Ground States of Molecules. 34.[1] MINDO/3 Calculations for Nonclassical Ions

Michael J. S. Dewar,* Robert C. Haddon, Andrew Komornicki, and Henry Rzepa

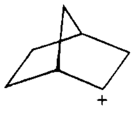
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received November 3, 1975

Abstract: MINDO/3 calculations are reported for the 2-norbornyl, 2-methyl-2-norbornyl, 5-norbornenyl, and 2-bicyclo[2.1.1]-hexyl cations and for π complexes isomeric with them. The classical structures are favored for 2-norbornyl and 2-methyl-2-norbornyl, whereas the π complexes are more stable for the other two. MINDO/3 calculations of ESCA spectra for the classical and π complex forms of 2-norbornyl indicate that the spectrum observed by Olah et al. corresponded to the former. MINDO/3 predicts a hitherto disregarded π complex structure to be the most stable form of 2-norbornyl. While this prediction may well be erroneous, the structure in question should be at least a low-energy species. STO-3G calculations are reported for several 2-norbornyl isomers.

Thirty years have elapsed since the π complex theory was first proposed,[2] to explain the course of various organic reactions. Soon afterwards it was suggested[3] on the basis of a simple Hückel calculation[4] that π complex isomers of carbonium ions might exist as stable species, perhaps even more stable than their "classical" isomers. The currently accepted π complex theory of metal-olefin complexes, involving back coordination, was also proposed at that time.[3]

The suggestion concerning metal-olefin complexes was soon confirmed by Chatt and Duncanson[5] and olefin π complexes now play a major role in organometallic chemistry. Evidence for the existence of stable π complex cations also soon came to light.[6] Unfortunately workers in this area refused to regard such species as π complexes or to represent them as such. This failure, combined with the use of an alternative and unsatisfactory "dotted line" symbolism,[6] has caused much confusion; for the large majority of "nonclassical carbonium ions" that have been postulated *are* π complexes and their behavior can be understood much better on this basis.[6] The only "nonclassical carbonium ions" that are not π complexes are certain species containing localized three-center bonds, e.g., edge-protonated cyclopropane and the trishomocyclopropenium cation.

A major difficulty in this area has been the lack of information concerning the structure of organic π complexes. Indeed, it is often difficult to prove that such species exist. One of the most violent chemical controversies in recent times has been concerned with the identity of the cation formed from *exo*-2-norbornyl derivatives.[6,7] A vast amount of time, money, and effort has been spent over the last 25 years on attempts to establish whether it is the classical 2-norbornyl cation (**1**) or the isomeric π complex **2**. Recently Olah et al.[8] claimed that they had "concluded the nonclassical ion controversy" by proving the ion to be **2**. However, their arguments have been questioned,[9] and, as we shall show presently, these criticisms are by no means unfounded.



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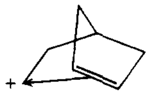

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Similar problems occur in all investigations of reaction mechanisms, due to the lack of direct procedures for studying the intermediates involved. This is an area where theoretical calculations should be of especial value, providing information that is otherwise unobtainable. Numerous attempts have indeed been made to study the nature and possible existence of "nonclassical carbonium ions" in this way.

The original[4] Hückel calculation was sufficient to show that π complexes might be relatively stable species and structure/stability relationships have been deduced for them using PMO theory.[10] What we now need is a quantitative procedure, able to tell us the stabilities of specific π complexes relative to classical isomers. Although various attempts have been published during the last 30 years, the methods used have been too inaccurate to provide such information.[11] They have at best confirmed qualitative conclusions that were already established.

Current procedures can be used in connections such as this only in an empirical way.[12] Such a procedure must be thoroughly tested before its conclusions can be trusted. In the present connection such tests are difficult since heats of formation are known only for a very few "nonclassical" species (CH_5^+,[13] $C_2H_7^+$,[13] protonated cyclopropane[14]) and geometries for none. We must at least be sure that our procedure reproduces the properties of "normal" molecules of as many different kinds as possible and also the limited data for the "nonclassical" ions. A further essential is that the geometries of the various species should be calculated by minimizing the total energy.[12] The use of assumed geometries is never acceptable and is particularly unacceptable here because the geometries of "nonclassical" carbocations are not known. These two considerations (accuracy and cost) eliminate nearly all the procedures currently available. Conventional semiempirical treatments (EH, CNDO, INDO) are too inaccurate, as also are ab initio methods based on the Roothaan[15a]-Hall[15b] (RH) SCF approach unless a very large basis set (6-31G*)[16] is used.

The only promising approach currently available is that based on the recently developed MINDO/3 semiempirical SCF MO method.[12,17] This has given good results for a very large number of "normal" molecules and ions and also for the three "nonclassical" species mentioned above.[18] Calculation of geometries is moreover a trivial matter for even quite large molecules; a complete geometry optimization for **1** or **2** takes ca. 10 min on our computer (CDC 6600). While the accuracy of MINDO/3 is admittedly less than one would like, it does at least seem to be much the same for molecules of most kinds. It does therefore at least offer hopes of giving meaningful results in comparisons of "classical" and "nonclassical" ions.

We have therefore carried out detailed MINDO/3 calculations for **1**, **2**, and other related "2-norbornyl" species and for a number of analogous cations where "nonclassical" isomers have been postulated or might occur. We also carried out RH calculations for some of the species for comparison, using a minimum basis set (STO-3G[19]). Here it would have been impractical to optimize geometries so we used the ones calculated by MINDO/3.

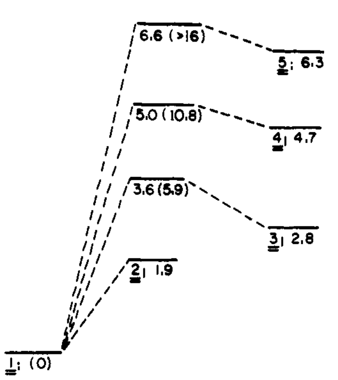


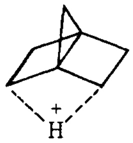
Figure 1. Relative energies (kcal/mol) for the 2-norbornyl cation isomers **1**–**5** and for the transition states for their interconversion; experimental values in parentheses.

