Electronic structure computations on the 2-norbornyl cations have recently been reported by Dewar et al. using his MINDO/3 semiempirical scheme[13] and their results differ significantly from ours. We find the total energies to be a strong function of the C_6–C_1–C_2 angle in the classical ion and their value is 8.5° greater than that in Figure 1. In the nonclassical ion they report C_6—C_1=C_6—C_2 bond lengths 0.2 Å shorter and C_1—C_2 lengths 0.05 Å longer than ours. The C_1=C_2 vs. C_6 charge distribution in the nonclassical ion is also qualitatively different. The MINDO/3 calculations[13] "do indeed show large formal charges at all three positions" (i.e., C_1, C_2, and C_6), in sharp contrast to our results which indicate that C_1 and C_2 carry the largest formal charge and C_6 carries the smallest. Dewar et al. report a charge difference of 0.085 e between C_1, C_2, and C_6, while we obtain differences of 0.300 at 4-31G and 0.133 at STO-3G.

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References and Notes

(1) STO-3G: W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969). 4-31G: R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54,** 724 (1971).
(2) H. C. Brown, *Tetrahedron*, **32,** 179 (1976).
(3) G. A. Olah, A. M. White, J. R. DeMember, A. Cammeyras, and C. Y. Lui, *J. Am. Chem. Soc.*, **92,** 4627 (1970); G. A. Olah, *Acc. Chem. Res.*, **9,** 41 (1976).
(4) P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96,** 599 (1974).
(5) P. Pulay, *Mol. Phys.*, **17,** 197 (1969).
(6) H. B. Schlegel, Ph.D. Thesis, Queen's University, 1975; H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, **63,** 3632 (1975).
(7) C. Altona and M. Sundaralingam, *J. Am. Chem. Soc.*, **92,** 1995 (1970).
(8) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14,** 385 (1972).
(9) B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21,** 309 (1973).
(10) W. L. Jorgensen and J. E. Munroe, *Tetrahedron Lett.*, 581 (1977).
(11) G. A. Olah, G. D. Mateescu, and J. I. Riemenschneider, *J. Am. Chem. Soc.*, **94,** 2529 (1972); G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95,** 8698 (1973).
(12) D. T. Clark, B. J. Cromarty, and L. Colling, *J. Am. Chem. Soc.*, following paper in this issue.
(13) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *J. Am. Chem. Soc.*, **99,** 377 (1977).

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A Theoretical Investigation of the Core Hole States of the 2-Norbornyl Cation

Sir:

Despite intense research activity into the classical or nonclassical nature of the 2-norbornyl system opinion is still as diverse as ever.[1-3] Theoretical calculations at various levels of sophistication agree in that the energy difference for isolated systems between the classical and nonclassical formulations is small.[4] It would, therefore, seem reasonable to focus attention on properties of the system which would provide a direct means of distinguishing between the two, and accordingly a whole host of spectroscopic techniques have been applied to this problem. However, the only such technique which would a priori appear capable of effecting this distinction is ESCA (XPS), for which the time scale precludes any ambiguities arising from rapidly equilibrating structures. Unfortunately, the issue has been clouded by technical difficulties in obtaining appropriate core-level spectra, and the available data[5-7] have been interpreted as supporting both possibilities. Comparison must eventually be made with model systems, from which inferences are then drawn concerning the interpretation of the experimental data. A fundamental difficulty has been the lack of suitable models for comparison, and it is the purpose of this communication to rectify this situation.

Table I. Binding Energy Shifts (in eV)

		ΔSCF	Equivalent cores	
		STO-4.31G	STO-3G	MINDO/3[19]
tert-Butyl cation				
Central carbon atom		3.8	3.7	3.4
Surround carbon atoms		(0)	(0)	(0)
Norbornyl cation				
Classical	C2	4.44	4.43	1.79
	C3	1.45	1.58	0.57
	C1	1.28	1.58	0.96
	C6	0.80	0.86	0.39
	C4	0.27	0.54	0.80
	C7	0.31	0.39	−0.13
	C5	(0)	(0)	(0)
Nonclassical	C1, C2	2.01	2.17	1.00
	C6	1.25	1.57	0.85
	C3, C7	0.33	0.49	−0.08
	C4	−0.12	0.15	0.53
	C5	(0)	(0)	(0)

Theoretical studies previously reported[8-12] indicate that relaxation energies accompanying core ionization are dependent on electronic structure, and differences in relaxation energies can contribute significantly to binding energy shifts, particularly for systems with considerable valence-electron symmetry. Electronic reorganization accompanying core ionization must, therefore, be taken into account and the most straightforward means of accomplishing this is by the ΔSCF method. An alternative but less sophisticated method involves the equivalent cores concept,[13-16] whereby shifts are computed from the heats of reaction of the appropriate isodesmic process. Previous calculations have indicated that shifts are accurately described at the ΔSCF STO-4.31G level, while for the less basis set dependent equivalent cores approach, calculations at the STO-3G level are generally adequate.

