of **24a** and **24b** as blue crystals (191 mg) in 87% yield: mp 231–234 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.39 (d, 1 H, H_6, J = 9.7 Hz), 7.92 (d, 1 H, H_4, J = 9.7 Hz), 7.71 (d, 1 H, H_8, J = 4.0 Hz), 7.53 (bd, 1 H, H_1, J = 3.9 Hz), 7.41 (brd, 1 H, H_2, J = 3.9 Hz), 7.40 (d, 1 H, H_9, J = 4.0 Hz), 7.23 (t, 1 H, H_5, J = 9.7 Hz), 4.31 and 3.74 (m, 4 H, *i*-Pr), 3.80 (brs, 2 H, H_3), 1.55, 1.46, 1.18 and 1.05 (d, 24 H, *i*-Pr) for 3*H* isomer of **24a**; 8.36 (d, 1 H, H_6, J = 10.0 Hz), 7.88 (d, 1 H, H_4, J = 10.0 Hz), 7.76 (d, 1 H, H_8, J = 4.2 Hz), 7.36 (t, 1 H, H_5, J = 10.0 Hz), 7.35 (d, 1 H, H_9, J = 4.2 Hz), 6.90 (brs, 2 H, $H_{2,3}$), 4.00 (brs, 2 H, H_1) for 1*H* isomer of **24a**; 8.37 (d, 1 H, H_6, J = 9.8 Hz), 7.93 (d, 1 H, H_4, J = 9.8 Hz), 7.82 (d, 1 H, H_8, J = 4.2 Hz), 7.62 (brd, 1 H, H_1, J = 5.4 Hz), 7.18 (brd, 1 H, H_2, J = 5.4 Hz), 3.89 (brs, 2 H, H_3) for 3*H* isomer of **24b**; 8.31 (d, 1 H, H_6, J = 9.5 Hz), 4.17 (s, 2 H, H_1) for 1*H* isomer of **24b** (other signals could not be assigned because of overlap with those of other isomers, but from the integral ratio of methylene protons the ratio of 3*H*-**24a**, 1*H*-**24a**, 3*H*-**24b**, and 1*H*-**24b** isomers was determined to be 57:14:19:10); IR (KBr, cm^{-1}) 2970, 1900, 1548, 1090; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 224 (4.50), 269 (4.65), 305 (4.68), 359 (4.14), 562 (3.10), 600 (sh, 3.08), 660 (sh, 2.70). Anal. Calcd for $C_{28}H_{37}N_2ClO_4$: C, 67.12; H, 7.44; N, 5.59. Found: C, 66.51; H, 7.32; N, 5.65.

3-[Bis(diisopropylamino)cyclopropenylidene]cyclopent[*e*]azulene (25). A mixture of **24a** and **24b** (56 mg, 0.11 mmol) was chromatographed on basic alumina (Woelm B Akt II) with benzene–acetone (7:3) to give **25** as reddish purple crystals (14 mg) in 32% yield: mp 171–175 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.11 (d, 1 H, H_4 or H_6, J = 9.3 Hz), 7.94 (d, 1 H, H_4 or H_6, J = 9.8 Hz), 7.23 (dd, 1 H, H_8, J = 4.2, 3.2 Hz), 7.03 (d, 1 H, H_2, J = 4.4 Hz), 6.84 (d, 1 H, H_7 or H_9, J = 4.2 Hz), 6.74 (d, 1 H, H_1, J = 4.4 Hz), 6.65 (t, 1 H, H_5, J = 9.5 Hz), 6.59 (d, 1 H, H_7 or H_9, J = 3.2 Hz), 3.99 (m, 4 H, *i*-Pr), 1.31 (d, 24 H, *i*-Pr); IR (KBr, cm^{-1}) 3050, 2950, 1890, 1592, 1522, 1300; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 243 (4.25), 273 (4.27), 299 (sh, 4.20), 403 (4.03), 526 (3.73); MS *m/e* (M^+) calcd 400.2878, obsd 400.2851.