Procedure

The MINDO/3 method has been described in detail.[17] The calculations reported here were carried out using the standard MINDO/3 program, including the associated DFP geometry procedure. The calculations for the more important norbornyl species were also carried out using the MINDO/2 program of McIver and Komornicki,[20] adapted to MINDO/3. This calculates geometries using the Murtagh-Sargent algorithm.[21] All geometries were found by minimizing the energy with respect to all geometrical variables, no assumptions being made. Transition states were located by the reaction coordinate method.[22] In the case of **2**, the method of McIver and Komornicki[23] was also used. The ab initio calculations were carried out by the standard Roothaan-Hall[15] restricted Hartree-Fock procedure, using the STO-3G basis set.[19]

Results and Discussion

The 2-norbornyl cation **1**, and the related π complex **2**, are known to interconvert extremely rapidly,[8,24,25] the reaction remaining fast on the NMR time scale down to −150 °C. It has also been established that **1** can rearrange by 6 → 2 and 3 → 2 hydrogen shifts via the intermediate structures **3** and **4**. The rates of these reactions have been determined by NMR spectroscopy.[25] The 3 → 2 migration of hydrogen via the endo π complex **5** is much slower[25] than the analogous rearrangement via **4**.



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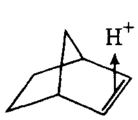

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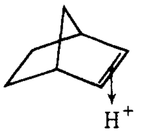

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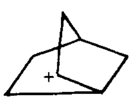

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Using MINDO/3, we calculated the geometries and energies of **1**–**5** and of the transition states involved in the degenerate rearrangements of **1** via **3**, **4**, and **5**. The three latter species represent local minima on the potential surface. On the other hand **2** is *not* a stable species, according to MINDO/3, but rather the (symmetrical) transition state for the corresponding degenerate rearrangement **1** ⇄ **6**. Our calculated energies, relative to that of **1**, of the various stable species and transition states are shown in Figure 1, together with experimental values derived from measured activation energies.

MINDO/3 predicts the most stable of the isomers to be the classical ion **1**, the π complex **2** lying higher in energy although by less than 2 kcal/mol. As noted above, none of the experimental evidence leads to any definite conclusions in this respect, apart from the work of Olah et al.[8] to which we will return presently. It now seems fairly certain that the large difference in rate of solvolysis between *endo*- and *exo*-2-norbornyl esters, and the high stereospecificity of the latter reactions, are due to factors other than a concerted rearrangement of nascent **1** to **2** while all the other chemical evidence can be explained likewise in terms of rapidly equilibriating classical ions.[9,26]

It should be emphasized that the inherent accuracy of MINDO/3 is too low for any definite predictions to be made on the basis of such small differences between calculated energies.[12,17] Here, however, the results for **3**–**5** do serve as a kind of internal calibration. Not only does MINDO/3 give activation energies for rearrangement via **2**–**5** that are in the correct order, but the values calculated in the three latter cases are also too low. This suggests that in this series MINDO/3 is if anything tending to underestimate the stabilities of the π complexes **3**–**5** relative to the classical ion **1**. The fact that the π complex **2** is predicted to be *less* stable than **1** does therefore seem to be significant.

One could in any case have predicted, in the absence of any experimental information, that the "nonclassical" ion **2** could not possibly be appreciably more stable than **1**. If this conclusion had been available 20 years ago, it would have been apparent that the difference in solvolysis rate between endo and exo esters could not be due entirely, or even mainly, to concerted rearrangement of **1** to **2**. It would also have been clear that this is a poor system in which to look for evidence for the intervention of a "nonclassical" ion. And finally, similar calculations would have indicated much more suitable candidates for the purpose; indeed, two are suggested by the calculations described below. It is difficult to estimate the saving of effort that could have been effected in this way. Nearly 500 papers have appeared, reporting studies of the 2-norbornyl system, without a final solution being reached.

Figure 2 shows the geometries calculated by MINDO/3 for **1**, **2**, and **3** together with the corresponding distribution of formal charge.

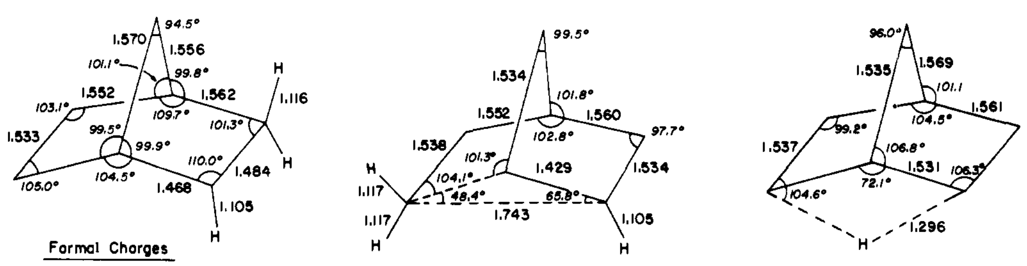
The structure calculated for **2** corresponds nicely to that expected[2-4,6,10,27] for a π complex. The basal (C_1C_2) bond is intermediate between single and double in length (1.43 Å) and the C_1C_6 and C_2C_6 distances (1.74 Å) are much greater than the length of a CC single bond. The length of the basal bond is indeed close to that observed in typical inorganic π complexes such as the ion $C_2H_4 \rightarrow PtCl_3^-$ (CC length, 1.37 Å[28]). It is also amusing to note that the length of the μ bond, i.e., the distance from the apical atom (C_6) to the basal (C_1C_2) bond, is 1.59 Å, similar to the length of a CC single bond. According to the π complex theory,[3,6,10] the bond in question *is* a single covalent bond, linking the apical atom to the (CC) basal unit.

Similar remarks apply to the proton π complexes **4** and **5**. Here again the basal (C_2C_3) bonds are short. The geometries are not reproduced since they present no other features of interest. The geometry of **3**, an edge-protonated nortricyclene, is also much as one would expect (Figure 2c). The CH distances in the three-center bond (C_6HC_2) are naturally greater than those in normal two-center CH bonds.

Attempts have been made to distinguish between **1** and **2** on the basis of the NMR spectrum of the ion in magic acid at low temperatures, the most significant of these being a ^{13}C NMR study by Olah et al.[8] The problem here is to distinguish between a rapidly equilibriating mixture of classical isomers (**1** ⇄ **6**) and a static π complex (**2**). Our calculations (Table I) imply that the corresponding time-averaged distributions of formal charge are very similar so it seems unlikely that any definite conclusions could be reached in this way.[29] Olah et al.[8] showed only that the observed ^{13}C NMR spectrum is consistent with formulation of the ion as the π complex **2**, not that it must have this structure.

