

atoms. This phenomenon, which has been observed in Knight shift experiments,^{23,24} has been interpreted²⁶ in terms of donation to the ammonia 3s (Rydberg) orbital. It is, however, the main tenant of the "inadequate" basis set technique that Rydberg-type orbitals are removed from the MO-manifold by the effect of the condensed phase. These two interpretations actually vary only in nomenclature. The ammonia 4a₁ (σ^*_{NH}) orbital in a valence-only basis has the same symmetry as the Rydberg 3s, which would be the 4a₁ in a full basis set. The choice of the 3s was largely dictated by the observation of a small negative spin density on the amino-hydrogens, suggesting that these atoms were close to a node. The spin polarization effect outlined above explains these results without involving either a node near hydrogen or a total negative spin density on the hydrogen atoms. The antibonding 4a₁ orbital, which becomes as diffuse as it is allowed to be by the restrictions on the basis set, takes over the role that the Rydberg 3s would play in the gas phase.

The relatively high solvation energies calculated for e⁻(O-(CH₃)₂) and e⁻(CH₂(CH₃)₂) arise from electrostatic and spin polarization of the methyl groups and from the BSSE effect discussed above.

The calculational technique outlined here has the advantage of simplicity but suffers from the use of a localized electron basis

(26) See, for instance: Smith, D. R.; Symons, M. C. R.; Wardman, P. J. *Phys. Chem.* **1979**, *83*, 1762.

set, which makes energy comparisons with free electrons difficult. The following conclusions arise from this work: a) Compact basis functions are essential in describing solvated electrons. Diffuse functions should be avoided in the absence of external potentials or other means of localizing the electron. b) The essential features of the geometry and an estimate of the solvating power of a given solvent are given by calculations on an electron interacting with a single solvent molecule. c) It must be recognized that total spin densities do not reflect experimentally measured coupling constants or Knight shifts. The spin density near the core is determined by spin polarization not by direct spin delocalization.

Although at present crude, the calculations reported here are suitable for inclusion in a semicontinuum type of scheme^{3,4} and are, therefore, open to improvement. An exciting prospect suggested by this technique, however, is that solvated electron reactions may for the first time be amenable to calculation.

Acknowledgment. Helpful discussions with Prof. M. C. R. Symons, Dr. B. P. Roberts, and Prof. J. A. Pople are gratefully acknowledged. Thanks are also due to Prof. P. v. R. Schleyer for his support and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

Supplementary Material Available: The optimized Z matrixes and Cartesian coordinates for the most stable e⁻(H₂O)₄, e⁻(NH₃)₃, and e⁻S (S = organic solvents) structures (9 pages). Ordering information is given on any masthead page.

Magnetic Properties in Terms of Localized Quantities. 5. Carbocations

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Abstract: The IGLO method (individual gauge for localized molecular orbitals) for the calculation of magnetic susceptibility and chemical shift tensors χ and σ is applied to a number of small- to medium-sized carbocations. There are two classes of cations: (a) cations where intramolecular charge delocalization is possible to a large extent, i.e., aromatic, so-called "nonclassical", and allylic cations (here the agreement between theory and experiment is good); and (b) cations with a localized charge, which have strong interactions with solvents and counterions, and where we cannot expect that under experimental conditions isolated cations are present. For these ions chemical shifts calculated for the isolated species are by far more deshielding than those observed experimentally. The IGLO method is shown to provide a useful tool for the elucidation of molecular structures. For cations with unknown geometry, like C₄H₇⁺ or C₇H₁₁⁺, we have calculated NMR parameters for various proposed structures. For C₄H₇⁺ that is assumed to be either a bicyclobutonium or a bisected cyclopropylcarbinyl ion, our calculations indicate that the assumption of a bisected cyclopropylcarbinyl geometry is not consistent with the observed NMR data. Though higher in energy at the SCF level, a bicyclobutonium structure leads to a much better agreement between calculated and observed chemical shift data for C₄H₇⁺. The methyl-substituted C₄H₆CH₃⁺ cation definitely has the structure of a methylbicyclobutonium ion. Concerning the structure of the 2-norbornyl cation a final decision is possible. Its experimental NMR spectra are in good agreement with those computed for the nonclassical structure and very different from that calculated for several classical geometries.

