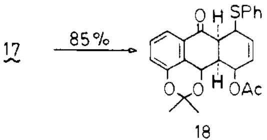
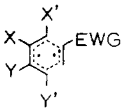
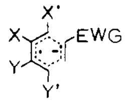


18
mp 195-7°

We attribute the differences to competing considerations of polar factors and odd electron distribution as illustrated by the two extreme forms **19** and **20** for the transition state. In the



19



20

thermal reaction, odd electron distribution as in **19** provides the dominating effect that determines regiochemistry. Since sulfur can stabilize a radical more effectively than oxygen,[15] it controls. However, if polar factors dominate, then oxygen would be anticipated to be the controlling element. In the Lewis acid catalyzed reaction polar factors should become more important relative to electron density. If the Lewis acid coordinates to the dienophile in promoting the Diels–Alder reaction, then a reversal from the thermal chemistry should be observed. Indeed, **1** and **2** show a complete reversal in regiochemistry of addition with juglone. On the other hand, the Lewis acid can coordinate with the diene in addition to or in lieu of the dienophile. Under such circumstances, it should preferentially coordinate to the acetoxy group and thus diminish the contributing effect of oxygen. In such a case, the reduced interaction of oxygen would enhance the observed regiochemical control exercised by sulfur. With dienophiles that don't tie up the Lewis acid as effectively as juglone, such as the acroleins and acrylates, the above effect leads to a reinforcement of the sulfur directing ability. Qualitatively, the magnitude of the catalytic rate enhancement supports this picture. Whereas the reaction of **1b** with juglone changes from 4 h at 110 °C (thermal) to 1.5 h at −10 °C (catalyzed), that of **1b** with α-methacrolein only changes from 16 h at 80 °C (thermal) to 16 h at room temperature (catalyzed).[16] While the frontier orbital PMO approach reaches the same conclusions with respect to the thermal reactions, it is unclear how such a rationale relates to the Lewis acid catalyzed reaction.[3]

In any event, by using sulfur as a control element and the effect of Lewis acids, great versatility in directing the orientation of Diels–Alder reactions is available.[17] The highly functionalized adducts obtained with dienes **1** and **2** are extremely valuable for further elaboration based upon β-keto sulfide chemistry[18] and sulfoxide pyrolyses[18] and sigmatropic rearrangements.[19] The juglone adducts have special applicability since they can serve as potential intermediates directed toward the tetracycline antibiotics and the anthracycline antitumor agents such as daunomycinone.[6] The asymmetry of ring A of juglone is translated to asymmetry of ring C which, in turn, can allow regiocontrolled introduction of the final ring.

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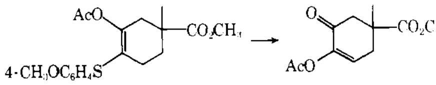
(5) This structure was fully supported by spectroscopic analysis and elemental analysis and/or high resolution mass spectroscopy.

(6) 2-Arylthiocyclobutanone[1] is acetylated (Ac_2O, $(C_2H_5)_3N$, room temperature) and pyrolyzed through a hot tube (350 °C at 1-mm pressure) mounted horizontally. **1b**: IR 1767 cm^{-1}; NMR δ 7.46 and 6.94 (AA′BB′, 4 H), 5.61 (s, 2 H), 5.14 (br, 1 H), 5.06 (br, 1 H), 3.85 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR δ 168.2, 159.8, 150.4, 139.1, 134.5, 122.8, 115.1, 114.9, 105.6, 55.2, 20.5.

(7) Cf. preparation of 1,4-diacetoxybutadiene, M. E. Jung, *J. Chem. Soc., Chem. Commun.*, 956 (1974). For a correction of the stereochemical assignment of this diene, see J. F. W. Keanna and P. E. Eckler, *J. Org. Chem.*, **41**, 2625 (1976).

(8) The acyloin from the Diels–Alder adduct of cyclopentadiene and maleic anhydride has the hydroxyl group in the endo configuration in contrast to the assignment of Jung. Tosylation (TsCl, C_5H_5N, room temperature), displacement (PhSNa, $(C_6H_{13})_4NBr$, DMF, 0 °C), reduction ($NaBH_4$, ethanol, 0 °C), acetylation (Ac_2O, C_5H_5N, 0 °C), and pyrolysis (horizontal hot tube, 460 °C at 1 mm) gave **2**: mp 65–66 °C; IR 1771, 1646, 1571 cm^{-1}; NMR δ 7.32 (d, J = 12.1 Hz, 1 H), 6.31 (d, J = 14.7 Hz, 1 H), 6.23 (dd, J = 14.7, 10.3 Hz, 1 H), 6.06 (dd, J = 12.1, 10.3 Hz, 1 H); ^{13}C NMR δ 167.7, 138.9, 135.8, 129.8, 129.7, 128.3, 127.3, 125.6, 114.8, 20.4.