Since the results for **1**–**5** seemed interesting, we decided to extend the calculations to some related carbocations.

First we examined the 2-methyl-2-norbornyl cation **7**. According to the π complex theory, an alkyl substituent in a basal position of a π complex should stabilize it less than it does the



Formal Charges

C_1	-0.036	H_1	0.064
C_2	0.397	H_2	0.046
C_3	-0.055	H_3	0.099 (0.079)
C_4	0.040	H_4	0.046
C_5	0.018	H_5	0.040 (0.020)
C_6	0.090	H_6	0.042 (0.007)
C_7	0.049	H_7	0.014

(a)

Formal Charges

C_1, C_2	0.142	H_1, H_2	0.067
C_3, C_7	0.015	H_3, H_7	0.039 (0.049)
C_4	0.035	H_4	0.052
C_6	0.057	H_6	0.070
C_5	0.023	H_5	0.035

(b)

Formal Charges

C_1	-0.009	H_1	0.075
$C_{2,6}$	0.176	$H_{2,6}$	0.073
$C_{3,5}$	0.007	$H_{3,5}$	0.035 (0.053)
C_4	0.031	H_4	0.053
C_7	0.039	H_7	0.032

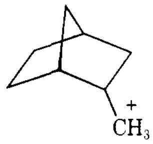
(c)

Figure 2. Calculated geometries (bond lengths in Å) and distributions of formal charge (in units of the electronic charge) for **1–3**.

Table I. Comparison of the Formal Charges Calculated for the π Complex **2** with the Mean of Those for the Classical Structures **1** and **6**

	Position						
	1	2	3	4	5	6	7
2	0.142	0.142	0.015	0.035	0.023	0.057	0.015
½(**1** + **6**)	0.181	0.181	−0.003	0.040	0.018	0.090	−0.003

isomeric classical carbonium ion in which the alkyl group is attached to the cationic center.[6,10] Since **1** was predicted to lie below **2** in energy, we would expect a much greater difference in the same direction between **7** and the π complex **8**. Indeed,



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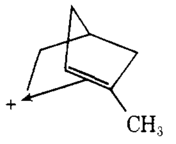

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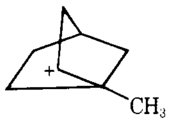

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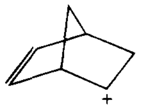
our MINDO/3 calculations predict **7** to be the most stable species, the corresponding methyl derivatives of **2–5** rearranging to **7** without activation. An estimate of the energy difference between **7** and **8** could be obtained only by assuming **8** to be similar to **2** in structure, the methyl group alone being optimized. The energy difference found in this way was 12 kcal/mol. We did not calculate the isomeric classical structure **9** in which the methyl group is attached at position 1 in **1** because MINDO/3 is known to give poor results for tetraalkylmethanes. There can, however, be little doubt that **9** must lie well above **7** in energy since **9** is a secondary carbonium ion whereas **7** is a tertiary one. We would therefore expect the ion to exist only as the classical isomer **7**. Olah et al.[31] have shown this to be the case. Figure 3 shows the calculated geometry and distribution of formal charge for **7**; they present no unexpected features.

A methyl group in the 2-position of **1** thus selectively stabilizes the classical isomer. The opposite effect might be expected in the analogous unsaturated ion **10**, the 5-norbornenyl



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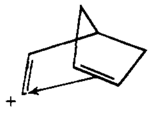

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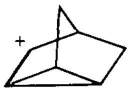

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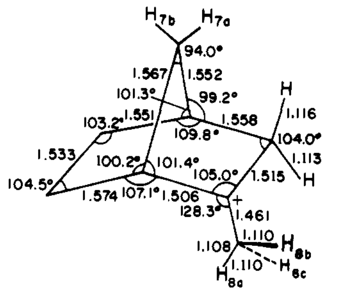
cation. Here there should be little interaction between the double bond and the cationic center in the classical isomer **10**.



Formal Charges

C_1	-0.034	H_1	0.042
C_2	0.373	H_2	0.072 (0.059)
C_3	-0.046	H_3	0.040
C_4	0.040	H_4	0.033 (0.013)
C_5	0.024	H_5	0.035 (-0.003)
C_6	0.079	H_6	0.006
C_7	0.048	H_7	0.037
C_8	-0.057	H_{8a}	0.061
		H_{8b}	0.088
		H_{8c}	0.092

Figure 3. Calculated geometry and distribution of formal charge in **7** (cf. Figure 2).

In the isomeric π complex **11**, however, the apical group is unsaturated; back coordination[3,10] is now possible between the filled π MO of the apical vinyl group and the empty antibonding π MO of the basal (C_1C_2) unit (Figure 4). This should lead to a stabilization of **11** relative to **10** and our calculations confirm this. Here the classical ion **10** is barely stable, being separated by a barrier only 0.1 kcal/mol high from the π complex **11** which lies 12 kcal/mol lower in energy. Olah and Liang[32] have shown that the ion does indeed exist as the symmetrical π complex **11** in SbF_5-SO_2ClF solution. Here a distinction between the classical (**10**) and π complex (**11**) structures can be drawn on the basis of the ^{13}C NMR spectrum of the ion because back coordination in the π complex leads to a large positive charge at C_5.

This ion can be formulated as a cyclopropylcarbonium ion **12** instead of a π complex. A similar situation occurs whenever the apical atom in a π complex has p or π electrons that can be used for back coordination.[3,6,10] Thus ethylene oxide can be formulated either as a cyclic ether (**13**) or as a π complex (**14**). In such cases the distinction depends on the degree of back coordination.

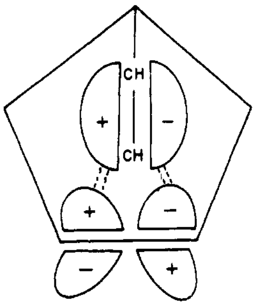


Figure 4. Back coordination in a π complex with an apical vinyl group, due to interaction of the filled vinyl π MO with the antibonding π MO of the basal ethene unit.