1,7- and 3,7-Bis[bis(diisopropylamino)cyclopropenylio]cyclopent[*e*]azulenides (26a and 26b). To a solution of **25** (21 mg, 0.051 mmol) and triethylamine (10 mg, 0.10 mmol) in dry dichloromethane (5 mL) was added chlorobis(diisopropylamino)cyclopropenium perchlorate (19 mg, 0.051 mmol) at room temperature. After stirring under argon overnight, the reaction mixture was concentrated in vacuo to give a reddish purple solid, and recrystallization from dichloromethane–ether afforded a 2:3 mixture of **26a** and **26b** (37 mg) as dark reddish purple crystals in 98% yield: mp 163–168 °C dec; ^{1}H NMR ($CDCl_3$, ppm) δ 8.15 (d, 1 H, H_6, J = 9.5 Hz), 7.86 (d, 1 H, H_4, J = 9.5 Hz), 7.48 (d, 1 H, H_2 or H_8, J = 4.0 Hz), 7.23 (d, 1 H, H_2 or H_8, J = 4.4 Hz), 6.93 (d, 1 H, H_3 or H_9, J = 4.4 Hz), 6.83 (t, 1 H, H_5, J = 9.5 Hz), 6.69 (d, 1 H, H_3 or H_9, J = 4.0 Hz), 4.13 (m, *i*-Pr), 1.56, 1.54, and 1.43 (d, *i*-Pr) for **26a**; 8.04 (d, 2 H, $H_{4,6}$, J = 9.6 Hz), 7.26 (d, 2 H, $H_{2,8}$, J = 4.5 Hz), 6.93 (t, 1 H, H_5, J = 9.6 Hz), 6.91 (d, 2 H, $H_{1,9}$, J = 4.5 Hz), 4.13 (m, *i*-Pr), 1.56, 1.54, and 1.43 (d, *i*-Pr) for **26b** (the protons of isopropyl group of **26a** overlap with those of **26b**); IR (KBr, cm^{-1}) 2970, 1880, 1508, 1460, 1340, 1090; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 255 (4.23), 322 (4.37), 374 (4.05), 424 (4.00), 564 (4.34). Anal. Calcd for $C_{43}H_{63}N_4ClO_4$: C, 70.23; H, 8.63; N, 7.62. Found: C, 70.22, H, 8.73; N, 7.47.

Acknowledgment. We thank Professor Jun-ichi Aihara for the calculation of resonance energy, ring current, and magnetic susceptibility of **4**, **15**, and **16**.

Registry No. 4, 88726-17-4; **7**, 14311-05-8; **8a**, 88726-13-0; **8b**, 88726-14-1; **9a**, 88726-15-2; **9b**, 88726-16-3; **10a**, 228-82-0; **10b**, 13777-90-7; **13a**, 88726-18-5; **13b**, 91861-71-1; **14a** (isomer 1), 91861-72-2; **14a** (isomer 2), 91861-73-3; **14b** (isomer 1), 91861-74-4; **14b** (isomer 2), 91861-75-5; **18**, 30388-20-6; **19a**, 91861-76-6; **19b**, 91861-77-7; **20**, 91861-78-8; 3*H*-**24a**, 91861-81-3; 1*H*-**24a**, 91861-83-5; 3*H*-**24b**, 91861-85-7; 1*H*-**24b**, 91861-87-9; **25**, 91861-79-9; **26a**, 91861-89-1; **26b**, 91861-91-5; chlorobis(diisopropylamino)cyclopropenium perchlorate, 74507-77-0; dimethyl disulfide, 624-92-0; **17**, 3724-43-4.

The $C_4H_7^+$ Potential Surface[1]

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Abstract: MINDO/3 calculations are reported for the $C_4H_7^+$ systems. Contrary to conclusions from ab initio calculations but in agreement with experiment, the cyclopropylcarbinyl cation and "cyclobutyl cation" are *both* predicted to correspond to minima on the potential surface, the latter being indeed the lower in energy and having a nonclassical structure with a relatively strong transannular bond, corresponding to 1-protonated bicyclobutane. The cyclopropylcarbinyl cation is best formulated as a π complex. Interconversion of the two isomers was studied and also their conversions to the α-methylallyl cation. The formation of 1-substituted 3-butenes does not take place via 3-buten-1-yl cation.

Thirty years have now elapsed since Roberts[2] first showed the cyclopropylcarbinyl cation (**1**) to have a nonclassical structure. During this period numerous experimental[3-5] and theoretical[6-10] studies have been reported of **1** and the rearrangements it, and its derivatives, undergo.

