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^{13}C NMR OF ARYL SUBSTITUTED CATIONS:
THE SIGMA-BRIDGED COATES CATION
AND THE 2-ADAMANTYL CATION

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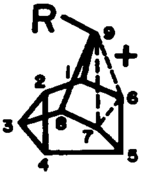
Abstract: A series of aryl substituted Coates and 2-adamantyl cations were generated and their ^{13}C NMR spectra determined to be consistent with sigma-bridged structures for the former, and unbridged structures for the latter.

Of all the cations mentioned in the literature, the Coates cation (1) and some derivatives of it are the only systems which have been considered sigma bridged by all in the field.[1] Hence we decided to test our probe[2] for detecting bridged systems by correlating $^{13}C^+$ chemical shifts of the aryl substituted Coates cations (2a-e) with the $^{13}C^+$ chemical shifts of classical systems (such as (3)). The important results of this study are tabulated in Table 1.

In a similar study on the 2-aryl-2-adamantyl cations (4a-h), we wished to test our probe for its sensitivity in detecting weakly bridged systems. The 2-adamantyl series was chosen for this study because it has been suggested that the parent 2-adamantyl cation (5) is best represented as a weakly bridged structure (6)[3] whose ground state energy must be close to that of the classical structure (5). The results for this system are given in Table 2.



1 (R = H)
2 (R = Ar)
7 (R = CH_3)

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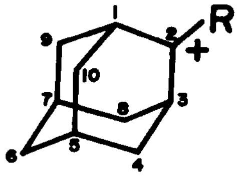

4 (R = Ar)
5 (R = H)

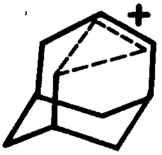

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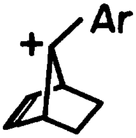
Table 1. ^{13}C NMR chemical shifts of the aryl substituted Coates cation (2a-e) downfield from TMS

Cation	Aryl Group	C1,8	C2,3 C6,7	C4 C5	C9
2a	$4\text{-}CH_3\text{-}C_6H_4$	38.27	36.33	40.47	107.80
2b	C_6H_5	37.45	37.59	40.47	89.08
2c	$3\text{-}F\text{-}C_6H_4$	36.91	38.58	40.40	76.86
2d	$4\text{-}CF_3C_6H_4$	36.71	39.30	40.49	70.88
2e	$3,5\text{-}(CF_3)\text{-}C_6H_3$	36.69	40.04	40.63	65.11

Table 2. ^{13}C NMR chemical shifts of the aryl substituted 2-adamantyl cations (4a-h) downfield from TMS

Cation	Aryl Group	C1,3	C2	C,4,8,9,10	C5,7	C6
4a[4]	$4\text{-}OCH_3\text{-}C_6H_4$	44.8	237.9	45.3	36.3	28.9
4b	$4\text{-}CH_3\text{-}C_6H_4$	49.3	260.8	48.3	36.8	29.8
4c	$4\text{-}F\text{-}C_6H_4$	51.2	265.2	49.4	37.0	30.0
4d	C_6H_5	51.9	271.8	49.8	36.8	30.1
4e	$3\text{-}Br\text{-}C_6H_4$	54.1	277.1	51.3	36.8	30.3
4f	$4\text{-}CF_3\text{-}C_6H_4$	56.8	283.6	52.9	37.1	30.8
4g	$3,5\text{-}(CF_3)_2\text{-}C_6H_3$	58.5	286.2	54.2	37.0	30.9
4h	$3,5\text{-}Cl_2\text{-}4\text{-}N(CH_3)_2\text{-}C_6H_2$	62.4	290.4	56.9	37.5	31.9

Figure 1 is a plot of the $^{13}C^+$ chemical shifts of (2a-e) against the corresponding $^{13}C^+$ chemical shifts of the aryl substituted cyclopentyl cations (3).[2] The most striking feature of this plot is the inverse relationship between the chemical shifts of the cationic carbons of classical systems and nonclassical systems as a function of electron demand (slope = -1.55). This is in strong contrast to similar plots of classical versus classical systems whose slopes have always been positive and close to unity.[5] A similar relationship has been reported to us by Olah[6] concerning the highly bridged 7-aryl-7-norbornenyl cations (8). Thus a general property emerges for the ^{13}C NMR shifts of aryl substituted bridged cations which supports our earlier interpretations on other possible bridged systems.[5]



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An unexpected result of this study is the insensitivity of the other bridged atoms in (2a-e) (carbons 2,3,6, and 7) towards the degree of bridging. Olah's[6] results on the aryl substituted 7-norbornenyl cations (8) are again consistent with ours and show in both cases that the ^{13}C NMR chemical shifts of these atoms have about a four ppm dependence over the range of substituents studied. Most likely this is a consequence of the ^{13}C NMR dependence on the amount of charge present at these sites being cancelled by the effect of hybridization on chemical shifts.

To test whether weakly bridged systems could remain bridged upon substitution by highly electron demanding aryl groups, we generated the data given in Table 2 for the 2-adamantyl system and plotted its $^{13}C^{+}$ chemical shifts against those of (3) (see Figure 2). An excellent correlation of positive slope is obtained indicating that even the 3,5-dichloro-4-N,N-dimethylammoniophenyl substituent is not electron demanding enough to cause the system to become bridged. Hence, if the 2-adamantyl cation (5) is bridged, we have found it to be sufficiently weak to be undetected by our probe. The excellent linearity and near unit slope (0.93) evidenced in Figure 2 for a correlation between two systems of such different steric requirements[7] implies that differential solvation or counterion association, if present, is not influencing the ^{13}C chemical shifts significantly for these tertiary aryl cations.