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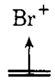

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16, $X = CH_2$, NH, O, S

If back coordination is important, the resulting structure will behave as though it contained a classical three-membered ring. Otherwise the structure is best represented as a π complex. Thus corner-protonated cyclopropanes (e.g., **2**) behave as π complexes, back-coordination being impossible, and the same is true in cases where the apical group is extremely electronegative and hence a poor donor (e.g., the ethylenebromonium ion **15**). If back coordination is strong, as is the case when the apical atom is neutral (CH_2, O, NH, S) and has unshared pairs of electrons, then a "classical" ring (**16**) results.

Consider now the case where the apical group in a π complex is unsaturated, e.g., vinyl (**17**). Here back coordination involves the π MO of the apical vinyl group (Figure 4). Since only half this MO can interact with the antibonding basal MO, one might expect back coordination to be correspondingly less effective. The ion should then behave like the π complex (**17**) rather than the isomeric cyclopropylcarbonium ion (**18**). The ion should be correspondingly more stable than one would expect for the "classical" structure, accounting for the well-known stabilizing effect of α-cyclopropyl substituents in carbonium ions.

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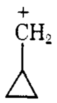

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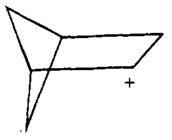
Figure 5a shows the geometry and distribution of formal charge calculated, with no assumptions, for the cyclopropylcarbonium ion. The calculation started with the geometry expected for the classical structure **18**. The final geometry is seen to be entirely different, corresponding indeed to that expected for the π complex **17**. The bonds in the three-membered ring are now quite different in length, the length of one (1.43 Å) being similar to that of the basal (C_1C_2) bond in **2** while the other two are very long (1.60 Å). Moreover the length of the CC bond in the apical "vinyl" unit is also intermediate between single and double. Back coordination sucks away some of the bonding π electrons from the apical group and so reduces the amount of double bond character in the vinylic double bond.

Figures 5b and 5c show the geometry and distribution of formal charge calculated for **10** and **11**. Those for **11** correspond nicely with the π complex formulation, both the C_1C_2 and C_5C_6 bonds being intermediate between single and double in length while C_1C_6 and C_2C_6 are both very long. Note also the relatively large positive charge at C_5; the ^{13}C NMR spectrum indicates[8] the presence of such a charge.

Another way in which the π complex form of a carbocation might be selectively stabilized is by introducing ring strain.[6,10] The μ bond linking the apical and basal units in a π complex is relatively weak. Ring strain can therefore be relieved at relatively little cost in the case of a π complex by deforming the μ bond. This indeed is clearly the reason why nonclassical structures play such a role in the norbornyl ring system. Ring strain can be relieved on passing from a classical structure, such as **1**, to an analogous π complex, such as **2**. Increasing the ring strain in **1** should therefore tend to make the π complex isomer the most stable.

We therefore carried out calculations for a lower homologue of **1**, i.e., the 2-bicyclo[2.1.1]hexyl cation **19** and the related π complex **20**. As expected, **20** proved the more stable of the two, although both were represented by local minima in the potential surface. The calculated difference in energy between **19** and **20** was 1.54 kcal/mol, while conversion of **19** to **20** was predicted to require activation (0.32 kcal/mol). The calculated geometries and distributions of formal charge are shown in Figure 6. Those for **20** are seen to correspond nicely to the π complex formulation.



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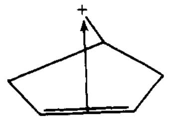

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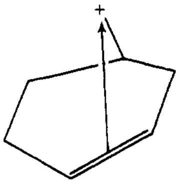
Wiberg et al.[33] have studied the NMR spectrum of this ion in $SbCl_5/SO_2ClF$. Even at −130 °C the methylene groups are all equivalent, implying either a very rapid interconversion of classical ions (**19**) via the π complexes (**20**) or rapid interconversion of the π complexes, either directly or via **19**. Wiberg et al. favored a direct interconversion of π complexes; our results indicate that the rearrangement takes place by reversible conversion of classical ions (**19**). The calculated activation energy (2 kcal/mol) is much less than the limit (6 kcal/mol) set by the NMR evidence.[33]

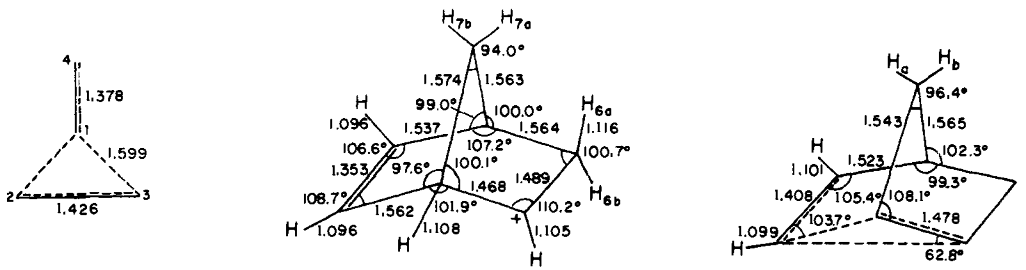
It has been generally assumed that any degenerate rearrangement of the 2-norbornyl cation (**1**) takes place via one or other of the species **2–5**. Our calculations for **19** and **20** suggested that the higher homologue (**21**) of **20** might be another reasonably stable isomer of **1**. It is derived from **1** by passage of C_7 to a bridging position between C_1 and C_2, on the exo side of **1**, whereas conversion of **1** to **2** involves an endo migration of C_6. We therefore carried out calculations for **21** in the hope that its energy might be low enough for it to be a possible intermediate in reactions of **1**. Greatly to our surprise, it not only turned out to be a stable species but more stable than any of the other 2-norbornyl isomers, **1–5**. The calculated heat of formation was less than that of **1** by 3.5 kcal/mol.



21

The experimental evidence[6,7] seems at first sight to refute the implied suggestion that **21** might be the most stable 2-norbornyl species, because solvolysis of *endo*-2-norbornyl esters does not take place with retention of configuration, and because solvolysis of an *exo*-2-norbornyl ester gives essentially no endo product. These objections are, however, not conclusive.

