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MINDO/3 Study of 7-Norbornyl, 7-Norbornenyl, and 7-Norbornadienyl Cations

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The geometries, charge distributions, and heats of formation for 7-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations have been calculated by the use of the semi-empirical MINDO/3 SCF MO method. Each of these cations is symmetrical with respect to the plane which contains the C(7)–H(7) bond and bisects the C(1)–C(7)–C(4) angle. Both the 7-norbornenyl and the 7-norbornadienyl cations take the nonclassical bridge-structure: the C(2)–C(3) and C(2)–C(7) distances are about 1.43 and 1.67 Å respectively, and the C(2)–C(1)–C(4)–C(7) dihedral angle is about 75°. The classical 7-norbornyl cation also is quite unsymmetrical with regard to the C(1)–C(7)–C(4) plane: the C(2)–C(1)–C(4)–C(7) and C(7)–C(1)–C(4)–C(5) dihedral angles are 94° and 144°, respectively. The calculated barriers to the bridge flipping in the 7-norbornyl and 7-norbornadienyl cations are 3.2 and 33.0 kcal/mol respectively. Although the latter is much higher than its observed value of 19.6 kcal/mol, it seems possible that solvation considerably lowers the barrier height. The present article also touches upon the solvolyses of derivatives of these carbocations.

The chemical behavior of the 7-norbornenyl and 7-norbornadienyl cations, known as unusually stable nonclassical ions, has been closely examined through kinetic, stereochemical, and spectroscopic experiments.[1–4] On the other hand, the theoretical studies which have hitherto been made on these carbonium ions do not necessarily afford enough information to explain their chemical properties.[5–7] For example, the geometries of the cations have not yet been calculated without any assumptions. In order to obtain detailed information about these interesting carbonium ions, we have begun to study them by the MINDO/3 self-consistent-field molecular-orbital method.[8] The present paper will give the calculated geometries, charge distributions, and heats of formation for 7-norbornyl (**1**), 7-norbornenyl (**2**), and 7-norbornadienyl (**3**) cations, and will discuss the stability of these carbocations and the solvent effect on it.

Method of Calculation

The calculations reported here were performed using the MINDO/3 parameters listed in Ref. 8, on a FACOM 230-75 computer at the Computing Center of Hokkaido University. Geometries of carbocations were obtained by minimizing their total energies with respect to all atomic coordinates, using a program written by the present authors. For any cation or molecule, the optimization procedure was repeated until a change in its total energy became less than 0.001 kcal/mol. Transition states were distinguished from other stationary points by two conditions: (a) they have only one negative eigenvalue of the force constant matrix and (b) their transition vector corresponds to the vibration which transforms the reactants into the products.[9]

A difference in solvation energy of two carbocations was estimated by the use of the following equation:

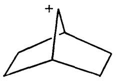
$$\Delta E_s = \Delta[-(1-1/D)(\sum_i q_i^2/2r_i + \sum_{i<j} q_i q_j/r_{ij})], \qquad (1)$$

where D denotes the dielectric constant of the solvent, q_i and q_j represent the net charges of the i-th and j-th atoms in each cation respectively, r_i designates the ionic radius of the i-th atom, and r_{ij} stands for the distance between the i-th and j-th atoms.[10] In this study, the ionic radii of carbon and hydrogen atoms were approximated by their usual van der Waals radii, 1.70* and 1.20 Å, respectively. In applying Eq. 1 to carbocations, we made the following modification: when the interatomic distance, d_{ij}, was less than the sum of the ionic radii, r_i+r_j, the latter was used as r_{ij}; otherwise, as usual, d_{ij} was adopted as r_{ij}. This means that it was assumed that the solvent neither assisted nor prevented the approach of the i-th and j-th atoms from their van der Waals distance to their bond distance. The following example shows that using bond distances as r_{ij}'s may lead to serious errors in the calculation of solvation energies for carbocations.

Let us consider a monoatomic system, A, with an ionic radius of R and a net charge of q and a diatomic system, B, where two atoms with ionic radii of R and net charges of $q/2$ are separated by a bond distance of d. From Eq. 1, the solvation energy for B, relative to that for A, is given by $\Delta E_s = -(1-1/D)(1/d-1/R)q^2/4$, which is negative because usually d is less than R. On the other hand, since B can be well approximated by a monoatomic system with a radius of R' (greater than R) and a net charge of q, the magnitude of the solvation energy for B should be smaller than that for A by $-(1-1/D)(1/R'-1/R)q^2/2$, *i.e.*, ΔE_s should be positive. Such a conflict probably comes mainly from overestimation of solvent effects in the process of forming the covalent bond. For this reason, we made the above-mentioned modification in Eq. 1 as a first approximation. However, it must be kept in mind that, in any way, ΔE_s gives only a rough estimate of a difference in solvation energy.