I. Introduction

During the past 30 years an impressive amount of experimental information on NMR chemical shift data of carbocations under stable ion conditions either in solution or in the solid state¹⁻⁴ has been accumulated. Ab initio calculations on carbocations have been restricted to potential energy hypersurfaces or to the de-

termination of equilibrium geometries^{5,6,17} and references therein. Theoretical calculations of chemical shift tensors have so far been missing, with the exception of ref 7, although cations present a

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Table I. Magnetic Susceptibilities of Carbocations^a

no.	ion	basis DZ		basis II					
		χ	χ	χ^d	χ^p	nonlocal	principal values		
							χ^{11}	χ^{22}	χ^{33}
1	CH ₃ ⁺	-0.15	0.32	9.99	-7.24	-2.44			
2	CH ₅ ⁺ C _s	16.44	18.86	15.50	2.22	1.14			
	C ₂ H ₃ ⁺								
6	classical	13.63	11.81	20.18	-7.74	-0.63			
7	nonclassical	23.14	21.02	20.53	-0.49	0.98			
	C ₂ H ₅ ⁺								
8	C _s	16.34	14.87	23.04	-6.18	-1.99			
9	C _{2v}	20.93	18.78	22.88	-3.48	-0.62			
	C ₂ H ₇ ⁺								
10	C _s	35.50	30.29	27.39	2.27	0.64			
11	C ₁	33.99	28.95	26.95	0.96	1.03			
12	cyclopropenyl	22.11	20.54	29.33	-6.96	-1.83	40.98	10.31	10.31
13	allyl	27.26	20.37	33.90	-9.99	-3.54	38.21	11.89	11.00
27	cyclopropyl	21.98	17.51	32.06	-9.09	-3.13			
19	isopropyl	30.41	27.85	35.49	-5.78	-1.87	38.61	24.93	20.00
20	tert-butyl	44.10	40.30	47.71	-5.18	-2.22	49.55	35.67	35.67
18	cyclobutenyl	37.06	32.99	41.33	-6.57	-1.77	47.89	27.28	23.80
14	1-methylallyl	36.88	33.48	46.44	-10.01	-2.94			
15	2-methylallyl	36.70	32.67	46.30	-9.74	-3.89	48.78	27.20	22.02
16	1-ethylallyl	52.01	45.68	58.34	-9.56	-3.10	63.52	38.92	34.61
17	1,3-dimethylallyl	51.60	46.21	59.28	-9.37	-3.69	62.98	41.63	34.03
28	cyclopentyl	52.40	45.84	56.47	-7.21	-3.42	58.07	42.21	37.25
21	cyclopropylcarbinyl	45.53	40.15	45.95	-5.29	-0.5	44.13	40.08	36.25
25	bicyclobutonium	51.42	45.17	44.89	-0.48	+0.75	52.43	42.22	40.85
26	methylbicyclobutonium	64.00	57.16	57.13	-0.35	+0.39	64.45	56.06	50.98
22	cis-1-methylcyclopropylcarbinyl	60.78	53.56	58.56	-4.36	-0.64	57.31	55.06	48.30
23	trans-1-methylcyclopropylcarbinyl	60.08	53.29	58.67	-4.60	-0.77	56.84	53.33	49.70
24	1,1-dimethylcyclopropylcarbinyl	74.92							
29	guanidinium	47.80	42.40	42.15	0.02	0.23	43.67	41.76	41.76

^aUnits are ppm cgs/mol. Sign convention: diamagnetic cations have $\chi > 0$.

challenge to theory, since, unlike neutral hydrocarbons, slight changes in their geometry cause large variations of the NMR parameters.

On the other hand, one can understand why conventional ab initio methods have not been applied to carbocations for which chemical shift data are experimentally accessible. Usually these molecules contain more than three carbon atoms, and moreover they are not very symmetric. Coupled Hartree-Fock (CHF) theory with a single origin of the vector-potential for the external magnetic field would require extremely large bases⁹ and is hence not applicable.

Only those methods that use local gauge origins, i.e., our IGLO method,^{12,13} Ditchfield's GIAO method¹⁰ or Hansen's and Bouman's LORG approach,¹¹ the latter of which seems to be rather close to our IGLO ansatz, are expected to yield reliable NMR data for medium-sized carbocations. The GIAO method, however, though applicable, seems to be rather time-consuming.

In our previous papers we have applied the IGLO method¹² mainly to neutral molecules,¹³ and the results of our calculations

were rather promising. Not only are isotropic NMR shifts reproduced quite well for a large number of molecules but also the calculated and experimental shift tensors even for some strained molecules are in excellent agreement.

A short description of our method, the types of basis sets and the geometries used, is given in section II. The IGLO results for χ , $\sigma(\text{C})$, and $\sigma(\text{H})$ for various types of carbocations are discussed in section III, and our conclusions are given in section IV.