It is well recognized that the solvolysis of secondary alkyl esters is strongly assisted by backside nucleophilic attack by the solvent. If a solvolysis involves a concerted rearrangement



Formal Charges

C_1	-0.050
C_2	0.141
C_4	0.294

(a)

Formal Charges

C_1	0.056	H_1	0.045		
C_2	-0.005	H_2	0.093		
C_3	0.000	H_3	0.088		
C_4	-0.006	H_4	0.062		
C_5	0.389	H_5	0.047		
C_6	-0.051	H_{6a}	0.091	H_{6b}	0.079
C_7	0.062	H_{7a}	0.007	H_{7b}	0.044

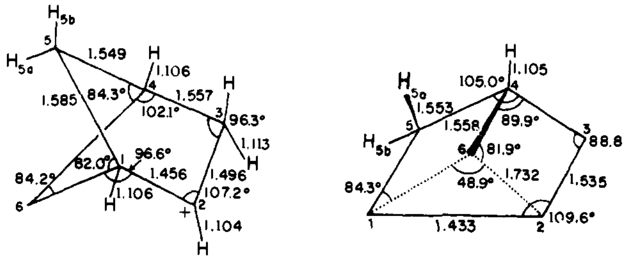
(b)

Formal Charges

C_1	-0.004	H_1	0.061		
C_2	0.280	H_2	0.068		
C_3	-0.079	H_3	0.099		
C_4	0.106	H_4	0.071		
C_6	0.043	H_{7a}	0.030	H_{7b}	0.039

(c)

Figure 5. Calculated geometry and distribution of formal charge (cf. Figure 2) in: (a) **17**; (b) **10**; (c) **11**.



Formal Charges

C_1	-0.043	H_1	0.075
C_2	0.389	H_2	0.054
C_3	-0.041	H_3	0.085
C_4	0.024	H_4	0.062
C_5	0.093	H_{5a}	0.052
		H_{5b}	0.011

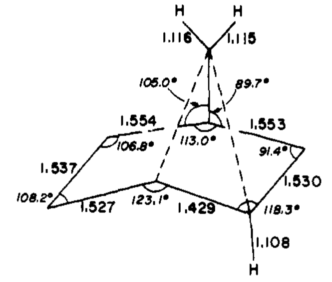
(a)

Formal Charges

C_1	0.154	H_1	0.072
C_3	0.025	H_4	0.063
C_4	0.041	H_{5a}	0.051
C_6	0.067	H_{5b}	0.049
		H_6	0.063

(b)

Figure 6. Calculated geometry and distribution of formal charge (cf. Figure 2) in: (a) **19**; (b) **20**.



Formal Charges

C_1	0.157	H_1	0.055
C_2	0.154	H_2	0.056
C_3	0.024	H_3	0.048 (0.042)
C_4	0.035	H_4	0.048
C_5	0.033	H_5	0.030
C_6	0.023	H_6	0.038 (0.045)
C_7	0.054	H_7	0.067 (0.061)

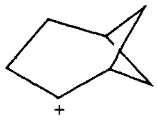
Figure 7. Calculated geometry and distribution of formal charge in **21** (cf. Figure 2).

of the nascent carbonium ion to a π complex, the rearrangement must compete with solvation. In the rearrangement of **1** to **2**, attack is from the endo side of **1** which is sterically hindered. Here the solvent is at a corresponding disadvantage. In the rearrangement of **1** to **21**, on the other hand, attack is from the unhindered exo side. Here solvent attack may predominate.

The second objection, i.e., the failure to observe endo products, applies equally in the case of **1** and **2** and was indeed one of the arguments used formerly to support the π complex formulation of the intermediate ion. It is now recognized that steric effects could lead to preferential exo attack on **1**, and a similar argument would suggest that attack by a nucleophile on **1** or **2** to give exo product could be much easier than attack on **21** to give endo product. The difference could well outweigh a small energy balance in favor of **21**.

These arguments assume that the equilibria between **1**, **2**, and **21** are very rapidly established. The MINDO/3 calculations imply that all three species have very similar energies and that the activation barriers between them are negligible. If so, the NMR[8] and ESCA[8] evidence is not inconsistent with **21** being the most stable form of the ion and it is easily seen that the evidence concerning isotopic scrambling can also be explained on this basis. Indeed, none of the available evidence excludes this possibility which nevertheless seems to have escaped serious consideration. Obviously MINDO/3 cannot make any definite predictions in this case because the differences in energy between **1**, **2**, and **21** are so small and because **21** differs significantly in structure from the other isomers, **1-5**. Nevertheless it seems very likely that even if **21** is not the most stable isomer of **1**, it may be close to it in energy. Analogous ions may then play an important role in other related systems.

In view of these results, we also studied the classical ion **22** which can be formed from **1** by a Wagner-Meerwein rear-



22

rangement via **21**. The calculated heat of reaction for **1** → **22** (−3.7 kcal/mol) seems too negative, a not unexpected result since **22** is a cyclobutane derivative and MINDO/3 underestimates the strain energy in cyclobutanes. Admittedly the error seems likely to be less for **22** than for cyclobutane itself since the four-membered ring in **22** is necessarily buckled.

MINDO/3 incorrectly predicts cyclobutane to be planar, due to an underestimation of eclipsing interactions.

As mentioned earlier, the only other procedure that might give reliable values for relative energies in cases such as this is the Roothaan-Hall method, using a very large basis set (6-31G*). Such a calculation for so large an ion would be prohibitively expensive; indeed, we found that we could not calculate a $C_7H_{11}^+$ species, even with the smaller 4-31G basis set,[34] on our computer without extensive modification of the program. It would in any case be quite impossible to optimize geometries in such a calculation so the results would mean very little. However, for interest, we did carry out calculations for **1**, **2**, and **21**, using the STO-3G basis set.[19] Even here it was out of the question to optimize geometries; we therefore used the ones calculated by MINDO/3. The relative energies of the three species found in this way were (in kcal/mol):

1, 0; **2**, +5.7; **21**, +21.2

These results seem to support the MINDO/3 values for **1** and **2** but to imply that MINDO/3 has in fact greatly underestimated the energy of **21**. However, little confidence can be placed in them because the use of assumed geometries in cases such as this can lead to large errors and STO-3G is in any case known[35] to underestimate the stabilities of nonclassical carbonium ions relative to classical isomers.

The only hope of distinguishing between the various possibilities seemed therefore to lie in a closer analysis of the ESCA spectra reported by Olah et al.,[8] which, they claimed, supported the π complex formulation (**2**) of the norbornyl cation, on the grounds that the separation of the two peaks in the ESCA spectrum was less than that observed for genuine "classical" carbonium ions and on a claim that the integrated areas under the peaks were in the ratio 2:5, corresponding to **2** if the positive charge is localized on the basal atoms of the π complex.

