On the Use of ^{13}C N.M.R. Spectroscopy as a Tool in Detecting Long Range π-Interactions in Carbanions

George B. Trimitsis* and Paul Zimmerman

Department of Chemistry, University of Pittsburgh at Johnstown, Johnstown, PA 15904 U.S.A.

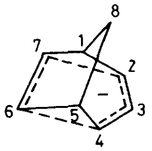
^{13}C N.m.r. spectroscopy is not completely reliable as a primary tool for the detection of long range π-interactions in potentially homoconjugatively stabilized carbanions.

^{1}H N.m.r. spectroscopy has been used in several instances as a diagnostic tool for the detection of long range π-interactions in carbanions.[1] In general, upfield shifts of *ca.* 1—2.5 p.p.m. in the resonances of the protons directly attached to a suitably placed carbon–carbon double bond have been interpreted as evidence for charge delocalization in the carbanionic systems under investigation.[1] In the case of the bicyclo-octadienyl anion (**1**), the most widely cited example of a homoaromatic carbanion,[1a,2] the protons on the olefinic carbons C-6, -7 were found to have moved upfield by an average of 2.25 p.p.m.

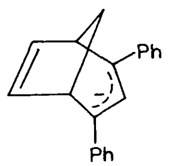
Table 1. ^{13}C Chemical shifts[a] (δ) and selected ^{13}C–H coupling constants (in Hz) for carbanion (**2**)[b] and hydrocarbon (**3**).[c]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
(**2**)	41.7	94.3	115.7	94.3	41.7	118.0 (165 Hz)	118.0 (165 Hz)	37.6
(**3**)	44.5	141.3	126.3	42.1	46.4	130.5 (156 Hz)	140.5 (166 Hz)	43.6

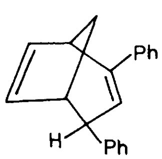
[a] The spectra were obtained using a Bruker ASPECT 2000 spectrophotometer operating at 75.46 MHz; THF (δ 25.3 and 67.4 relative to Me_4Si) was used as an internal standard. [b] The chemical shifts for the aromatic carbons were as follows: δ C-1′ 144.9, C-2′ 117.2, C-3′ 128.2, and C-4′ 111.8. [c] The chemical shifts for the phenyl group at C-2 were as follows: δ C-1′ 145.5, C-2′,-3′ 124.9—128.4, C-4′ 126.9; those for the phenyl group at C-4 were as follows: C-1″ 142.2, C-2″,-3″ 128.9—124.4, and C-4″ 124.4.



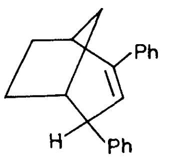
(**1**)



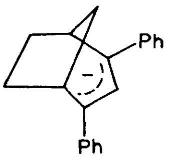
(**2**)



(**3**)



(**4**)



+ (3) ⇌ (2) + (4) (1)

relative to the same protons in the parent hydrocarbon, bicyclo[3.2.1]octa-2,6-diene.

More recently the reliability of ^1H n.m.r. spectroscopy as the primary tool in determining long range π-interactions in carbanions has been questioned by our findings in connection with anion (**2**),[3] the 2,4-diphenyl analogue of intermediate (**1**). Thus, while hydrocarbon (**3**) and its saturated analogue (**4**) were found to have comparable kinetic[3] and thermodynamic†[4] acidities for the allylic hydrogen at C-4, indicating the absence of long range π-interactions in carbanion (**2**), the ^1H n.m.r. spectrum of the latter displayed a substantial upfield shift for 6-, 7-H, as well as other close similarities to the ^1H n.m.r. spectrum of anion (**1**).[3a]

Two very recent publications have attempted to examine the question of homoaromaticity in carbanion (**1**) by means of ^{13}C n.m.r. spectroscopy.[5] Although both groups reported sizeable upfield shifts (average Δδ 45 p.p.m.) and a lowering of the ^{13}C–H coupling constants [av. ΔJ(C–H) 13 Hz] for C-6, -7 of anion (**1**) relative to its parent hydrocarbon, there was considerable disagreement about the extent of homoaromaticity in (**1**).[6]

A potentially important consideration that was not taken into account in either of the above studies is the extent to which delocalization of the negative charge in the allylic portion of a carbanion such as (**1**) may affect the chemical shift and the coupling constants of C-6, -7 *in the absence* of long range interactions.[3] In order to assess this factor, we have examined the ^{13}C n.m.r. spectrum of carbanion (**2**) and report our findings herein.

A solution of the diphenylbicyclo-octadienyl anion (**2**) (0.54 M) was prepared from the parent hydrocarbon (**3**) in [$^2H_8$]tetrahydrofuran (THF) by treatment of the latter with n-butyl-lithium at 0 °C as described earlier,[3a] and its ^{13}C n.m.r. spectrum was recorded using a Bruker ASPECT 2000 spectrometer. The chemical shifts of anion (**2**) together with those of the parent hydrocarbon (**3**) are summarized in Table 1.‡