The experimental studies indicate that **1** undergoes a rapid degenerate interconversion with the two isomers where different pairs of methylene groups are linked, and also rapid interconversion with the cyclobutyl cation (**2**, **3**). Under ionizing conditions, ionizable derivatives (**4**, **5**) of **1** or **2** (**3**) interconvert rapidly, while a slower rearrangement leads to the corresponding 3-butenyl derivative, **6**. It has usually been assumed that the latter is formed via the corresponding cation (**7**).

Calculations[6] by the Roothaan–Hall (RH; "ab initio SCF") method, using the STO-3G basis set, predicted **1** to be the only minimum of the type $(CH)(CH_2)_3^+$ on the $C_4H_7^+$ potential

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(1) Part 68 of the series Ground States of Molecules. For Part 67, see: Dewar, M. J. S.; Healy, Eamonn F.; Stewart, James J. P. *J. Compt. Chem.*, in press.

(2) For reviews see the following: (a) Richey, G. "Carbonium Ions", Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26. (b) Wiberg, K. B.; Hess, B. A.; Ashe, A. J., ref 2a, Chapter 26. (c) Brown, H. G. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapter 5.

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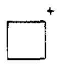

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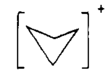

3

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8

surface, **2** (**3**) collapsing to **1** without activation. The latter conclusion has been confirmed by calculations[7] with larger basis sets (4-31G, 6-31G, 6-31G*), but these also predicted the existence of a second minimum, corresponding to a structure similar to **1** but lacking its plane of symmetry.

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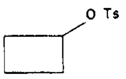

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Extensive studies[11,12] have, however, shown that the RH procedure gives unsatisfactory results for "nonclassical" carbocations because their formation from classical analogues usually involves large changes in correlation energy. Adequate allowance must be made for this by one of the standard procedures, i.e., inclusion of very extensive CI, CEPA, etc. Calculations of this kind become very expensive, even for ions as small as those considered here, if they are carried out properly.[13]

By good fortune, MINDO/3[14] happens to perform exceptionally well for simple carbocations, giving results[15] similar to those from the most sophisticated ab initio procedures[11,12] at an infinitesimal fraction of the cost in computing time. In view of the continuing interest in the $C_4H_7^+$ system, we therefore decided to use it in a detailed survey of the relevant parts of the corresponding potential surface. Here we report our results. The only previous MINDO/3 calculations for such species seem to be a study[15] of **1** which confirmed its formulation as a π complex, a calculation[16] of the barrier to rotation in **1**, and calculations by Bauld et al.[17] for **2** (**3**), carried out in another connection. The latter are, however, of interest in that they indicate a strong transannular bonding interaction between C_1 and C_3 in **2** (**3**).

Procedure

The MINDO/3 procedure has been fully documented.[14] The calculations were carried out with full geometry optimization, using the MOPAC[18] package of computer programs. Transition states were located by the reaction coordinate method[19] and refined by minimizing the norm of the energy.[20] Each stationary point was characterized by calculating and diagonalizing the corresponding Hessian (force constant) matrix.[20] All these procedures are included in MOPAC.

Results

Calculations were carried out for 1, **2**, **3**, **7**, and the α-methylallyl cation, **8**. The cyclobutyl cation was studied both without constraints (**3**) and with enforced planarity (**2**). **1**, **3**, and **8** proved to be minima on the potential surface, their Hessian matrices having no negative eigenvalues, while **2** proved to be the transition state for interconversion of **3** and its mirror image. The latter conclusion followed from the fact that the Hessian matrix had one negative eigenvalue, from the form of the corresponding

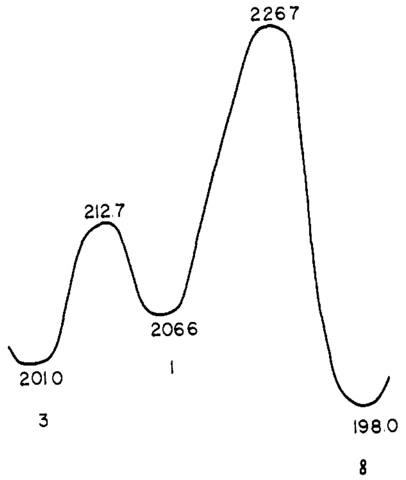

Figure 1. The MINDO/3 calculated reaction profile for interconversion of **1**, **3**, and **8**.