It has been pointed out[9] that the original spectrum[31] cited by Olah et al. does not in fact deconvolute in the manner indicated but rather into two peaks with areas in the ratio 1:6. Olah et al. subsequently claimed[8] that a spectrum obtained under conditions leading to higher resolution could be deconvoluted into two Gaussians with areas in the ratio 2:4.95. It is, however, apparent from the published spectrum that this is the case only if the resolution is into Gaussians of different widths, that at higher energy being the broader. This, however, is impossible if the ion has the π complex structure **2** because the high-energy peak would then correspond to ionization from two equivalent carbon atoms while the low-energy peak would represent a superposition of ionizations from carbon atoms in three different environments. The latter could be broader than the former, but not narrower. It has been suggested[9b] that the high-energy peak in fact contains peaks due to impurities; if so, the ratio of integrated areas would be much less than that corresponding to **2**. Alternatively, the ion might have the so far neglected π complex structure **21** where the basal carbon atoms are *not* equivalent. The spectrum cannot in any case correspond to **2**. It should be noted that arguments based on intensities of bands in ESCA spectra must carry much more weight than arguments based on band separations. As Siegbahn et al.[38] have shown, the intensities of ESCA bands are so accurately proportional to the numbers of atoms contributing that they can be used to estimate elementary compositions of molecules with quite high accuracy. The separation of bands in ESCA spectra cannot on the other hand be predicted with any assurance since there is as yet no really accurate theory of ESCA shifts.

Table II. Relative C(1s) Ionization Potentials of Cations Calculated Using the Equivalent Core Approximation[40]

		I(calcd)[a]	I[b]
1	C_1	5.501	296.301
	C_2	6.332	297.132
	C_3	5.108	295.908
	C_4	5.343	296.143
	C_5	4.550	295.340
	C_6	4.931	295.731
	C_7	4.415	295.215
2	C_1, C_2	5.757	296.557
	C_3, C_7	4.674	295.474
	C_4	5.285	296.085
	C_5	4.754	295.554
	C_6	5.602	296.402
21	C_1	5.898	296.698
	C_2	5.758	296.558
	C_3	4.775	295.575
	C_4	5.438	296.238
	C_5	4.723	295.523
	C_6	5.073	295.873
	C_7	5.150	295.950
24	C_1	7.345	298.145
	C_2, C_5	5.810	296.610
	C_3, C_4	5.347	296.147
23	C_1	5.462	296.262
	C_2	8.864	299.664
7	C_1	4.892	295.692
	C_2	6.755	297.555
	C_3	4.473	295.273
	C_4	4.898	295.698
	C_5	4.149	294.949
	C_6	4.442	295.242
	C_7	3.966	294.766
	C_8	4.751	295.551

[a] Difference (in eV) in the C(1s) ionization potential between the cation and methane. [b] Assuming a value of 290.8 eV for methane, cf. K. Siegbahn et al., "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.

On qualitative grounds, one might in fact have expected the ESCA spectrum of **2** to show bands in the ratio 3:4 rather than 2:5, in view of the fact that the formal charge in a π complex should be spread over the three atoms concerned. Our calculated charge densities for **2** (Figure 2) do indeed show large formal charges at all three positions. As a further check, we decided to calculate the ESCA spectra of the various relevant ions. Recent work has shown[39] that ESCA spectra can be calculated with reasonable accuracy by MINDO/3, using Jolly's[40] equivalent core approximation, the average error in the relative ionization energies being ca 0.8 eV. We therefore calculated the relative C(1s) ionization potentials of **1**, **2**, and **21** in this way. Also, since no calculations had been carried out previously for carbonium ions, we calculated values for three such ions of known structure for which ESCA data were available, namely *tert*-butyl cation (**23**), cyclopentyl cation (**24**), and the 2-methyl-2-norbornyl cation (**7**). The results are shown in Table II, together with conversions to chemical shifts and absolute gas phase ionization energies.

$C(CH_3)_3^+$

23

24

In **23** there are just two C(1s) ionizations. We calculated the difference between them to be 3.4 eV, in reasonable agreement with experiment (3.9 eV[41]).

In the other cases there are a number of C(1s) ionizations but these are not resolved in the observed ESCA spectra. In order to compare our results with experiment, we therefore synthesized spectra from our calculated ionization potentials,