Results and Discussion

Geometries. Figure 1 shows the calculated geometries for the carbocations **1**, **2**, and **3**. Though no assumption was made about their symmetries, each of these cations has, within the limits of the computational errors, a plane of symmetry which contains the C(7)-H(7) bond and bisects the C(1)–C(7)–C(4) angle. The



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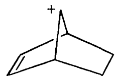

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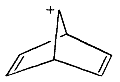

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* One-half the thickness of benzene rings in crystals.

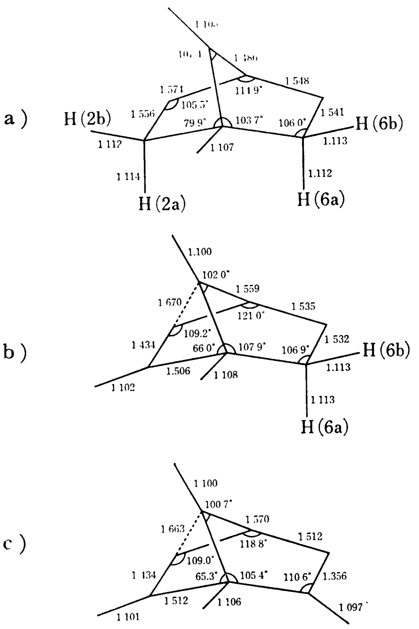


Fig. 1. The calculated geometries (bond lengths in Å) for (a) **1**, (b) **2**, and (c) **3**.

conformations of **1**, **2**, and **3** viewed along the C(1)–C(4) directions are given in Fig. 2. It should be noted here that not only the nonclassical ions **2** and **3**, but also the classical ion **1** is unsymmetrical with respect to the C(1)–C(7)–C(4) plane. As will be shown by an appreciable lengthening of the C(1)–C(2) and C(3)–C(4) bonds, this deformation probably occurs so as to help delocalization of the C(1)–C(2) and C(3)–C(4) σ-bonding electrons into the vacant C(7) 2p-orbital.

The degree of unsymmetry of **2** and **3** is much greater than that of **1**. Both the remarkable lengthening of the C(2)–C(3), C(1)–C(7), and C(4)–C(7) bonds and the close approach of the C(7) atom to the C(2) and C(3) atoms clearly indicate that the vacant C(7) 2p-orbital and the C(2)–C(3) π-bonding orbital interact strongly with each other to form a kind of bridged ion. It may be useful for an understanding of this orbital interaction to examine how the two overlapping orbitals in **2** and **3** differ from isolated 2p- and π-orbitals. First, it is found that the C(7)–H(7) bond deviates from the C(1)–C(7)–C(4) plane onto the side opposite to the C(2)–C(3) bond. This will make the C(7) 2p-orbital expand toward the C(2)–C(3) π-bonding orbital, resulting in an increase in the overlapping. On the other hand, both C(2)–H(2) and C(3)–H(3) bonds deviate from the C(1)–C(2)–C(3)–C(4) plane onto the same side as the C(7) atom. Considered simply from the viewpoint of expansion of the π-bonding orbital, such deviations of the two C–H bonds would be unfavorable to the p-π overlapping under consideration, but nevertheless they appear to strengthen this overlapping by directing the C(2) and C(3) 2p atomic orbitals, of which the C(2)–C(3) π-bonding orbital consists, more effectively toward the C(7) 2p-orbital (see Fig. 3).

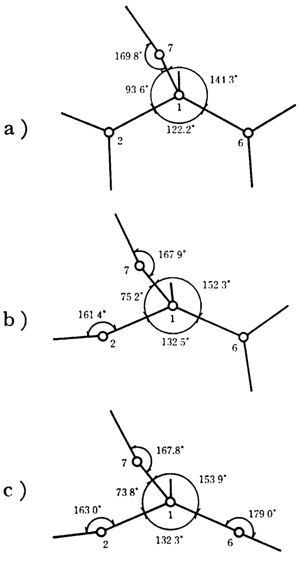


Fig. 2. The conformations viewed along the C(1)-C(4) directions: (a) **1**, (b) **2**, and (c) **3**.