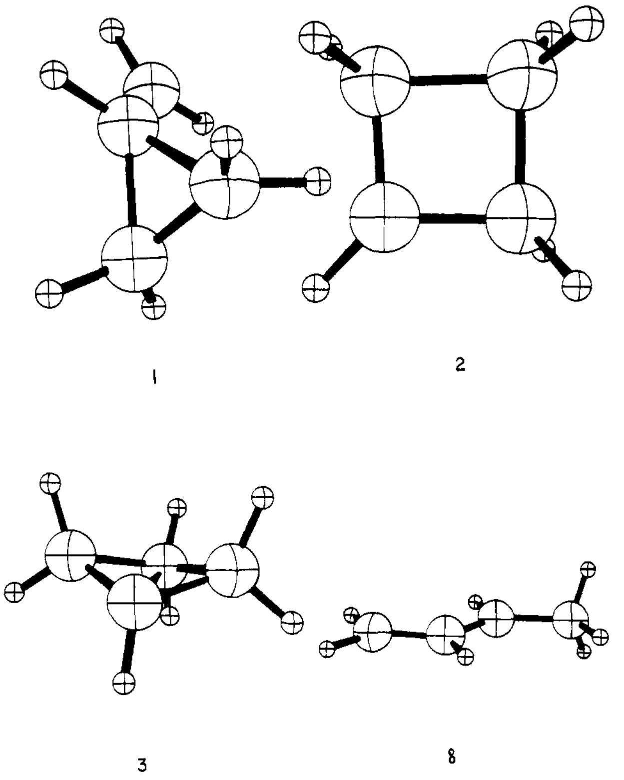

Figure 2. ORTEP plots of the MINDO/3 calculated geometries for **1**, **2**, **3**, and **8**.

Table I. MINDO/3 Calculated Heats of Formation and Hydride Ion Affinities

	ΔH_f	HIA
1	206.56	275.6
2	210.60	
3	200.97	266.4
7	collapsed with activation to **8**	collapsed with activation to **8**
8	197.97	
CH_3^+	260.3^a	337.1
$CH_3CH_2^+$	214.6^a	304.9
CH_3CHCH_3	186.4^a	283.4
$CH_3CHCH_2CH_3$	176.1^a	277.0
allyl cation	222.2^a	286.2

[a] Reference 13.

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(12) Raghovochari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. It should be noted that the authors failed to refer to the MINDO/3 calculations and indeed failed to cite results from *any* other calculations, even those of ref 11.

(13) Geometries should be calculated by minimizing the total energy with respect to all geometric parameters without making any assumptions. All stationary points found in this way should be characterized by calculating and diagonalizing[19] the Hessian (Force Constant) matrix.

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(18) Available from the Quantum Chemistry Program Exchange (QCPE).

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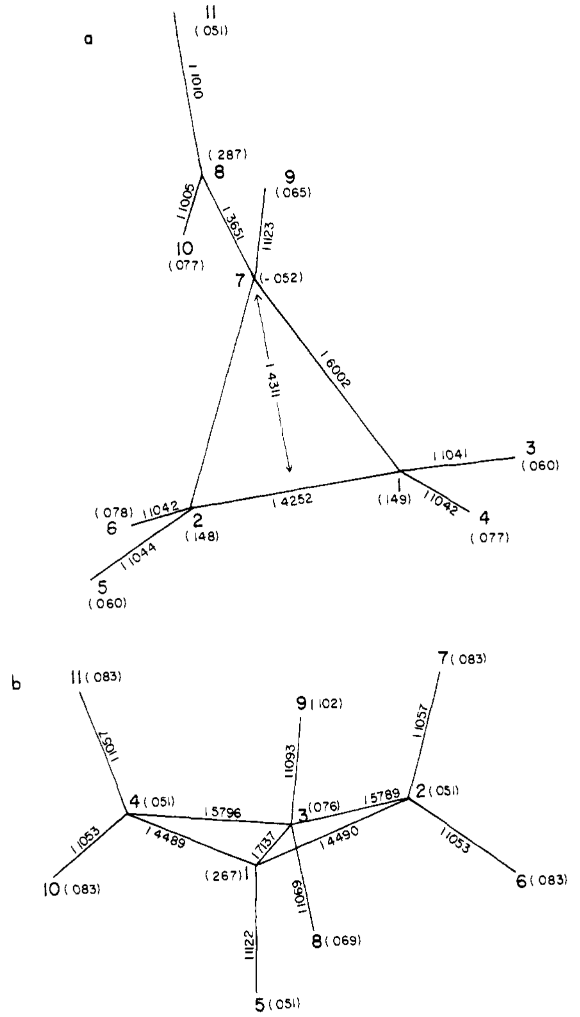