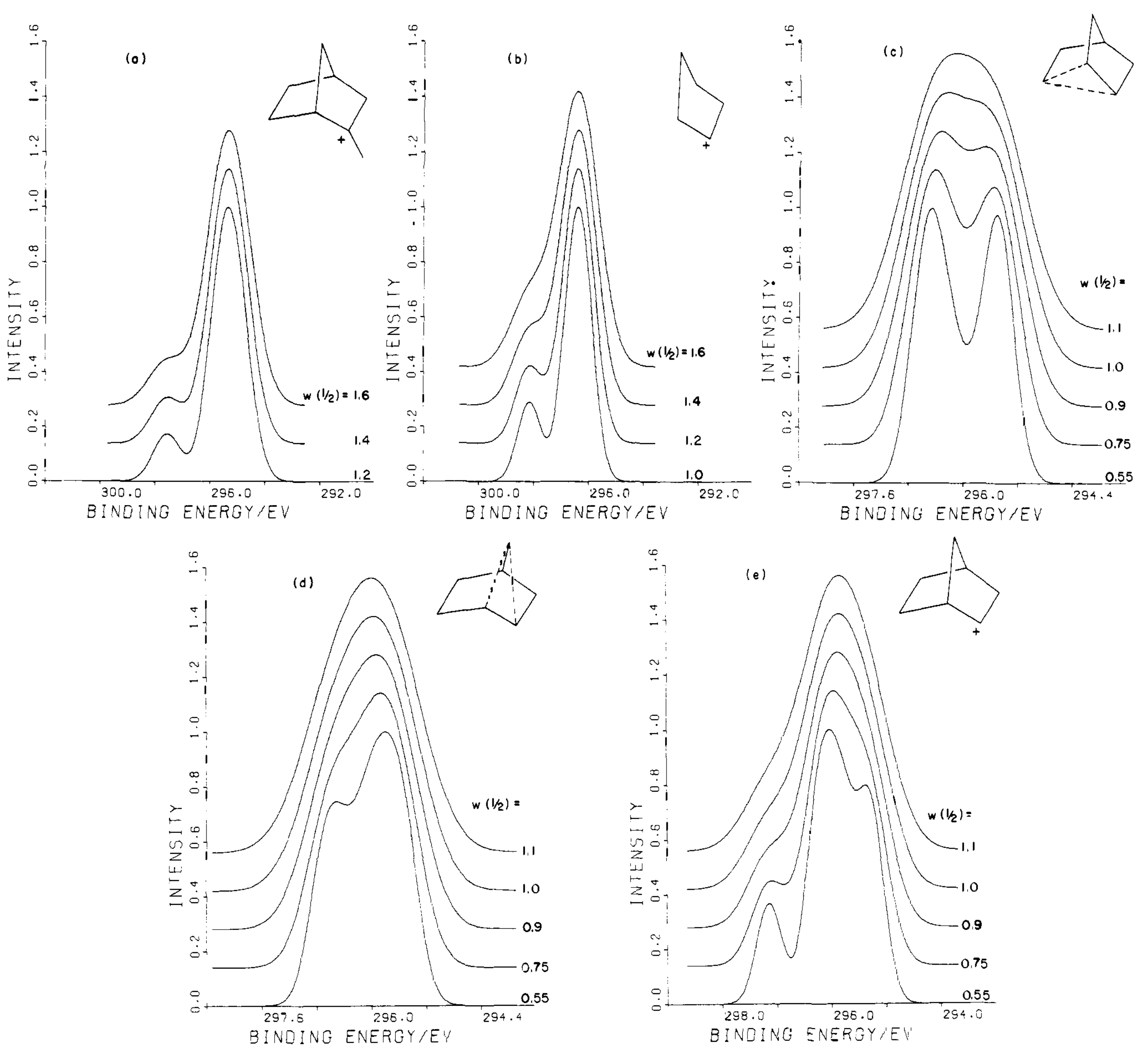


Figure 8. ESCA spectra calculated from C(1s) ionization energies estimated by MINDO/3, assuming Gaussian-like shapes, for (a) **7**; (b) **24**; (c) **2**; (d) **21**; (e) **1**; at various values of $W(\frac{1}{2})$, in eV.

assuming Gaussian line shapes with similar peak heights and with similar widths ($W(\frac{1}{2})$) at half peak height.

In the case of **7**, the best match to the observed[31] spectrum was given by $W(\frac{1}{2}) = 1.4$ eV. The calculated spectrum (Figure 8a) is very similar to the observed one; the separations of the two peaks are calculated to be 2.3 eV, somewhat less than that in the observed one (3.7 ± 0.2 eV[31]), but within the limits of error of MINDO/3.

The ESCA spectrum for **24** has not been published but is stated[31] to consist of two peaks with a separation of 4.3 ± 0.5 eV. Our calculated spectra are shown in Figure 8b. The separation of the two peaks was found to be 1.8 ± 0.1 eV and was fairly insensitive to the spectral resolution used.

These results suggest that MINDO/3 reproduces the observed spectra in a reasonable manner, allowing for the limited accuracy of MINDO/3 estimates of ESCA chemical shifts. The calculated peak separations are clearly too small and not uniformly so. This could well be due to the use of the core approximation in which 1s–2s interactions are neglected. These must lead to variations in the 1s ionization potential with the total 2s electron density of the atom in question, a factor not taken into account in our calculations. The electronic band spectrum of polyethylene, calculated[42] by MINDO/3, shows an analogous error, the calculated 2s band extending to too high energies. The effect of the neglected 1s–2s interactions is to depress the energy of the 1s AO's at the expense of a corresponding increase in energy of MO's derived from 2sAO's, particularly those with the highest binding energies. Effects of this kind should affect the quantitative ESCA ionization energies calculated by MINDO/3 but not their relative values. Indeed, the ESCA spectrum for **7** (Figure 8a) calculated by MINDO/3, using an appropriate line width, resembles very closely the experimental one although the MINDO/3 band separation is again too small.

The C(1s) ionization potentials of **2** fall into two groups of three, with the seventh in between. As expected on the basis of the calculated formal charges, the values for all three carbon atoms involved in the π complex (C_1, C_2, C_6) are similar. It is evident that our calculated values are totally inconsistent with experiment.[8,31] This is emphasized by the calculated ($W(\frac{1}{2}) = 0.55$–1.1 eV) spectra shown in Figure 8c, which consist of two peaks of similar size, the one at higher energy being somewhat the larger. The observed spectrum,[8,31] on the other hand, consists of a single peak with a shoulder low down on the high-energy side.

The calculated spectra ($W(1/2) = 0.55-1.1$ eV) for **21** (Figure 8d) are nearer to the observed one in appearance, but too narrow. This could possibly be due to our calculated ionization potentials having too small a spread (see above). Also the shoulder at the high-energy side of the band is too indistinct.

Deconvolution of these spectra into two Gaussians, using a least-squares procedure,[43,44] gave two bands with integrated band areas of 2.8 ± 0.1:4.2 ± 0.1, depending on the value of $W(1/2)$, and with an almost constant peak separation of 0.78 eV. Olah et al.[8] state that deconvolution of their revised spectrum with a curve analyzer[44] gave two bands with areas in the ratio 2:4.95 and a peak separation of 1.44 eV. Scaling our spectrum to give this peak separation, and using a more realistic value for $W(1/2)$ of 1.4 eV, gives a calculated line shape very similar to the one shown in Figure 8d at a resolution of $W(1/2) = 0.75$ eV. While the agreement seems very good, the calculated and observed spectra are in fact significantly different in appearance. The shoulder in the calculated one occurs much higher up on the side of the main peak, suggesting that the two bands differ less in area than those in the observed spectrum.

Figure 8e shows the spectra calculated for **1** from the MINDO/3 C(1s) ionization energies, at various spectral resolutions. The best fit to the original[31] spectrum is given by $W(1/2) = 1.0$ eV and to the revised[8] one by $W(1/2) = 0.9$ eV. Deconvolution of these spectra into two Gaussians gave bands with areas in the ratio 0.7 ± 0.1:6.3 ± 0.1 and a peak separation of 1.40 ± 0.03 eV. The latter value agrees very well with that quoted by Olah et al.[8] while the ratio of band areas is close to that estimated by Kramer[9b] by deconvolution of the original[31] ESCA spectrum. The calculated and observed spectra are moreover very similar in appearance, the shoulder appearing at about the same height in each case.