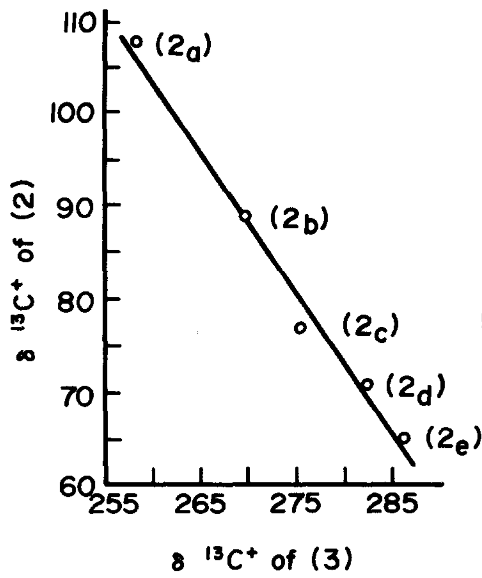


Figure 1. Plot of the ^{13}C NMR chemical shifts of the cationic carbons of 3 vs. 2.

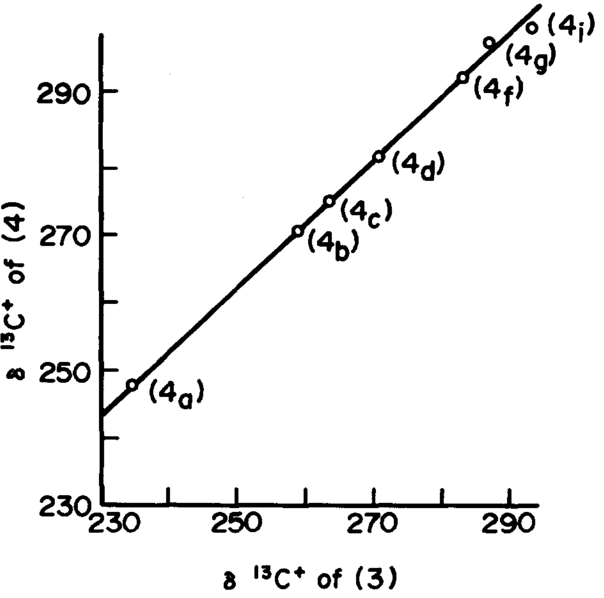


Figure 2. Plot of the ^{13}C NMR chemical shifts of the cationic carbons of 4 vs. 3.

The symmetry indicated by the NMR spectra of (2a-e) is a consequence of a rapid bridge flipping process shown in Figure 3. Even at -110°C, the highly bridged cation (2e) gave no indication in its NMR spectra of being "frozen out". In contrast to this behavior, both the unsubstituted Coates cation (1) and the methyl substituted Coates cation (7) coalesce at temperatures of over 0°C and -10°C respectively.[1] Figure 2 is an energy diagram for bridge flipping of (1), (2) and (7), and readily explains the rapid equilibration of (2).

Figure 2 implies that while aryl groups stabilize classical cations more so than alkyl groups, the reverse is true for nonclassical ions. The net result, therefore, of placing an aryl group on a bridged system is to bring its ground state energy closer to that of its classical structure. Indeed, if the relative energies of the bridged and unbridged structures are close enough, a bridged ion may become classical by the placement of even strongly electron demanding aryl substituents on it as indicated by Figure 2.

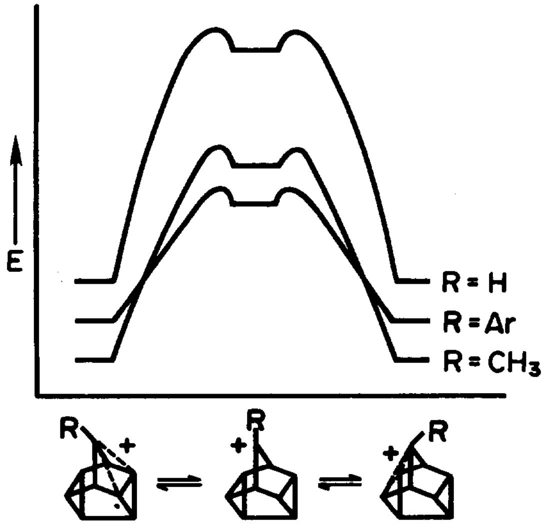
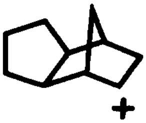


Figure 3. Energy diagram for the bridge flipping of (1), (2) and (7).

In conclusion, we have established a solid basis for our earlier interpretations[2,5] of aryl substituted cations and also found that our probe should be limited to only highly bridged systems. Unfortunately, we have yet to determine the exact threshold for the degree of bridging that is detectable but we feel from these and earlier results that it lies between that of the 2-adamantyl and the 3,5-trimethylene-2-norbornyl cation (9).[5]



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References

1. R. M. Coates and E. R. Fretz, J. Am. Chem. Soc., 97, 2538 (1975), and references cited therein.
2. D. G. Farnum and A. D. Wolf, J. Am. Chem. Soc., 96, 5166 (1974).
3. D. Farcasiu, J. Am. Chem. Soc., 98, 5301 (1976), and references cited therein.
4. The nmr spectrum of the p-anisyl substituent was found to be dependent on the acid concentration. ^{13}C NMR chemical shift values ranged from 237.9 ppm (1 equivalent of magic acid) to 280.4 ppm (about 6 equivalents of magic acid). D. Kelly and H. C. Brown have reported to us difficulties in reproducing the nmr spectra of a number of p-anisyl substituted cations.
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