As a starting point, data for the *tert*-butyl cation (Table I) may be considered. The reported core-level spectra[17] consist of a doublet structure (intensity ratio 1:3) with a C 1s binding energy shift of 3.9 ± 0.2 eV. The ΔSCF STO-4.31G computed shift is in good agreement with experiment, in contrast with the previously published estimate[17] of 4.45 eV from small basis set calculations employing Koopman's theorem.[18] The STO-3G equivalent cores shift is in good agreement with the hole-state calculation, whereas the extensively parametrized MINDO/3 equivalent cores shift[19] does relatively poorly.

The good agreement between theory and experiment is significant, since although the mode of sample preparation used for the ESCA investigations involves a relatively uncharacterized system, possibly involving ion pairs in a frozen solvent matrix, it is almost inconceivable that agreement could be entirely fortuitous. Previous work,[20,21] however, suggests that shifts (but not absolute binding energies) computed for an isolated ion should correlate directly with experimental data pertaining to the solid state.

Allen and Goetz[22] have detailed an extensive nonempirical LCAO–MO–SCF investigation at the STO-3G and STO-4.31G level on the electronic structures of classical and nonclassical 2-norbornyl cation. As a basis for the detailed interpretation of the experimental ESCA data, the core-hole spectra at the ΔSCF STO-4.31G and equivalent cores STO-3G level have been calculated, employing the optimized geometries obtained by Allen and Goetz. The computed shifts and assignments for the C 1s binding energies are shown in Table I. The main feature is the considerably larger span in binding energies for the classical ion than for the nonclassical ion (4.4 eV compared with 2.1 eV, respectively, for the ΔSCF STO-

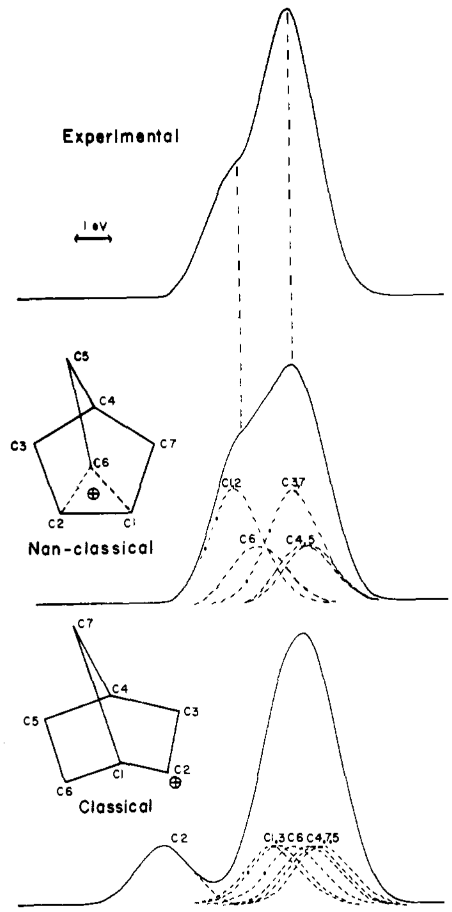

Figure 1. C 1s core-hole-state spectra for the 2-norbornyl cation, simulated using a fwhm of 1.8 eV for composite line widths.

4.31G basis). Further, the hole-state and ab initio equivalent cores results are in excellent agreement, with regard to both the span in binding energy and relative ordering, whereas the recently published MINDO/3[19] results are strikingly different in both these aspects.

Core hole-state spectra may be synthesized by taking components of appropriate line shape and line width. Figure 1 shows such simulated spectra for the ΔSCF STO-4.31G basis, the STO-3G equivalent cores spectra being essentially identical. Even with relatively poor resolution, a clear-cut distinction exists between the classical and nonclassical species. An interesting feature of the nonclassical spectrum is the intermediate binding energy calculated for C-6, which implies that any attempt to deconvolute the experimental spectrum into just two components is untenable.[5,6] For the classical spectrum, the high binding energy calculated for C-2 leads to a well-resolved spectrum with intensity ratio 1:6.