These results seem to suggest very strongly that the ion cannot have the π complex structure (**2**) assigned to it by Olah et al. They also seem to strongly support its identification with the classical structure **1**. The only loophole lies in the possible tendency of MINDO/3 to underestimate ESCA band separations in carbocations; the alternative π complex structure **21** might then prove to be correct. There are clearly no other possibilities and the classical structure **1** seems on balance by far the most likely.

Since this conclusion is diametrically opposite to that of Olah et al.,[8] who believed they had proved the ion to be **2** and excluded the structure **1**, some further comment seems appropriate.

Olah et al.[8] based their argument on the fact that the band separation in the ESCA spectrum of the ion was much less than those observed for "normal" classical carbonium ions, together with the premise that the ESCA spectra of **1** and **7** should be similar in this respect. This premise seemed eminently reasonable at the time and their argument correspondingly incontrovertible. We at least accepted it as such. Our MINDO/3 calculations indicate, however, that the ESCA spectra of **1** and **7** are not in fact similar and that the band separation in **1** should on the contrary be less than that in classical ions such as **7**, **26**, or **27**. This removes the apparent conflict between arguments based on the peak separation and those based on ratios of band intensities; for it seems clear that the ratio in the original spectrum was closer to 1:6 than 2:5 and, as mentioned earlier, there are doubts concerning the validity of conclusions drawn from the revised one.

Why should **1** be abnormal? The charge distributions calculated for it and for **7** are indeed similar (Figures 2 and 3), which one might have thought would lead to them having similar ESCA spectra. The explanation seems to lie in the fact that the nonclassical structures **2**, **3**, and **4** (and perhaps also **21**) differ little from **1** in energy, and that **1** is consequently unusually polarizable. If then we remove a 1s electron from C_2, an extensive electronic reorganization takes place, distributing the positive charge over the adjacent carbon atoms and also C_6. The stabilizing effect of this reorganization reduces the energy required to remove the 1s electron and the separation between the ESCA bands corresponding to C_2, and to the other carbon atoms, consequently decreases. In resonance terminology, we would say that the ion is a hybrid of the various structures, with **1** strongly predominating. When a 1s electron is removed from C_2, the resulting ion is stabilized by an increased contribution by the nonclassical structures. In the case of **7**, the effect is much less because the classical structure is now much below the others in energy. It is interesting that the peak separation in the ESCA spectrum of **7** is nevertheless somewhat smaller than those for "normal" tertiary carbonium ions,[8] although much greater than that for **1**. These arguments suggest that similar small band separations may be observed in the case of other classical carbonium ions where one or more nonclassical structures lie only a very little higher in energy.

Since this paper was first submitted (October, 1975), a valuable review[45] by Olah has appeared, summarizing his experimental work in this area and the conclusions he draws from it. However, since this contains no experimental results or arguments that Olah has not already published, we do not feel it materially alters the situation.

Summary and Conclusions

Our most important conclusion is that the claim by Olah et al.[8] that they had "concluded the nonclassical ion controversy", by proving the "2-norbornyl" cation to have the π complex structure **2**, was somewhat premature. We would hesitate to claim that we in turn have solved this long standing and not very interesting problem; however, it does now seem likely that the ion in fact has the classical structure **1**, as Brown has maintained for many years (cf. ref 9).

A possible alternative seems to be the unsymmetrical π complex **21**. It is curious that this possibility has never been seriously considered, given that it appears to be consistent with all the available experimental evidence (except perhaps the ESCA spectrum). While it seems to us unlikely that the ion really is **21**, it is to the credit of MINDO/3 to have drawn attention to the possibility, regardless of the final outcome.

Apart from this dark horse, the calculations reported here seem to have provided a satisfactory account of the relative stabilities of the various isomers **1–5** of the 2-norbornyl cation and also of the relative stabilities of classical and nonclassical species in the other systems studied (**7/8**, **10/11**, **19/20**). Combined with the previous results for some simple nonclassical carbocations[18] these seem to suggest that MINDO/3 provides a remarkably successful description of such species. Indeed, given the uncertainties due to possible differential solvent effects, it is difficult to see that any treatment could do significantly better in the absence of a quantitative theory of ionic solvation.

Finally, our calculations entirely vindicate the π complex theory of ions such as **2**, the calculated geometries and charge distributions being just those that would be expected on this basis and on the basis of crystallographic studies of metal-olefin π complexes. It seems unfortunate that organic chemists should continue to reject a representation of such species which has not only been generally adopted by inorganic chemists for the last 25 years but also has significant and useful structural and mechanistic implications.[6,10]

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A Derivation of the Shapes and Energies of the Molecular Orbitals of 1,3-Dipoles. Geometry Optimizations of These Species by MINDO/2 and MINDO/3

Pierluigi Caramella,[1a] Ruth Wells Gandour, Janet A. Hall, Cynthia Gray Deville, and K. N. Houk*[1b]

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received March 3, 1976*

Abstract: The energies and shapes of the frontier molecular orbitals of 1,3-dipoles determine the reactivities and regioselectivities of these species. The reasons that the frontier molecular orbitals of 1,3-dipoles have the shapes and energies they do are deduced here by qualitative perturbation theory. MINDO/2 and MINDO/3 calculations on all the parent 1,3-dipoles have been performed with geometries optimized by the procedure of McIver and Komornicki for MINDO/2 and by the procedure of Dewar for MINDO/3. The geometrical trends observed for the nitrilium betaines deviate significantly from those commonly assumed, but fit experimental data for HCNO, and ab initio STO-3G calculations on these systems. The resulting Koopmans' theorem ionization potentials and electron affinities from MINDO/2 are in close agreement with our earlier empirical estimates, and indicate the suitability of MINDO/2 for calculation of ionization potentials and electron affinities of these systems.

The rates and regioselectivities of reactions of 1,3-dipoles with alkenes and alkynes have been studied experimentally for many years,[2] but a theoretical framework for the understanding of these reactions was developed only recently.[3-6] In spite of the simplicity of the frontier molecular orbital treatment of these reactions, the understanding of why the method works is truly attainable only after it is understood why the frontier molecular orbitals of 1,3-dipoles and dipolarophiles

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