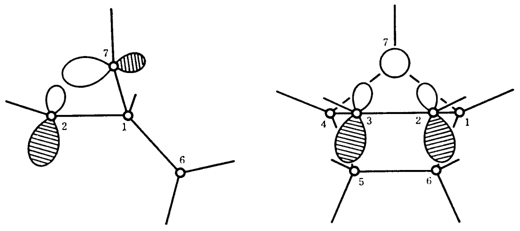


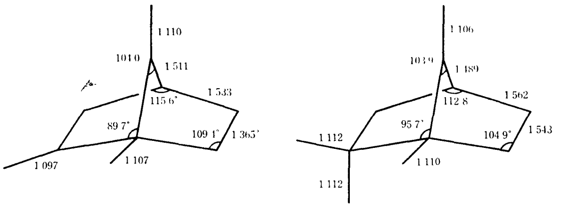
Fig. 3. The overlapping of the C(2) and C(3) p-orbitals with the C(7) vacant orbital in **2**.

Table 1. The distributions of net charges (in units of the electronic charge)

Atom	1	1[a)]	2	3	3[b)]
C(1), C(4)	−0.011	−0.030	0.062	0.087	0.032
C(2), C(3)	0.045	0.048	0.106	0.106	0.004
C(5), C(6)	0.040	0.048	0.038	−0.013	0.004
C(7)	0.352	0.425	0.086	0.084	0.398
H(1), H(4)	0.073	0.065	0.060	0.058	0.061
H(2a), H(3a)	0.054	0.039	0.081	0.086	0.094
H(2b), H(3b)	0.037	0.028			
H(5a), H(6a)	0.031	0.039	0.031	0.091	0.094
H(5b), H(6b)	0.031	0.028	0.035		
H(7)	0.048	0.044	0.086	0.083	0.025

a), b) The transition states for the bridge flipping in **1** and **3** respectively.

Distributions of Net Charges. The distributions of net charges, which are listed in Table 1, show that the C(2)–C(3) π-bonding electrons in **2** and **3** are so remarkably delocalized that the C(2) and C(3) atoms carry greater net charges than the C(7) atom. This result is consistent with the experimental observation that, in the ^{13}C NMR spectra of **2** and **3**, the absorption of the C(2) and C(3) atoms occurs at lower fields than that of the C(7) atom.[4)] Although, in both **2** and **3**, the C(2) and C(3) atoms bear the greatest net charge of $+0.106e$, even this does not reach one-third of the net charge ($+0.352e$) on the cationic center in **1**. Thus,

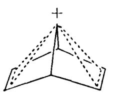


(a) (b)

Fig. 4. The calculated transition state geometries for the bridge flipping in (a) **3** and (b) **1**.

the positive charge of **2** and **3** can be regarded as being spread over almost the whole cation. It is interesting that, in spite of such a pronounced dispersal of the positive charge, the C(5) and C(6) atoms in **3** still bear slight negative net charges (−0.013*e*).**

Bridge Flipping. Figure 4(a) shows the calculated geometry of **3** in the transition state for the bridge flipping. This geometry was calculated on the assumption of C_{2v} symmetry, which was later verified by testing whether the geometry obtained satisfied the two conditions of transition states or not (see the section on Method of Calculation). In the case of the neutral norbornadiene molecule, MINDO/3 optimization affords a length of 1.356 Å to the C(2)–C(3) bond and a value of 121.8° to the C(2)–C(1)–C(4)–C(7) dihedral angle, while the corresponding values of **3** in the transition state are 1.365 Å and 116.2° respectively. This structural variation, caused by extraction of a hydride ion, seems to support the presence of such an interaction between the vacant C(7) 2p-orbital and the C(2)–C(3) or C(5)–C(6) π-bonding orbital, as is shown in **4**. The distribution of net charges, given in the last column of Table 1, also indicates that an appreciable amount of the π-bonding electrons flows into the C(7) 2p-orbital; the C(2), C(3), C(5), and C(6) atoms carry slight positive net charges (+0.004*e*).