When considering the experimental data, contamination problems suggest that emphasis should be placed on shifts rather than relative intensities.[2] Even a cursory perusal of the synthesized spectra suggests that the experimental data are not interpretable in terms of a classical parent 2-norbornyl cation. Comparison between the calculated nonclassical spectrum and a smoothed version (normalized to a flat baseline) of the experimental data, however, is quite striking. The most logical conclusion to draw is that the published spectra pertain to a nonclassical 2-norbornyl cation, for which the surface has been contaminated by extraneous hydrocarbon.[23] With a knowledge of electron mean free paths[24] (~20 Å for kinetic energies appropriate to the experimental data) and taking a monolayer as ~5 Å thick, the experimental data would be quantitatively described in terms of the calculated line profile for the nonclassical ion with a fractional (~0.6) monolayer coverage of hydrocarbon contamination. To this extent, the calculations outlined here resolve experimental ambiguities.

The distinction between classical and nonclassical energies is so fine as to be sensitive to minor electronic perturbations. Thus, a methyl substituent, stabilizing a positive charge, might be anticipated to prefer a classical structure. From calculations on 2-propyl and *tert*-butyl cations,[25] a decrease in C-2 binding energy of ~0.9 eV is expected, giving a shift of ~3.5 eV for a classical 2-methylnorbornyl cation, in good agreement with the reported ESCA shift of 3.7 eV.[5,6]

References and Notes

(1) H. C. Brown, *Tetrahedron*, **32**, 179 (1976).
(2) G. A. Olah, *Acc. Chem. Res.*, **9**, 41 (1976).
(3) G. M. Kramer, *Adv. Phys. Org. Chem.*, **11**, 177 (1975).
(4) D. W. Goetz and L. C. Allen; 23rd International Congress of Pure and Applied Chemistry, Vol. 1, Boston, 1971, p 51.
(5) G. A Olah, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **94**, 2529 (1972).
(6) G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973).
(7) G. D. Mateescu and J. L. Riemenschneider, *Proc. Int. Conf. Electron Spectrosc.*, 661 (1971).
(8) D. B. Adams and D. T. Clark, *Theor. Chim. Acta*, **31**, 171 (1973).
(9) D. T. Clark, I. W. Scanlan, and J. Müller, *Theor. Chim. Acta*, **35**, 341 (1974).
(10) D. T. Clark and I. W. Scanlan, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1222 (1974).
(11) D. T. Clark and J. Müller, *Chem. Phys. Lett.*, **30**, 394 (1975).
(12) D. T. Clark, and J. Müller, *Theor. Chim. Acta*, **41**, 193 (1976).
(13) W. L. Jolly and D. N. Hendrickson, *J. Am. Chem. Soc.*, **92**, 1863 (1970).
(14) W. L. Jolly, *J. Am. Chem. Soc.*, **92**, 3260 (1970).
(15) D. T. Clark and D. B. Adams, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1819 (1972).
(16) D. B. Adams and D. T. Clark, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 201 (1973).
(17) G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Am. Chem. Soc.*, **92**, 7231 (1970).
(18) T. A. Koopmans, *Physica*, **1**, 104 (1933).
(19) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *J. Am. Chem. Soc.*, **99**, 377 (1977).
(20) Cf. D. T. Clark in "Electron Emission Spectroscopy", W. Dekeyser, Ed. D. Reidel Publishing Co., Dordrecht, Holland, 1973, pp 373–507.
(21) D. T. Clark, J. Peeling, and L. Colling, *Biochim. Biophys. Acta*, **453**, 533 (1976).
(22) D. W. Goetz, H. B. Schlegel, and L. C. Allen, *J. Am. Chem. Soc.*, preceding communication in this issue.
(23) Cf. D. T. Clark, W. J. Feast, W. K. R. Musgrave, and I. Ritchie, "Advances in Polymer Friction and Wear", Vol. 5A, L. H. Lee, Ed., Plenum Press, New York, N.Y., 1974, p 373.
(24) Cf. D. T. Clark and H. R. Thomas, *J. Polym. Sci., Polym Phys. Ed.*, in press.
(25) D. T. Clark and B. J. Cromarty, *Prog. Theor. Org. Chem.*, in press.
(26) Thanks are due to the Science Research Council for provision of a research studentship, and to the Atlas Computing Laboratory for computing facilities.

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Direct Oxidation in High Yield of Some Polycyclic Aromatic Compounds to Arene Oxides Using Hypochlorite and Phase Transfer Catalysts[1]

Sir:

Because arene oxides,[2] or their subsequent metabolites,[3] have been implicated as the intermediates responsible for the carcinogenicity and mutagenicity of polycyclic aromatic hydrocarbons,[4] there has been considerable interest in developing convenient methods for their synthesis[5] and in understanding how they are formed physiologically. As part of a continuing program to investigate oxygen atom transfer (oxenoid) reactions[6] in model and enzymic systems, we have been exploring[7,8] the use of several reagents for the direct oxidation of arenes to arene oxides.[9] In this communication we report that various arene oxides can be prepared under mild conditions and in high