(9) Assignment of regiochemistry was established by spectroscopy and/or chemical behavior analogous to the methods employed for cycloadditions of **3**. See ref 1. For example **4** (R = CH_3, EWG = CO_2CH_3) was converted to i.



i

(10) Assignment of regiochemistry follows from spectroscopic data. For example in adduct **8** (R = CH_3) the methine adjacent to sulfur (δ 3.68) only shows coupling to the vinyl proton, whereas the methine adjacent to oxygen (δ 5.37) shows coupling to the methylene group and a vinyl proton.

(11) H. H. Inhoffen, H. Muxfeldt, H. Schaefer, and H. Kramer, *Croat. Chem. Acta*, **29**, 329 (1957); H. Musfeldt, *Angew. Chem.*, **74**, 825 (1962).

(12) Also see A. J. Birch and V. H. Powell, *Tetrahedron Lett.*, 3467 (1970).

(13) Experiment performed by C. Caldwell in these laboratories. A ratio of **12**:**13** of >20:1 is observed.

(14) The NMR spectrum of this compound clearly establishes the regiochemistry as well since the benzylic methine (δ 5.44 (d, J = 5.6 Hz) and acetoxy methine (δ 5.56 (dd, J = 5.5, 4.3 Hz)) couple to the same bridgehead proton at δ 3.14 as determined by spin decoupling. The methine next to sulfur (δ 3.90) couples (J = 5.0 Hz) to the bridgehead proton adjacent to the carbonyl group (δ 3.55).

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(16) The effect of Lewis acid complexation of the diene in addition to or in lieu of the dienophile on rate is difficult to predict. Using a frontier orbital PMO approach, it can be argued that a relative rate acceleration or deceleration will be observed.

(17) By modifying the substituents on S and O, control by O in the presence of Lewis acids with simple dienophiles as high as 10:1 can be obtained.

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Ab Initio Electronic Structure Calculations for Classical and Nonclassical Structures of the 2-Norbornyl Cation

Sir:

We report geometry optimized ab initio molecular orbital calculations employing both the STO-3G and the more flexible 4-31G basis sets[1] for the 2-norbornyl cation to help resolve the long-standing controversy as to whether the classical[2] or nonclassical[3] model best represents the known experimental data.

Geometry optimization for both ions was carried out at the STO-3G level using initial configurations obtained from the

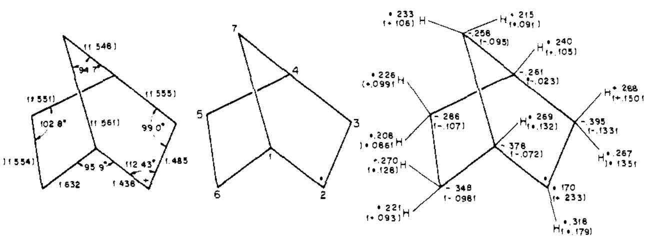

Figure 1. Classical structure for 2-norbornyl cation obtained from energy optimization with ab initio molecular orbital calculations using the 4–31G s,p basis set: left side, geometry; middle, numbering of the carbon atoms; right side, Mulliken atomic charges (electrons) with 4-31G basis. Charges from STO-3G s,p basis at same geometry in parentheses.

known geometries[4] of $C_3H_7^+$ plus classical mechanics calculations. Each C–C bond length and the C_6–C_1–C_2 bond angle were independently varied by successive iteration until self-consistency was achieved. C–H bond lengths and bond angles for the C_6, C_1, and C_2 carbons were then varied and found to deviate an almost negligible amount from their positions as originally set by the classical mechanics calculations. This optimization procedure was then checked by applying the force relaxation method to the optimized structures.[5] Forces on the atoms were calculated using the program FORCE[6] and the corresponding average displacements were found to be small: ±0.002 Å for bond lengths and ±0.02 Å for nonbonded C–C distances. These displacements result in changes of ±0.004 e/atom for the Mulliken atomic charges and 0.48 kcal/mol in the energy difference between the classical and nonclassical conformations. This affirms the accuracy of our optimization procedure. The residual forces on the atoms (0.01 mdyn root mean square) indicates that the structures obtained by the force relaxation method are within 0.001 au (0.63 kcal/mol) of true minima. Geometry optimization at 4-31G was initiated from the STO-3G optimized structure and followed the same procedure. Fifteen separate calculations were made at this level for each of the ions.

For the classical $C_7H_{11}^+$ ion the STO-3G minimum energy geometry is analogous to the methyl-staggered 1-propyl cation. In the terminology of Altona and Sundaralingam,[7] it possesses a contra twist of C_3 and C_5 relative to C_2 and C_6. The optimization at 4-31G was begun with the contra twist conformation and the final result is shown in Figure 1 along with net atomic charges from Mulliken population analysis. Because of the well-known problems arising from the atomic partitioning of the overlap integrals and the sensitivity to basis set, we also computed charges with the STO-3G basis at the optimized 4-31G geometry (Figure 1, values in parentheses). Both bases yield the same pattern of charge differences between the atoms.

