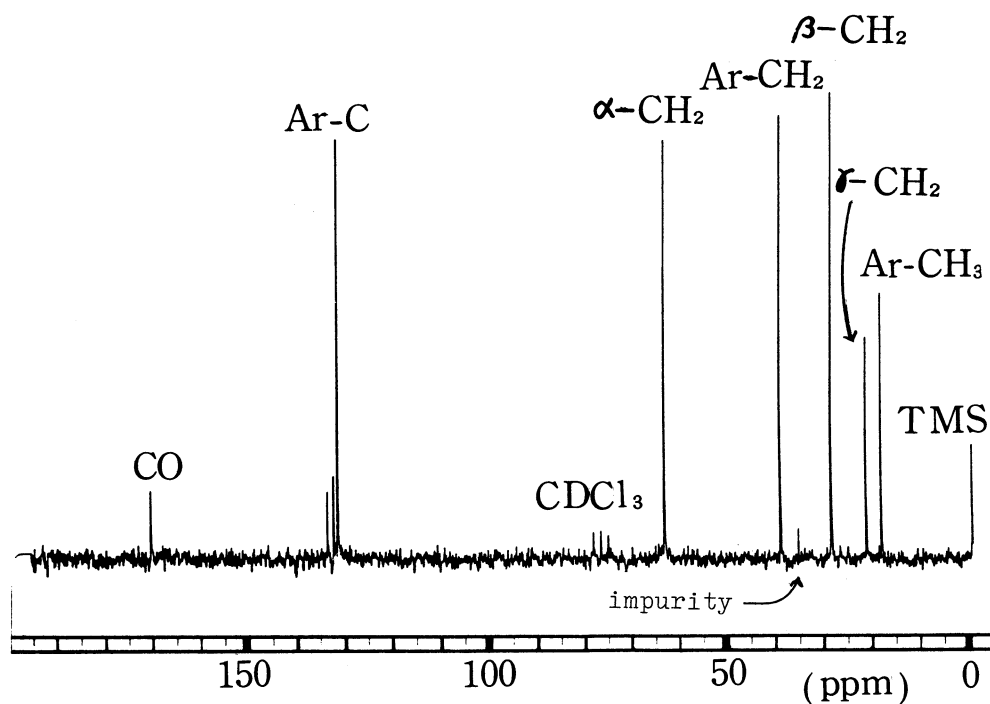
The dioxadioxo[n]paracyclophanes (I_n) constitute an excellent model in assessing the ring current effect of the benzene ring for the following reasons. The assignment becomes easier because of the presence of lesser number of carbon atoms in ansa chains in addition to the fact that oxygen atoms enlarge the

differences in chemical shifts. The usage of I_n with the odd number of carbon atoms in the ansa chain can still facilitate the assignment by taking advantage of the lesser intensity of the signal due to the central carbon atom. Thus the defect of [n]paracyclophanes, which are otherwise suitable, as model compounds for testing the ring current effect is mostly removed in the series of I_n .



Comparison of the data of I_n with those of the open-chain analogs (II_n) will cancel out many other factors than the ring current effect which affect the chemical shifts of NMR signals, thus providing more reliable assessment of the extent of the ring current. Indeed, the difference in chemical shifts between the corresponding methylene protons in I_n and those in II_n has been shown⁵⁾ to be close to the values expected from the calculation with the use of Johnson-Bovey equation.⁶⁾ We now wish to report the results of such comparisons.

The assignment of bridge-methylene carbon signals of I_{11} is shown in Fig. 1 as a typical example. Two signals at 63.9 and 39.7 ppm from internal TMS are assigned to α -carbons relative to ether oxygens of the ester groups and benzyl-methylene carbons, respectively, from the known chemical shift rules for various kinds of carbons and the molecular symmetry.⁷⁾ The signal at 18.8 ppm is also assigned to aromatic methyls by consideration of the chemical shift. The signal intensity unequivocally leads to the assignment of the signal at 21.9 ppm to the central bridge-methylene carbon (γ to the ether oxygens). The remaining signal at 29.1 ppm is now assigned to β -carbons.

Fig. 1 ^{13}C NMR spectrum of I_{11} in CDCl_3

Assignments of ^{13}C signals of I_{13} and I_{15} were performed by taking the γ -effect,⁸⁾ which causes the high-field shift, into consideration in addition to the above-mentioned factors. The ^{13}C signals of II_n were assigned similarly.

The results are tabulated in Table 1.

Table 1. ^{13}C Chemical Shifts of I_n and II_n in CDCl_3 at Room Temperature (ppm from Internal TMS)

Compound Carbon	I_{11}	II_{11}	I_{13}	II_{13}	I_{15}	II_{15}
ArCH_2	39.7	39.1	39.6	39.1	39.2	39.2
$\alpha\text{-CH}_2$	63.9	64.4	63.3	64.5	64.2	64.8
$\beta\text{-CH}_2$	29.1	28.2	28.1	28.5	27.9 or 27.3	28.6 or 29.1
$\gamma\text{-CH}_2$	21.9	22.3	25.6	25.7	25.7	25.8
$\delta\text{-CH}_2$			27.2	28.8	27.3 or 27.9	29.1 or 28.6
$\epsilon\text{-CH}_2$					29.2	29.3
ArCH_3	18.8	20.8	19.0	20.8	18.8	20.8
		19.0			19.0	19.1

The differences in chemical shifts between the central carbon atoms of I_n and II_n , together with those of the corresponding protons are shown in Table 2.

Table 2. Chemical-Shift differences between Central Carbons in the Ansa Chain of I_n and II_n and Those of Protons [$\delta_{CH_2}(II_n) - \delta_{CH_2}(I_n)$]

n	$\Delta\delta_{^{13}C}$ (ppm)	$\Delta\delta_{^1H}^{5)}$ (ppm)
11	0.4	0.92
13	1.6	0.43
15	0.1	0.16

Clearly the data of ^{13}C are scattered, although the data of protons show steady rise in the chemical shifts as the ring-size becomes smaller, the phenomenon being common in the series of [n]paracyclophanes of the similar size.^{2,4b,9)} It may also be pointed out that the chemical shifts of the central carbon of the ansa chain is not necessarily at the highest field, even if the carbons affected by the γ -effect is excluded. These results indicate that the ring current effect is not playing an important role in determining the chemical shifts. At best, the ring current effect must be of limited importance in this system. It seems that a macrocyclic system is necessary to realize the large ring current effect for the ^{13}C NMR spectroscopy.¹⁰⁾

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