Nuclear Magnetic Resonance Spectroscopy. Ring-Current Effects on Carbon-13 Chemical Shifts
(dihydropyrenes/bridged annulenes)

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ABSTRACT A comparison of the $^{13}$C nuclear magnetic resonance chemical shifts of some 15,16-dialkyl-15,16-dihydropyrenes with the corresponding 15,16-dialkyl-2,7,15,16-tetraphydropyrenes provides a measure of the effect of ring current on carbon-13 chemical shifts in which other effects may be expected to be negligibly small. The general conclusion is that the absolute magnitude of the ring-current effect is the same for carbon-13 as for protons when they occupy the same position in space relative to the aromatic $\pi$-electron cloud.

Early in the investigation of nuclear magnetic resonance the concept of a ring current was introduced to explain the observed chemical shifts of protons in the vicinity of aromatic rings (1). In the case of protons this ring current effect is usually large compared to the other factors affecting the value of the chemical shift, and this is dramatically evident for the simple and bridged annulenes (2-4). However, for heavier elements the ring-current effect is less significant and is normally wholly overshadowed by other kinds of influence. Thus, attempts to evaluate the ring-current effects on $^{13}$P- or $^{13}$C-chemical shifts have commonly been frustrated by lack of suitable models in which these other factors would be nullified or unimportant. For example, Jones and Grant have invoked a paramagnetic ring-current to explain the unusually low field signals of the quaternary carbons in the carbon magnetic resonance spectrum of biphenylene, 1 (5, 6) and have proposed that the upfield shifts of the internal quaternary carbons of pyrene, 2 (7), and acepleiadylene, 3 (8), are due to the diamagnetic ring current of the $4n + 2 \pi$-electron peripheral systems in these molecules. However, without suitable models these shifts are within the range that can be rationalized by other factors such as electronegativity or ring strain.

In other studies on [12]paracyclophane, 4 (9) and 1,6-methano[10]annulene, 5 (10, 11), the general conclusion reached was that the ring-current effect on carbon-13 chemical shifts is small compared to other factors such as geometry, hybridization, and charge. Although in these studies comparison was made to reference models, the models available were not ideal. For example, comparison of 5 with either 6 or 7 as reference models involves changes in geometry. One particular effect of change in the peripheral geometry is to alter the $\pi$-orbital interaction of the C-1 and C-6 carbons (12-14) and the chemical shift of the bridging methano carbon should be sensitive to these changes (15, 16).

In their study on 1,6-methano[10]annulene Jones, Masumune, and their colleagues (10) suggested that the bridged annulenes would be especially suitable for analyzing the ring-current contributions to carbon-13 chemical shifts. These molecules have atoms placed within the cavity of the aromatic $\pi$-electron cloud and it is already known that the ring-current contribution to the chemical shift of protons placed internally to the $\pi$-electron cloud is exceptionally large (2-4). In a study directed toward this end Günther, Vogel, and their colleagues (11) measured the $^{13}$C-nuclear magnetic resonance (NMR) spectrum of the bridged [14]annulene 8 and estimated its ring-current contribution by comparison to that of the dihydro derivative 9, as a model. Their conclusion was that the ring-current contribution to the chemical shift of carbons a and b is approximately 8.9 and 6.9 parts per million (ppm), respectively. Although these values are probably quite good, there is some change in geometry between 8 and 9 so, even though small, some contribution to the chemical shift differences is due to factors other than ring current.

In the course of our investigations of the physical and chemical properties of the dihydropyrenes (17), we prepared a series of compounds ranging from the parent molecule, trans-15,16-dihydropyrene, through various dialkyl derivatives, structures 10 a-c. Also at hand were the corresponding 2,7-dihydro derivatives, structures 11 a-c. These molecules seem ideally suited for analyzing the ring-current effect on carbon-13
chemicals shifts and so we undertook such a study.

First of all, the aromatic molecules, 10 \( \alpha \)-c, are bridged [14]annulenes in which the carbons under consideration are internal substituents lying within the shielding region of the aromatic \( \pi \)-electron cloud. Further, examination of molecular models indicates clearly that the comparison molecules, 11 \( \alpha \)-c, lacking an aromatic ring current, are otherwise essentially unchanged with regard to the geometry of the internal framework. Thus, to a very close approximation all of the factors affecting chemical shift, other than ring current, are the same for the two series of compounds. Secondly, the varying distances of the atoms of the internal alkyl groups from the plane of delocalization of the aromatic \( \pi \)-electron cloud allows a mapping of the ring-current effect over a range of positions in space. Finally, the presence of both hydrogen and carbon in the same region permits a comparison of the effect of the same ring current for two different nuclei. This point is of some interest since predictions from the theory of nuclear magnetic resonance suggest that the magnitude of the ring-current effect for different nuclei should be the same if the nuclei are located at the same position in space relative to the aromatic \( \pi \)-electron cloud.