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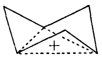

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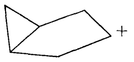

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The barrier to the bridge flipping in **3** was estimated to be 33.0 kcal/mol by our MINDO/3 calculation. Since its observed value at 45 °C is 19.6 kcal/mol or more,[11] the calculated barrier seems to be somewhat too high. The difference may be ascribed in part to the MINDO/3 approximation and in part to the solvent effects. As will be seen in Table 1, the C(7) atom bears much more net charge in the transition state than in the stable form. Hence, **3** can acquire more stabilization energy due to solvation in the former. This difference in solvation energy was estimated at 5.7 kcal/mol for $D=\infty$ by using Eq. 1. Jorgensen has recently shown that the presence of one molecule of hydrogen chloride can reduce the difference in energy between the more stable cation, **5**, and the less stable one, **6**, by more than 9 kcal/mol.[12,13] This suggests that solvation may facilitate the bridge flipping in **3** to a considerable extent.***

The calculated barrier to the bridge flipping in **1** was only 3.2 kcal/mol. Moreover, the calculation of solvation energy showed that this barrier might be lowered in solvents with $D=\infty$ by 2.0 kcal/mol. Therefore, it seems difficult to observe the bridge flipping of **1** in solution. The calculated geometry and distribution of net charges of **1** in the transition state for the bridge flipping are given in Fig. 4(b) and in the third column of Table 1 respectively. The C(7) atom of **1** in the transition state carries more net charge than that of **3** in the transition state, which is probably due to the absence of π-bonding electrons to delocalize directly into the ionizing center.

TABLE 2. THE CALCULATED HEATS OF FORMATION (IN kcal/mol)

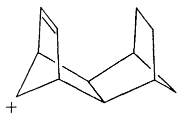
RX	RH	RCl	R^+	$\Delta\Delta H^{a)}$	$\Delta\Delta H^{b)}$	$\Delta E^{c)}$
9	7.0	−0.1	210.9	34.2	33.1	15.2
10	44.8	36.6	214.5	(0)	(0)	(0)
11	84.0	75.5	249.7	−4.0	−3.7	−3.9
12	91.6	83.2	253.7	−7.6	−7.4	
13	127.8	119.4	290.2	−7.3	−7.1	−4
14						−4.4
15						−4.3

a), b) The calculated relative enthalpies of the gas reactions $RH \rightarrow R^+ + H^-$ and $RCl \rightarrow R^+ + Cl^-$, respectively. c) The relative activation energies estimated from the observed rate constants for the solvolyses of RX. See Refs. 15—19.

Heats of Formation. The calculated heats of formation of **1**—**3** and **7**—**13** are summarized in Table 2. Since MINDO/3 is known to overestimate the heats of formation of **9** and **11** with X=H by about 21 and 25 kcal/mol respectively,[14] the other heats of formation also should be taken as being overestimated to approximately the same extent as those of the two hydrocarbons. Table 2 further contains the calculated enthalpies of the gas reactions,

$$R\text{-}X \longrightarrow R^+ + X^-. \qquad (2)$$

These enthalpy changes seem not to include such large



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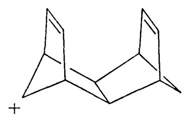

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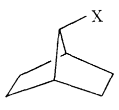

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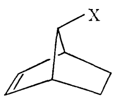

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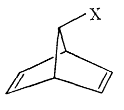

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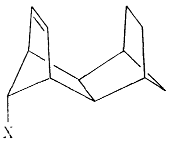
** MINDO/3 gives net charges of −0.040*e* to the C(5) and C(6) atoms in norbornadiene.

*** The effect of the entropy term on this bridge flipping seems not to be very important, since it is estimated at 2—3 kcal/mol(25 °C) from the entropies of activation for the acetolyses of **9** and **10**.



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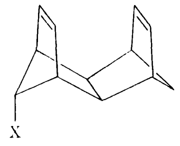

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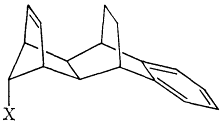
errors as the heats of formation themselves, because the errors of the latter are probably to a marked degree canceled out in deriving the former from the latter. In fact, it has been shown that MINDO/3 brings about an error of only 4 kcal/mol with respect to the heat of hydrogenation of norbornadiene into norbornane.[14)] Since, as will be seen in Table 2, the relative enthalpy of Reaction 2 does not change substantially according to whether the reactant is a hydrocarbon or an alkyl chloride, the results with the chlorides will hereinafter be discussed.

The relative activation energies observed for solvolyses of the compounds of interest are given in the last column of Table 2.[15–19)] The calculated enthalpies of the **11**→**3** and **13**→**8** reactions are in good agreement with their corresponding activation energies. This suggests that the formation of **3** and **8** should receive nearly as great solvent-assistance as that of **2**. It has recently been found that the relative energies of nonresonant, isomeric secondary and tertiary carbocations are similar in the gas phase and in solution.[20–22)] The cationic portion of **8**, not to mention that of **3**, is quite analogous in charge distribution to that of **2**, as will be seen in Table 3. Accordingly, although these three carbocations are neither nonresonant nor isomeric, it is possible that solvent effects on them may be similar.