Figure 3. MINDO/3 calculated bond lengths and formal charges for **1** and 3.

eigenvector, and that distortion of **2** along that eigenvector, followed by geometry optimization, led to **3** or its mirror image. The primary carbenium ion (**7**) was not a stationary point on the potential surface, collapsing without activation to **8**. This was not unexpected because similar studies of a number of primary, secondary, and even tertiary carbonium ions have shown that they are often likewise unstable, undergoing hydrogen migration to form π complexes. **7** would be expected to collapse to **8**, the latter being an allyl cation and correspondingly stable.

We also studied the interconversions of the various isomers. The results are indicated by the schematic MERP (minimum energy reaction path) shown in Figure 1. The barrier to interconversion of **1** and **3** is quite low while a much higher barrier separates **1** from **8**. No direct path of lower energy was found linking **3** to **8**.

Table I shows the energies of the various stationary points located on the potential surface, Figure 2 their geometries in the form of ORTEP plots, and Figure 3 the corresponding distributions of formal charge.

Discussion

Our results differ from the earlier ab initio ones[6-8] in that they not only predict both **1** and **3** to be stable species but also imply that **3** should be more stable than **1**. NMR studies[3] of the ion in superacid media indicate that there are at least two isomers present in equilibrium with one another, in agreement with our results and directly contradicting the ab initio ones. Gas-phase studies[4] have moreover confirmed the existence of two stable $C_4H_7^+$ species and have also indicated that one is the cyclopropylcarbinyl ion (**1**) while the other is some kind of cyclobutyl species, as our calculations also predict.

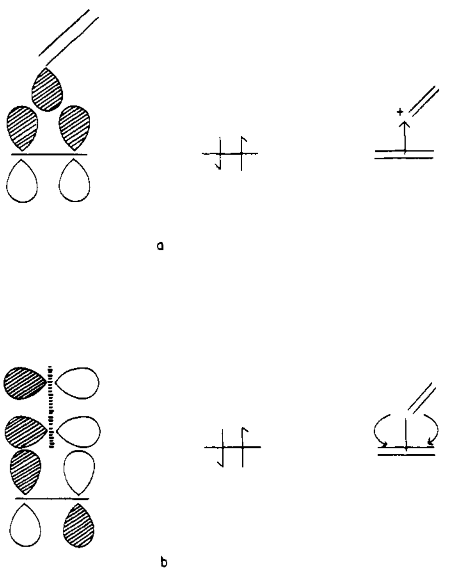

Figure 4. (a) Schematic representation of the π complex between vinyl cation and ethylene. (b) Back-bonding from the apical π MO to the basal π^* MO.

The stabilization of **1** and **3**, relative to analogous open-chain carbocations, can be estimated by calculating the corresponding hydride ion affinities (HIA), these being *minus* the heats of reaction for combination of the ions with H^-.

$$R^+ + H^- \rightarrow RH; \Delta H = -\mathrm{HIA} \qquad (1)$$

The necessary MINDO/3 heats of formation are shown in Table I, together with values of HIA calculated from them by using the experimental value[21,22] for the heat of formation of H^-. Geometrical constraints had to be applied in calculating ethyl cation because this rearranges without activation to the isomeric π complex. The results in Table I indicate that **1** and **3** are much more stable than analogous alkyl cations, a conclusion supported by the ease with which they can be prepared and studied. Both are clearly "nonclassical" species of some kind or other.

