

C O R R E S P O N D E N C E

Structure of the 2-Norbornyl Cation

In the recent collection¹⁻⁴ 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_0 symmetry. Attempts³ 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 reached³ 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 predicts⁵ 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 reported⁸ 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 least⁹ 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 likely¹⁴ 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 Societatis Scientiarum Upsaliensis*, Ser. IV, Vol. 20; Almqvist & Wiksells: 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 calculations³ predict the ratio to be 2:5 while MINDO/3⁶ 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) Yannoni, 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 ~ 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