CORRESPONDENCE

Structure of the 2-Norbornyl Cation

In the recent collection[1-4] of "last words" concerning the infamous 2-norbornyl cation (1), one vital piece of evidence seems to have been overlooked.

The evidence that 1 is not a normal classical ion seems strong,[1,3] even though there are problems concerning its thermochemistry.[2] The main point of contention is whether or not it has C_v symmetry. Attempts[3] to establish this by NMR or ESCA spectral studies depend on a knowledge of what the chemical shifts would be if the structure were unsymmetrical. The conclusions reached[3] were based on the assumption that if 1 were unsymmetrical, the chemical shifts would correspond to those for a classical carbocation. This assumption, however, is not only unjustifiable but certainly incorrect if 1 is in fact nonclassical. Nor can the parameters be deduced from analogy because no other unsymmetrical nonclassical carbocation has been reported and the parameters would in any case depend on the degree of asymmetry. The available calculations[3,5] are equally inconclusive because they lead to conflicting conclusions. In the case of small carbocations, MINDO/3 gives results comparable with those from "state of the art" ab initio methods.[6] Since the calculations for 1 were carried out by less sophisticated methods without full geometry optimization, the conflict with MINDO/3 cannot be taken as a refutation of the latter. MINDO/3 predicts[5] 1 to be unsymmetrical but with an unusual amount of charge delocalization, i.e., a "nonclassical classical" species.

It has long been known that the areas of peaks in ESCA spectra are accurately proportional to the numbers of atoms involved, so much so that ESCA spectra can be used to obtain quite good estimates of elemental compositions of molecules.[7] The time scale of ESCA is also exceedingly short so no complications can arise from time averaging in the case of 1. The ratio of the areas of the two peaks in the reported[8] ESCA spectrum of 1 should therefore provide unambiguous evidence concerning the relative number of positively charged and neutral carbon atoms. If 1 is symmetrical, the ratio should be at least[9] 2:5; if unsymmetrical, 1:6.

While Olah et al.[8a] stated that the ratio of peak areas in their original spectrum[8a] was 2:5, we,[5] and others,[10] have independently analyzed their published spectrum by various methods and agree in finding the ratio of peak areas in it to be almost exactly 1:6.[11] Olah et al.[3] refer to a recent independent ESCA study of 1 which, they state, led to essentially identical results. It is obvious that the ratio of peak areas in the spectrum they reproduce (which is indeed similar to the one in their original paper)[8a] is much less than in the accompanying spectrum simulated for the symmetric ion (where the ratio is of course 2:5). The fact that the separation of peaks in the ESCA spectrum of 1 was only half that observed in genuine classical carbocations is not significant because, as indicated above, the separation would be expected to be less in 1 if it is nonclassical.

The ESCA spectrum of 1, when correctly interpreted, therefore seems to leave no doubt that 1 is *not* symmetrical. The evidence thus seems to suggest that it is best formulated as an unsymmetrical π complex,[12a] analogous to those apparently involved[12b] as intermediates in biomimetic cyclizations.

The only piece of evidence not immediately accommodated by this interpretation is the solid-state low-temperature NMR spectrum.[13] However, since the barrier to interconversion of the two mirror image π complexes is likely[14] to be very low, interconversion could take place rapidly on the NMR time scale, even at 0 K, by heavy atom tunneling.[15]

(1) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.

(2) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432.

(3) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440.

(4) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448.

(5) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 377.

(6) (a) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432. (b) Koehler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1978**, *100*, 5297; **1979**, *101*, 3479.

(7) Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S. E.; Lindgren, I.; Lindberg, B. "ESCA; Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy", Nova Acta Regiae Societatie Scientiarum Upsaliensis, Ser. IV, Vol. 20; Almqvist & Wirksells: Uppsala, 1967, p. 141.

(8) (a) Olah, G. A.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2529. (b) Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8698.

(9) The ab initio calculations[3] predict the ratio to be 2:5 while MINDO/3[5] predicts 3:4.

(10) Kramer, G. *Adv. Phys. Org. Chem.* **1975**, *11*, 177.

(11) The spectrum reported later[8b] by Olah et al. was clearly contaminated by impurities because the high energy peak was much broader than the other. Since the former corresponds to a single carbon atom, or to 2 equivalent carbon atoms, it must be *narrower* than the other, which corresponds to several nonequivalent atoms.

(12) (a) See: Dewar, M. J. S.; Marchand, A. P. *Ann. Rev. Phys. Chem.* **1965**, *16*, 321. (b) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 1744.

(13) Yannonoi, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907.

(14) The barrier could even be less than kT at quite moderate temperatures.

(15) (a) Carpenter, B. K.; *J. Am. Chem. Soc.* **1982**, *104*, 1700. (b) Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 4040.

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Agreeing with Dewar on the 2-Norbornyl Cation

Professor Dewar is certainly entitled to view the 2-norbornyl cation as a π-complex (albeit unsymmetrical). This deviates, however, from our view only in the depiction of the delocalized bonding and hence makes no difference as far as the structure of the ion is concerned, which we agree is nonclassical (i.e., involving multicenter delocalized bonding).