As to the **9**→**1** reaction, the case is considerably different. The difference between the enthalpies of the **9**→**1** and **10**→**2** gas reactions was estimated at 33.1 kcal/mol by our MINDO/3 calculation, while the solvolysis experiments have shown that the activation energy for **9** is higher than that for **10** by 15.2 kcal/mol. The difference between these calculated and observed values, 17.9 kcal/mol, seems too large to be regarded as due merely to the usual electrostatic effects of the solvent; for example, from Eq. 1, it was shown that **1** might be only 4.8 kcal/mol more stabilized by solvents with $D=\infty$ than **2**. In order to explain this remarkable discrepancy between the gas reactions and the solvolyses, it is necessary to consider different mechanisms for the solvolyses of **9** and **10**. Although **10** presumably solvolyzes through the free, stable carbonium ion, **2**, the solvolysis of **9** may involve rate-determining formation of solvent-separated ion-pairs, as has been found for the 2-adamantyl derivative.[23)] The change of **9** into the solvent-separated ion-pair will not require as much energy as the ionization of **9** into the free carbonium ion, **1**. Consequently, the activation energy for the solvolysis of **9** may actually be much lower than could be expected from the mechanism which involves the free cation, **1**.

Table 3. The distributions of net charges (in units of the electronic charge) in **8** and **13** (X=H)

Atom	**8**	**13**
C(1), C(4)	0.067	0.073
C(2), C(3)	0.100	−0.038
C(5), C(6)	0.011	0.019
C(7)	0.087	0.058
C(8), C(11)	0.070	0.073
C(9), C(10)	−0.044	−0.038
C(12)	0.052	0.058
H(1), H(4)	0.050	−0.034
H(2), H(3)	0.074	0.014
H(5), H(6)	0.007	−0.038
H(7a)	0.078	−0.039
H(7b)		−0.033
H(8), H(11)	0.006	−0.034
H(9), H(10)	0.047	0.014
H(12a)	−0.011	−0.039
H(12b)	0.017	−0.033



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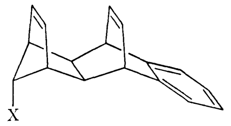

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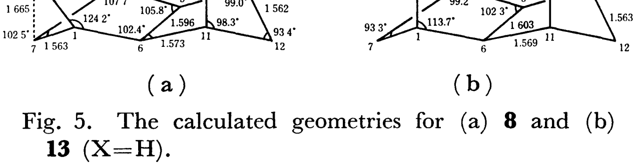
It is known experimentally that **13** solvolyzes about 10^3 times as fast as **10**.[24)] Fukui *et al.* have recently tried to explain this additional acceleration by applying their three-system interaction theory to the carbonium ion, **8**.[25)] On the other hand, it has been found that the solvolysis rate for **15** is slightly lower than that for **14**.[19)] Our calculations with **12** and **13** also show that, if both of their solvolyses proceed through free carbonium ions, **13** will solvolyze somewhat more slowly than **12**. These results suggest that the solvolytic rate enhancement of **13** and **15** may not necessarily be ascribed to additional stabilization of the intermediate carbonium ions, *i.e.*, anchimeric assistance by the double bond more distant from the cationic center, because **12** and **14** without such anchimeric assistance are more reactive than **13** and **15**. The calculated geometries of **8** and **13** are shown in Fig. 5. The two double bonds in **8** appear too remote from each other to have an effective orbital interaction; the distance between the C(2) and C(10) atoms was estimated at 3.51 Å. Further, no weakening of the C(9)–C(10) double bond in **8** can be detected in Fig. 5. The comparison between the charge distributions for **8** and **13** is given in Table 3, which also shows clearly the absence of detectable flow of the C(9)–C(10) π-electrons into the C(2)–C(3) π-orbital. Thus, it may be said that **8** is not appreciably stabilized



(a) (b)

Fig. 5. The calculated geometries for (a) **8** and (b) **13** (X=H).

by the presence of the C(9)–C(10) double bond. It should thus be concluded that the additional acceleration of the solvolyses of **13** and **15** is due mainly to the relief of steric repulsion between the two adjacent double bonds in the reactants.

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