As noted above, it has already been pointed out in print that the MINDO/3 calculations for **1** indicate it to be best represented as a π complex (**9**), formed by ethylene as the donor and vinyl cation as acceptor, the resulting structure being further stabilized by back-coordination of the π electrons of the apical vinyl group into the empty antibonding π MO of ethylene (see Figure 4). Both double bonds in **1** should be weakened by coordination with acceptors while that in the ethylene moiety should be further weakened by donation of electrons into the corresponding antibonding π^* MO. The calculated bond lengths (1.365 and 1.426 Å, respectively) conform to this expectation, both being intermediate between the C—C and C=C bond lengths with the basal bond the longer.

Since the μ bond in **9** is effectively a two-center double bond in which the ethylene moiety contributes one orbital to each component, its length should really be measured from the apical atom to the midpoint of the basal CC bond. The calculated value (1.431 Å) is reasonable on this basis whereas the distances between the apical and basal atoms (1.600 Å) are much greater than the length (1.53 Å) of a normal two-center C–C bond.

The structure calculated for **3** is less easily interpreted.

It clearly does not correspond to the classical cyclobutyl cation because the distance between C_1 and C_3 (1.714 Å) implies the existence of a bond between them. C_3 is thus covalently linked to five other atoms. Transformation[23] of the MOs calculated for **3** into optimally localized orbitals (Table II) indicates that four

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[21] The energies calculated by MINDO/3 or MNDO for anions where the charge is localized on a single atom are usually too negative. See: Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

[22] "Handbook of Chemistry and Physics", 64th ed.; CRC Press: Cleveland, Ohio, 1983–1984.

Table II. MINDO/3 Localized MOs for **3**

no. of centers	% composition of orbitals
2.033	C1, 54.85; C2, 43.69
2.034	C1, 54.81; C2, 43.72
2.486	C3, 44.68; C2, 43.81; C1, 10.34
2.486	C3, 44.66; C4, 43.81; C, 10.35
2.015	C2, 54.20; H6, 45.00
2.015	C4, 54.18; H10, 45.01
2.013	C3, 53.58; H8, 45.79
2.036	C4, 53.63; H11, 45.11
2.036	C2, 53.62; H7, 45.11
2.048	C1, 51.99; H5, 46.70
2.122	C3, 52.27; H9, 44.43; C1, 2.47

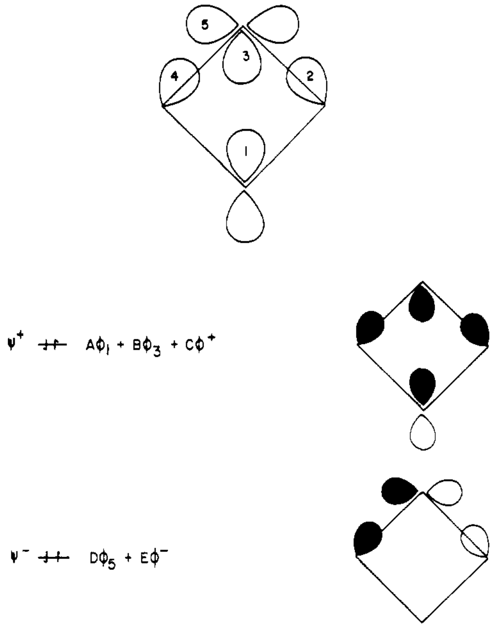

Figure 5. Three-center MOs which represent the "nonclassical" bonding in **3**.

of the valence electrons are delocalized while the others occupy localized two-centeer CC and CH bonds. The AOs available for forming the delocalized orbitals are indicated in Figure 5. Since **3** has a plane (Σ) of symmetry, its MOs must be either symmetric or antisymmetric, for reflection in Σ. The AOs ϕ_1 and ϕ_3 are symmetric and ϕ_5 antisymmetric, for reflection in Σ, while ϕ_2 and ϕ_4 can be replaced by symmetric and antisymmetric combinations, ϕ^+ and ϕ^-, given by:

$$\phi^+ = 2^{1/2}(\phi_2 + \phi_4) \qquad \phi^- = 2^{1/2}(\phi_2 - \phi_4) \qquad (2)$$

Two totally bonding MOs can then be constructed from these AOs, one (ψ^+) symmetric and the other (ψ^-) antisymmetric, being of the forms indicated in eq 3. All other MOs constructed from

$$\psi^+ = A\phi_1 + B\phi_3 + C\phi^+ \qquad \psi^- = D\phi_5 + E\phi^- \qquad (3)$$

ϕ_{1-5} are antibonding and so higher in energy than ψ^+ or ψ^-. These are therefore the MOs occupied in **3**. Figure 5 indicates their forms.