The carbon-13 spectra for compounds 10 \( \alpha \)-c and 11 \( \alpha \)-c are shown schematically in Fig. 1 with each signal from the carbons in the aromatic system being compared directly to the signal from the corresponding carbon in the localized model. The upfield shift \( (\Delta \delta = \delta_{\text{delocalized}} - \delta_{\text{localized}}) \) of the internal carbons in 10 \( \alpha \)-c, i.e., the ring current effect, is readily apparent, the magnitude diminishing with increasing distance from the aromatic \( \pi \)-electron cloud. The consistency of structures 11 \( \alpha \)-c as good localized models is evident from the similar upfield shifts exhibited by a given internal carbon (E, F, and G) throughout the series, especially so for the diethyl and di-n-propyl derivatives. Thus, one has confidence that the changes in geometry and electronic effects for the internal atoms are minimal in going from the aromatic compounds to their reference models, and so the upfield shifts can be attributed unambiguously to the influence of ring current.

To compare carbon-13 and proton ring-current effects we give a schematic summary of the proton chemical shifts in Fig. 2. These data from Figs. 1 and 2 are then combined to provide a graphical comparison of the two effects in Fig. 3.
In Fig. 3 the Δδ values for the internal carbons and protons are plotted against the out-of-plane distance (Z) of these atoms from the mean plane of delocalization. The values of Z are derived from measurements from Dreiding models using the conformation of the alkyl groups shown in Fig. 4. Both space-filling models and data from x-ray crystallographic analysis (20) indicate that this should be the favored conformation. Furthermore, for the case of the di-n-propyl derivative, 10 c, the AA'XX' coupling pattern for the proton magnetic resonance signals of the methylene protons is in accord with the conformation shown and results from hindered rotation about the F-G carbon–carbon bond (21).

Two approximations are obviously inherent in the comparison given in Fig. 3. Although the conformation of the alkyl groups shown in Fig. 4 is undoubtedly highly populated, other conformations, especially those involving rotation about the E–F bond, are neglected in our Z values. Another omission is the neglect of the variation of the in-plane distance (ρ) of carbons E, G, and H and protons g and h from the center of the E–E bond. The effect of these approximations, though, on the correlation of the two nuclei should be small, since both the carbon and proton chemical shift data are affected similarly. As can be seen from Fig. 3, the magnitudes of the upfield shifts due to ring current are very similar for the two nuclei for the same position in space and so provide a good correlation for the various atoms of the alkyl groups.

The values of the internal quaternary carbons, E, need to be considered separately, since they are the closest atoms to the center of the molecule. The solid line in Fig. 3 represents a theoretical plot of the Johnson and Bovey calculations for benzene (22, 23) converted from ring radii to Ångstroms. If ρ does not vary, the chemical shift due to ring current (Δδ) should reach a maximum finite value when Z = 0. Although these calculations for benzene are not directly comparable to the results obtained for the dihydrobenzenes, the shape of the theoretical curve should be similar. From general considerations it might be expected that the ring-current effect for atoms close to the center would be less than predicted by the theoretical curve. However, the quaternary carbon atoms E, only 0.4 Å from the mean plane, should show a greater ring-current effect than the H2 proton or the F carbons at 1.4 and 1.9 Å, respectively. Our interpretation of this discrepancy is that the quaternary carbons E, being closest to the center, are more susceptible to small changes in peripheral geometry as well as the change in hybridization at carbon A, than are the other internal atoms. Thus, the ring-current effect for carbons E is decreased slightly from its true value due to small changes in these other factors.

In summary, the ring-current effects on carbon-13 chemical shifts have been analyzed using a series of bridged [14]annulenes compared with their dihydro derivatives as nonaromatic models. For the same position in space relative to the mean plane of delocalization of the aromatic π-electron cloud, the magnitude of the ring-current effect on chemical shifts is essentially the same for carbon-13 as for protons and follows the theoretical curve predicted by Johnson and Bovey.

**Fig. 2.** Schematic representation of the ¹H NMR spectra of compounds 10 a–c and 11 a–c and the parent system trans-15,16-dihydpyrene. *2,7-trans-15,16-tetrahydropyrene has not been synthesized; the chemical shift given for H, is an estimate. All spectra were taken in deuterochloroform and chemical shifts are relative to tetramethylsilane.
Fig. 3. Correlation of the upfield shifts due to the diamagnetic ring current in 10 a-c for $^{13}$C (data from Fig. 1) and $^1$H (data from Fig. 2). The solid line represents the theoretical results of Johnson and Bovey (20) for benzene, converted from ring radii to Angstroms.

Fig. 4. Conformation of Dreiding model from which measurements of the out-of-plane distances (Z) were taken for use in Fig. 3.

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