The STO-3G optimum configuration for the nonclassical ion is analogous to corner protonated cyclopropane[4] and the final optimized 4-31G geometry along with the 4-31G and STO-3G (parentheses) atomic charges, are given in Figure 2. The charge distribution pattern is again essentially the same at both STO-3G and 4-31G. In particular, C_1 and C_2 are the most positive and C_6 the least positive of the carbon atoms, in agreement with the lack of delocalized positive charge at C_6 revealed by experiments where substitutions have been made at this position.[2,3] At STO-3G, the total energy of the nonclassical ion is 5.2 kcal/mol higher than the classical conformation while at 4-31G the difference is only 0.2 kcal/mol.

In the gas phase, this trend toward increasing stabilization of the nonclassical ion relative to the classical conformation with increasing accuracy of the wave functions has been well established for small cations. The differential stabilization obtained by augmenting the basis with d-polarization functions on the carbons is 7.0 kcal/mol in the ethyl cation[8] and 4.3 in $C_3H_7^+$. Use of p-polarization functions on hydrogens[8] increases the relative stability of the ethyl cation by a further 1 kcal/mol. Addition of instantaneous electron–electron correlation in the ethyl cation[9] differentially favors the bridged structure by 8 kcal/mol. Similar values are to be expected for $C_7H_{11}^+$.

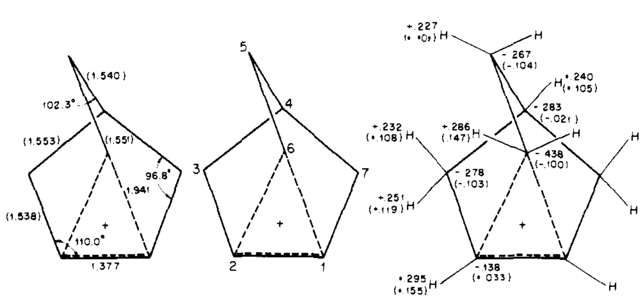

Figure 2. Nonclassical structure for 2-norbornyl cation obtained by energy optimization employing an initio molecular orbital wave functions with the 4-31G s,p basis: left side, geometry; middle, numbering of the carbon atoms; right side, atomic charges (electrons) from Mulliken population analysis. Charges resulting from STO-3G s,p basis at same geometry are given in parentheses.

Table I. Relative C 1s Orbital Energies at 4–31G Optimized Geometries (eV)

Classical $C_7H_{11}^+$		Nonclassical $C_7H_{11}^+$	
C_2	4.58	C_1,C_2	2.48
C_1	1.50	C_6	1.96
C_3	1.32	C_3,C_7	0.34
C_6	1.08	C_4	0.23
C_4	0.58	C_5	(0.0)
C_7	0.39		
C_5	(0.0)		

Considerable progress toward estimating differential solvation effects has been made recently by Jorgensen[10] using a semiempirical computation scheme. Employing five HCl molecules as a representative electron-donating solvent he found the bisected (classical) ethyl cation to be stabilized by 14 kcal/mol more than the bridged (nonclassical) conformation. He also pointed out that this finding is in qualitative agreement with the simple HOMO–LUMO perturbation theory treatment of electron donor–acceptor complexes. At the 4-31G optimum geometries both $C_7H_{11}^+$ ions have almost identical HOMO energies but the LUMOs differ by 2.7 eV (0.15396–0.05343 au) and this is comparable with his results for the ethyl cation. Two further points regarding Jorgensen's solvation estimates should be noted: (a) it is essential that the computations be repeated with ab initio wave function employing a basis similar to that used here; (b) as he noted, solvents which are poor electron donors (e.g., superacid) may produce considerably smaller differential solvation energies.

The experimental technique which has the best potential for differentiating between the classical and nonclassical structures is ESCA and Olah et al.[3,11] have reported a spectrum taken in superacid. Under the assumption that their spectrum may be resolved into two peaks, they find a separation of 1.47 eV. The relative C 1s one-electron energies from our 4-31G optimized solutions are listed in Table I and they clearly favor assignment of a nonclassical ion to the observed spectrum. This identification of ground-state one-electron energies with ESCA measurements implies the validity of Koopman's theorem and further calculations which allow charge rearrangement between the ground and ionized states of the two cations are reported in the following communication.[12] These calculations move the peak separation approximately ½ eV closer to agreement between the nonclassical ion and the experimental spectrum. The simulated spectra displayed there is quite similar to that which would result from using the values in Table I.

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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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-