As expected, the symmetrical nature of carbanion (**2**) renders its ^{13}C n.m.r. spectrum much simpler than that of the parent hydrocarbon (**3**) thereby making peak assignment quite straightforward. On the basis of chemical shift changes (Table 1), it can be seen that the negative charge resides on the allylic carbons C-2—C-4 and the two benzene rings. A closer examination of the values in Table 1, however, shows that the resonances of the vinylic carbons C-6 and C-7 also underwent sizeable upfield shifts (12.5 and 22.5 p.p.m., respectively), despite the fact that anion (**2**) is not expected to display long range π-interactions. These upfield shifts which are on average about 40% as large as those observed in the bicyclo-octadienyl anion (**1**), are only one of several similarities that exist between the ^{13}C n.m.r. spectra of anions (**1**) and (**2**). Thus, a comparison of the chemical shifts in Table 1 with those reported earlier for (**1**) reveals that just as in the case of (**1**), the resonance of C-8 in (**2**) experienced a 6.0 p.p.m. upfield shift [68% as large as that in (**1**)], while the chemical shift of C-3 moved upfield by 10.6 p.p.m., compared to a shift of 3.7 p.p.m. in (**1**).

The similarity of the ^{13}C n.m.r. spectrum of anion (**2**) to that of (**1**) may have led to the conclusion that (**2**) is also homoaromatic. Since this was shown earlier not to be the case,†[3] it must be concluded that factors other than long range π-interactions are contributing to the upfield shifts of the vinylic carbons C-6, -7.

Next, the ^{13}C–H coupling constants of C-6, -7 in carbanion (**2**) and its parent hydrocarbon (**3**) were examined (Table 1), and compared with those of anion (**1**) and its starting material.[5] It can be seen from Table 1 that the decrease in the J(^{13}C–H) values of C-6, -7 on going from (**3**) to (**2**) was not

---

† The relative thermodynamic acidities at C-4 of hydrocarbon (**3**) and its C-6, -7 saturated analogue were measured by allowing the system shown in equation (1) to come to equilibrium then quenching with excess of D_2O and examination by ^1H n.m.r. spectroscopy. Hydrocarbon (**3**) was found to be 2.25 times more acidic than its saturated analogue (ref. 4).

‡ Chemical shift assignments were made on the basis of appropriate model compounds (refs. 5 and 7).

large [ΔJ(C-6) 9, ΔJ(C-7) 1 Hz], and certainly smaller than that observed during the formation of (**1**) from its parent hydrocarbon[5] [ΔJ(C-6) 9, ΔJ(C-7) 16 Hz]. These findings are not unexpected, since carbanion (**2**) is devoid of long range π-interactions,†[3] while at least some charge is thought to reach the vinylic carbons in anion (**1**).[6a,8] Thus, it appears that ^{13}C–H coupling constants may give a more reliable prediction of charge delocalization in carbanions than ^{13}C chemical shifts, although neither one of these parameters is sufficiently conclusive to be used without corroborating evidence.

The authors wish to thank Dr. F-T. Lin for ^{13}C n.m.r. measurements and Dr. K. N. Houk for useful discussions. Both Drs. Lin and Houk are with the Chemistry Department, University of Pittsburgh, Pittsburgh, PA, U.S.A.

Received, 13th July 1984; Com. 1007

References

1 (a) M. Ogliaruso, R. Riche, and S. Winstein, *J. Am. Chem. Soc.*, 1966, **88**, 4731; (b) J. B. Grutzner and S. Winstein, *ibid.*, 1968, **90**, 6562; (c) W. A. Ball, *Tetrahedron Lett.*, 1968, 5531; (d) G. B. Trimitsis, E. W. Crowe, G. Slomp, and T. L. Helle, *J. Am. Chem. Soc.*, 1973, **95**, 4333; (e) A. G. Anastassiou and H. Kasmai, *J. Chem. Soc., Chem. Commun.*, 1975, 201.

2 J. M. Brown and J. L. Occolowitz, *J. Chem. Soc., Chem. Commun.*, 1965, 376; *J. Chem. Soc. B*, 1968, 411; J. M. Brown and E. N. Cain, *J. Am. Chem. Soc.*, 1970, **92**, 3821.

3 (a) G. B. Trimitsis and A. Tuncay, *J. Am. Chem. Soc.*, 1976, **98**, 1997; (b) *ibid.*, 1975, **97**, 7193.

4 R. Anderson, J. Suchocki, and G. B. Trimitsis, 36th Annual Eastern Colleges Science Conference, Williamsport, PA, U.S.A., May, 1982.

5 M. Christl, H. Leininger, and D. Bruckner, *J. Am. Chem. Soc.*, 1983, **105**, 4843; F. H. Kohler and N. Hertkorn, *Chem. Ber.*, 1983, **116**, 3274.

6 Recent theoretical studies are also in disagreement about the presence of homoaromaticity in (**1**) and in carbanions in general; see for example: (a) E. Kaufmann, H. Mayr, J. Chandrasekhar, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 1375; (b) J. B. Grutzner and W. L. Jorgensen, *ibid.*, p. 1372; (c) J. M. Brown, R. J. Elliott, and W. G. Richards, *J. Chem. Soc., Perkin Trans. 2*, 1982, 485.

7 J. P. C. M. van Dongen, H. W. D. van Dijkman, and M. J. A. de Bie, *Recl. Trav. Chim. Pays-Bas*, 1974, **93**, 29; D. H. O'Brien, A. J. Hart, and C. R. Russell, *J. Am. Chem. Soc.*, 1975, **97**, 4410.

8 R. Sustmann and R. W. Gellert, *Chem. Ber.*, 1978, **111**, 42.