

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY,
RING-CURRENT EFFECTS UPON CARBON-13 CHEMICAL SHIFTS^{1a}

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Ring currents have played a crucial role in modern chemistry, but they have been analyzed and discussed almost entirely in terms of their effect upon proton nmr chemical shifts.^{2,3} The application of carbon magnetic resonance spectroscopy to this area has received relatively little attention. In fact, only a few alternate and nonalternate aromatic hydrocarbons have been studied in an attempt to elucidate the effect of ring currents on the shifts of carbon nuclei.^{4,5} Unfortunately, the previous conclusions regarding ring-current effects on ¹³C shifts are not always unambiguous. For example, the observed cmr-shift data for biphenylene might be interpreted in terms of electronegativity and strain superimposed on a diamagnetic ring current, rather than by invoking a paramagnetic ring-current effect.⁶ Interpretation of the cmr data from biphenylene, pyrene and the majority of other compounds studied suffer somewhat from the lack of suitable model compounds, which are needed to derive "normal" chemical shifts.

In hope of accurately assessing the effect of ring currents upon carbon nuclei, we have measured the cmr shifts of [12]-paracyclophane (*1*).⁷ Abnormal shifts of the remote methylene carbons in *1* would seem to be attributable to ring-current effects, as electronegativity and strain effects should be negligible for these carbon atoms. Figure 1 shows the cmr shifts of *1* in CDCl₃ solution along with the appropriate reference compounds. The saturated carbons of *1* do show a range of shifts starting at 157.1 ppm and going to a high of 166.8 ppm. The protons in the methylene chain behave similarly.⁸

It is difficult to decide on appropriate model compounds to provide CH₂ groups with shifts for which ring currents (or other complicating effects) are not to be expected. Cyclopentadecane is possibly a good choice, especially because it is known that the internal methylene carbons in large cycloalkenes are almost identical to the analogous carbons in the corresponding cycloalkanes.¹³ Selection of 166.1 ppm as the ¹³C chemical shift of an isolated methylene

carbon in a large ring sets the maximal ring-current contribution to the carbon chemical shift at +0.7 ppm in *I*.

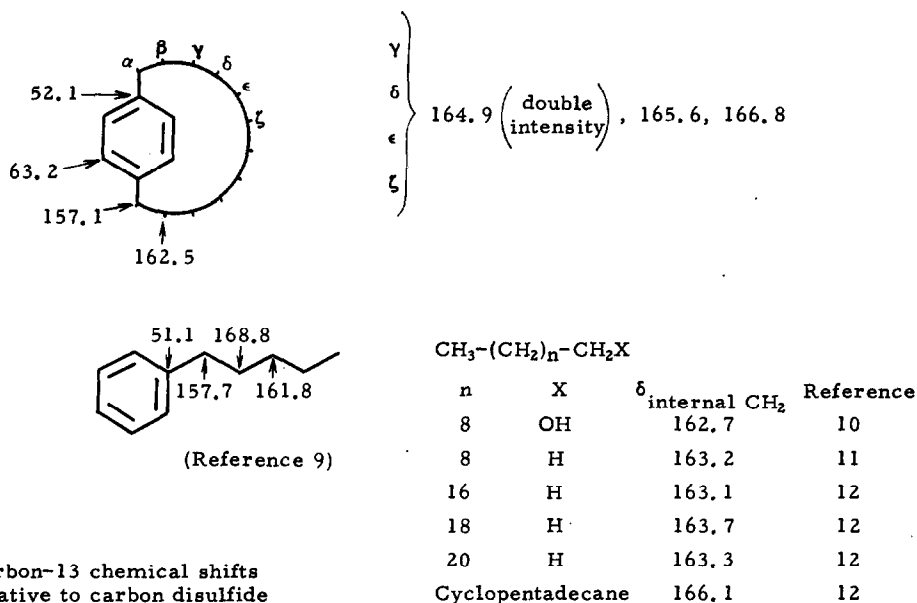
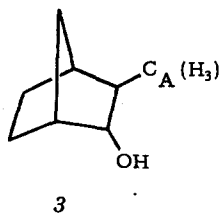
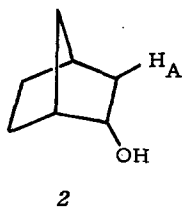


Figure 1. Carbon-13 chemical shifts relative to carbon disulfide

It does not seem reasonable to calculate the ring-current contribution by comparing the CH₂ shifts of *I* with 163.3 ppm, which seems to be the correct shift of a "normal" methylene carbon in an open-chain compound. This would lead to a ring-current contribution to the most upfield carbon of *I* to be +3.5 ppm, which must be too large, because the corresponding selection of 1.3 δ as the chemical shift of a "normal" methylene proton in an open-chain compound leads to about a +0.3 ppm maximal ring-current contribution to the proton chemical shifts of *I*. It is quite unreasonable that the ring-current contributions to the protons and the carbons should be different by a factor of 10.

It has already been demonstrated that when protons or carbons are in similar spatial positions, they are similarly influenced, in a chemical-shift sense, by field effects.^{14,15} Thus, H_A in structures such as *2* and C_A in structures such as *3* undergo almost identical lanthanide-induced shifts when the respective molecules are complexed with a paramagnetic shift reagent and contact effects are absent. Since the protons and carbon atoms in the methylene chain of *I* are located in similar spatial positions, with the carbon atoms being somewhat closer than the protons to the area of maximum ring-current effect, one would expect the carbon resonances to



to be shifted slightly more, but certainly not 3.5 ppm more, than the proton resonances. It is more reasonable that the internal carbon resonances in long-chain *n*-alkanes normally come at somewhat lower fields than the carbon resonances in the corresponding cycloalkane.

The observation of upfield shifts for the CH₂ resonances of *1* for those carbons over the ring, and the fact that these shifts are slightly greater than those observed for the methylene protons in *1*, accords indeed with a ring-current effect on the cmr shifts of *1*. However, the ring-current effect is obviously small and will normally be almost wholly overshadowed by other kinds of influences on cmr shifts.

REFERENCES

1. a. Supported by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences, and by the National Science Foundation.
b. National Institutes of Health Postdoctoral Fellow, 1971-1972.
c. Contribution No. 4504.
2. See E. Vogel in Special Publication No. 21, the Chemical Society, London, p. 113 (1967).
3. R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Topics in Current Chemistry*, 16, 103 (1971).
4. A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, 92, 2386 (1970).
5. A. J. Jones, P. D. Gardner, D. M. Grant, W. M. Litchman, and V. Boekelheide, *ibid.*, 92, 2395 (1970).
6. A. J. Jones and D. M. Grant, *Chem. Commun.*, 1670 (1968).
7. We thank Prof. Donald J. Cram for generously supplying us with a sample of *1*.
8. J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, 79, 846 (1957).

9. E. Lippmaa and T. Pehk, Eesti NSV Tead. Akad. Toim., Keem., Geol., 17, 210 (1968), (CA 69, 111930x).
10. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, J. Amer. Chem. Soc., 92, 1338 (1970).
11. D. M. Grant and E. G. Paul, ibid., 86, 2984 (1964).
12. J. J. Burke and P. C. Lauterbur, ibid., 86, 1870 (1964).
13. D. E. Dorman and K. Herwig, unpublished results.
14. G. E. Hawkes, D. Leibfritz, D. W. Roberts, and J. D. Roberts, paper submitted to J. Amer. Chem. Soc.
15. G. E. Hawkes, unpublished data.