The electrons occupying ψ^- form a three-center two-electron bond, analogous to the π bonds in allyl cation, the π bond orders in which are 0.7. Since the overlap between the AOs C_1 and C_3 is better than that between other pairs of AOs contributing to ψ^+, the electrons in it contribute a corresponding strong partial bond between C_1 and C_3, together with weaker bonds between C_1 and C_2, C_2 and C_3, C_3 and C_4, and C_4 and C_1. Thus C_1 and C_3 are linked, overall, by a strong partial bond, there being no other bonding between them; C_1 and C_2, and likewise C_1 and C_4, are linked both by a normal two-center covalent bond and by the partial bonding due to ψ^+; while C_2 and C_3, and C_3 and C_4, are linked by a strong partial bond, due to the electrons in ψ^-, and a weak one, due to the electrons in ψ^+. One would therefore expect (a) the bonds between C_1 and C_2, and between C_1 and C_4, to be stronger, and therefore shorter, than ordinary C–C bonds; (b) the C_1C_3 bond to be weaker, and therefore longer, than a normal C–C bond; (c) the C_2C_3 and C_3C_4 bonds to be intermediate in strength, and therefore length, their lengths being consequently not much different from those of normal C–C bonds. As Figure 3 shows, the calculated bond lengths conform nicely to these expectations. It is also easy to see why **3** has a puckered geometry. If it were planar, ϕ_1 would be a 2p AO and could not then interact with ϕ_3.

As noted above, the two-electron three-center bond due to ψ^- is similar to the corresponding π bond in allyl cation (**10**). If ψ^+ were localized between atoms C_1 and C_3, the positive charge in **3** would then be shared equally between C_2 and C_4, as it is between the terminal atoms in **10**. However, the electrons in ψ^+ are in fact spread over all four atoms. The charge in **3** is therefore correspondingly delocalized (Figure 3).

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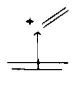
The geometry calculated for **3** implies that it could be regarded as protonated bicyclobutane, i.e., as bicyclobutanium ion, and that it may indeed be obtainable by dissolving bicyclobutane in supereracids.

The calculated MERP (Figure 1) for interconversion of **1**, **3**, and **8** implies that interconversion of **1** and **3** should be much faster than conversion of either to **8**. As noted above, the experimental evidence indicates clearly that this is the case. According to MINDO/3, **3** should be lower in energy than **1** and should therefore be the dominant form at equilibrium. This conclusion is also supported by the experimental evidence. As already noted, the ab initio calculations for this system predicted **3** not only to be higher in energy than **1** but not even to correspond to a minimum on the potential surface.

While MINDO/3 is known[15] to give very good estimates of heats of formation for simple π-complex carbocations, its performance for **3** is difficult to predict. One might, however, expect the MINDO/3 heat of formation for **3** to be too negative because MINDO/3 underestimates strain energies in small rings and might therefore equally underestimate the angle strain at C_1 in **3**. The calculated difference in energy between **1** and **3** certainly seems too large, given the existence of a measurable equilibrium between them, and the barrier to interconversion is also probably too large. If the left-hand side of the MERP in Figure 1 was raised to make the energies of **1** and **3** similar, the barrier to interconversion would be ca. 7–8 kcal/mol, a value consistent with the available evidence.

One last point needs to be explained, i.e., the fact that with long standing under ionizing conditions, cyclopropylcarbinyl and cyclobutyl derivatives isomerize to 3-buten-1-yl derivatives. This rearrangement cannot take place by rearrangement of **1** or **3** to **7**, both because the reactions would be much too endothermic and because **7**, if formed, would at once rearrange to **8**. No α-methylallyl derivatives are formed in these reactions.