Concerning the ESCA spectra, the significant point is the absence of a high binding energy peak characteristic of a trivalent carbocation center. This clearly rules out the classical ion, however fast it may equilibrate. It is highly questionable, however, whether one could distinguish an unsymmetrical nonclassical ion from the symmetrical one. In the reported ESCA spectra the two overlapping peaks are separated by 1.5 ± 0.2 eV (separation in model classical ions is $\sim$4.5 eV). The integration of peak areas in the original spectra (resolved by computer simulation) is close to 2:5 and not 1:6 as suggested in Dewar's letter. Regardless there seems to be no point to argue peak area ratios. Except for highly charged or strongly negatively substituted carbons, ESCA peaks always overlap and are broad (the intrinsic carbon line width

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is $\gtrsim$0.5 eV). In the spectrum of the 2-norbornyl cation the higher binding energy shoulder is assigned to the two partially charged olefinic carbons to which bridging occurs, whereas the pentacoordinated bridging carbon carrying little charge appears at lower energy overlapping with all other unresolved neutral carbons (including any possible background carbon impurity which would tend to enhance the peak intensity). Even if the ion were unsymmetrically delocalized, this pattern would hardly change.

We have not overlooked the question raised by Dewar concerning possible unsymmetrical nonclassical norbornyl cations equilibrating through a low barrier (see our Account). Yannoni and Myhre in their CPMAS solid state ^{13}C NMR studies were able to obtain the spectrum at 5 K (a truly pioneering result) and showed that if there is still equilibration the barrier is less than 0.2 kcal/mol, thus in the order of RT, representing at the most the energy of a vibrational transition.

As far as calculations are concerned, MINDO/3 hardly seems suitable to try to differentiate an unsymmetrical nonclassical ion from the symmetrical one.

Dewar concludes his letter with the statement: "However, since the barrier to interconversion of the two mirror image π-complexes is likely to be very low, interconversion could take place rapidly on the NMR time scale, even at 0 K, by heavy atom tunneling." Whether heavy atom tunneling is feasible in the norbornyl system may be questioned,[1] but the point is hardly worth discussing. No difference between symmetrical and unsymmetrical nonclassical ions has structural meaning, if the process involves a barrier equal to or less than the energy of a vibrational transition (or no energy at all).

The structure of the 2-norbornyl cation is clearly established as nonclassical and Dewar's letter, while raising some points with his customary flair, only reemphasizes the conclusion reached in our Account.

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(1) *Note Added in Proof.* A recent report (Myhre, P. C.; McLaren, K. L.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 5294) provides experimental evidence that tunneling is unimportant in the 2-norbornyl cation.

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Reviewers of Manuscripts in Broken English

Congratulations to Professor Bunnett on his fine editorial in *Accounts of Chemical Research* (**1985**, *18*, *1*). It was long overdue and should be read by every reviewer of Journals for the American Chemical Society.

We strongly support the idea that if English is to be the language of chemistry, the American academic community has a *responsibility* in helping make it so. That responsibility is first to determine the soundness of the science and secondly to aid authors, especially nonnative speakers, with comments directed at increasing clarity. Professor Bunnett rightly criticized the typical, unproductive, American attitude toward correctness in grammar and punctuation. It is far too easy to dismiss sound science on the basis of grammar rather than to evaluate carefully the value of the science. When we judge nonnative speakers in such a manner, we diminish ourselves by showing our arrogant linguistic attitudes toward those who happen not to be native speakers. We would do well to help others with English because in assisting an author with the complexities of English we demonstrate our competence.

Is it asking too much to request suggestions for revision of the language in a scientifically sound manuscript? Clearly it is not. We know from linguistics that most native speakers know enough about grammar, style, and structure of writing in their own field to be able to make constructive comments for nonnative speakers. To be constructive reviewer's comments need not use the terminology of formal grammar. Simple, direct suggestions in ordinary language are usually sufficient. If a reviewer finds an instance where expert advice is needed, the community of scholars should easily expand to include faculty interested in writing, linguistics, and English. Many faculty in those fields have spent as many years studying language as you have spent studying chemistry and are as happy to share their knowledge as you are.

If you are ever in the need of help in editing a foreign paper in physical organic chemistry, please let us be the first to offer our services in at least improving the quality to the level of an ungrammatical Minnesotan.

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How "Free" Are "Free Radicals"?

In our science some contemporary developments spread like brushfire while a number of obsolete and confusing practices, like old soldiers, do not die and hardly even fade away.

One of these obsolete practices is the common use of the term "free radical". When radicals (synonymous with "odd-electron species") were observed for the first time they were christened "free radicals" in order to distinguish their name from the then commonplace use of "radical" in the sense of "group", "moiety", or "substituent" as in "the methyl radical of acetic acid". This latter use of the word "radical" is wholly extinct now and thus there is no danger of this kind of confusion any more. On the other hand, today's sophisticated chemist has a need for the term "free radical" in the sense of not solvent caged, not part of a more or less loose radical pair, etc.

Thus, editors of chemical journals should see to it that the obsolete term "free radical" in the sense of "odd-electron species" is replaced by the unambiguous term "radical" and that a new term "free radical" is made available for detailed discussions of radical behavior.

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