The explanation probably lies in the properties expected for the π-complex ion, **1**. Such π complexes, where there is backcoordination between the apical and basal groups, can be written as classical species, e.g., **11** in the case of **1**. There should indeed be a continuous transition[24] between species best represented as π complexes (**9**) and species best represented in terms of three-membered rings (**11**). Combination of **1** with a nucleophile can



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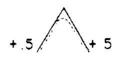

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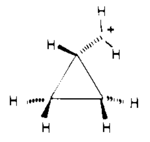

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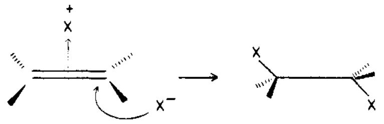
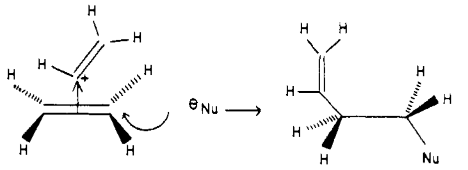
therefore take place at the exocyclic methylene to give derivatives of methylcyclopropane. However, π complexes can also react with nucleophiles by attack at a basal carbon atom, as in the second step in electrophilic addition to olefines; e.g.



A corresponding attack on the π complex corresponding to 1 can give a 3-butenyl derivative; e.g.



There is therefore no need to postulate rearrangement of 1 or 3 to the classical ion (7) in order to account for the formation of such products. This represents an example where the π-complex description of nonclassical carbocations is clearly superior to the "dotted line" representation.

Summary and Conclusions

The calculations reported here seem to account in a very satisfactory manner for the experimental evidence concerning the $C_4H_7^+$ system. MINDO/3 predicts both cyclopropylcarbinyl cation (1) and a modified form (3) of the cyclobutyl cation to be minima on the potential surface and also for the experimental evidence concerning their structures and interconversion. These results indicate once more the value of MINDO/3 in studies of reactions of carbocations and emphasize the inadequacy of other than "state-of-the-art" ab initio methods in this connection. The structures calculated for 1 and 3 are shown to conform to current qualitative ideas concerning molecular structure, and the calculations also account for the isomerization of cyclopropylcarbinyl and cyclobutyl derivatives to 3-buten-1-yl derivatives. This is without any need to postulate prior isomerization of the cyclopropylcarbinyl or cyclobutyl cations to the 3-buten-1-yl cation, which is predicted by MINDO/3 to rearrange without activation to the 3-buten-2-yl cation, as might indeed have been expected on general grounds.

A detailed analysis of the results of the calculations for 1 and 3 has also led to reasonable descriptions of their structures in terms of current qualitative theory. 1 is best represented as a π complex, formed by ethylene as donor and vinyl cation as acceptor, while 3 has a curous "nonclassical" structure which can be interpreted in terms of bonding known to occur in other nonclassical species.

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Flash-Photolytic Generation of Acetophenone Enol. The Keto–Enol Equilibrium Constant and pK_a of Acetophenone in Aqueous Solution

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Abstract: Acetophenone enol has been generated by Norrish type II photoelimination of γ-hydroxybutyrophenone, and its rate of ketonization has been measured in dilute aqueous HCl solutions. These data, in combination with the specific rate of acid-catalyzed enolization of acetophenone, give a value of the keto–enol equilibrium constant which is in good agreement with another result based upon enolization and ketonization rate constants measured in NaOH solutions. The average of these determinations gives $\mathrm{p}K_E = 7.90 \pm 0.02$. This, when combined with the known acid-dissociation constant of acetophenone enol, leads to $\mathrm{p}K_a^K = 18.24 \pm 0.03$ for the acidity constant of acetophenone ionizing as a carbon acid. The present results allow an estimate of the specific rate of proton transfer from H_3O^+ to the β-carbon atom of acetophenone enolate ion, $k = (4.2 \pm 1.2) \times 10^{10}\ M^{-1}\ s^{-1}$, which is so great as to suggest that this reaction occurs through proton transfer down hydrogen-bonded solvent bridges between acid and substrate.

Simple enols have long been of interest because they are essential intermediates in a number of important chemical and biological reactions, and also because they have a fascinating chemistry of their own.[1] Elucidation of this chemistry, however, has been impeded by the thermodynamic instability of simple enols, and also by the speed with which they revert to their keto tautomers.

We have recently shown that these difficulties may be overcome by the use of modern flash-photolytic methods.[2] It is well-known that Norrish type II photoelimination of structurally appropriate carbonyl compounds produces enols,[3] and the subsequent reactions of enols so generated may be monitored by rapid spectroscopic techniques. We have already reported our use of these methods to generate the enols of acetophenone, eq 1,[2a] and acetone[2b] in

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