II. Method, Basis Sets, and Geometries

Since our method has been outlined in detail elsewhere,^{12,13} we can restrict ourselves to a description of its main features. IGLO (individual gauges for localized molecular orbitals) is a theory of coupled Hartree-Fock type. It is formulated in terms of localized MOs with an individual gauge origin for each MO. This makes the formalism somewhat more complicated, but χ and σ are no longer computed as small differences of two artificially large numbers.

Our specific choice leads to gauge origins almost uniformly distributed over the molecule, and therefore it is well suited for calculations of the magnetic susceptibility (cf. Table I), a property of the molecule as a whole. One can imagine better choices for local properties like the chemical shieldings of individual atoms in a molecule. One might, of course, choose optimum gauge origins for χ and for each $\sigma(\text{N})$ separately, applying Sadlej's⁸ criterion to each of the perturbation operators, as Hoeller and Lischka did in their CHF calculations.^{9b} Then, however, we would lose one prominent feature of our method, namely the ability to get out of only one single calculation results of equal accuracy for the susceptibility as well as for the chemical shift tensors of all atoms in the molecule.

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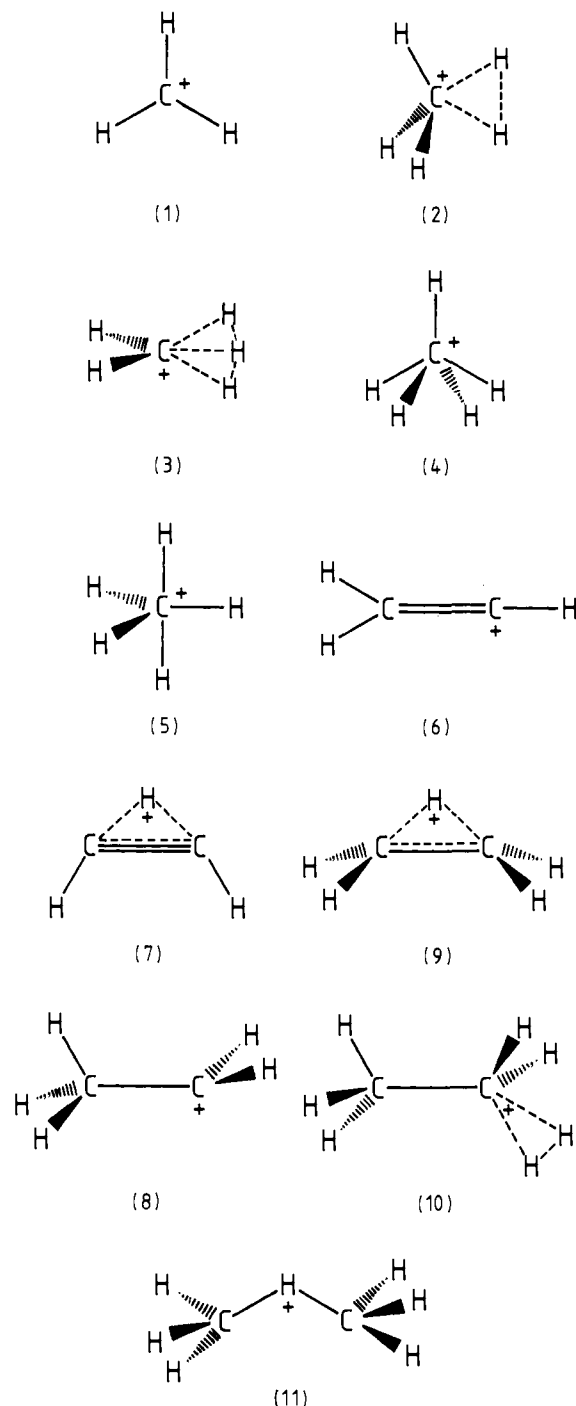


Figure 1. Structures of C_1 and C_2 cations.

Huzinaga¹⁶ Gaussian lobes were used for five different basis sets as follows:

- Basis DZ: C or N: 7s3p contracted to [4111,21]
 H: 3s contracted to [21]
 Basis DZ+d: as basis DZ, augmented by one set of d-functions for the 'heavy' nuclei (exponent: 1.0)
 Basis I: as basis DZ+d, but fully uncontracted p-functions
 Basis II: C or N: 9s5p1d contracted to [51111,2111,1], d-exponent: 1.0
 H: 5s1p contracted to [311,1], p-exponent: 0.7
 Si: 11s7p2d contracted to [5111111,211111,11], d-exponents: 1.40, 0.35
 Basis III: C or N: 11s7p2d contracted to [5111111,211111,11], d-exponents: 1.40, 0.35
 H: 6s2p contracted to [3111,11], p-exponents: 1.30, 0.33

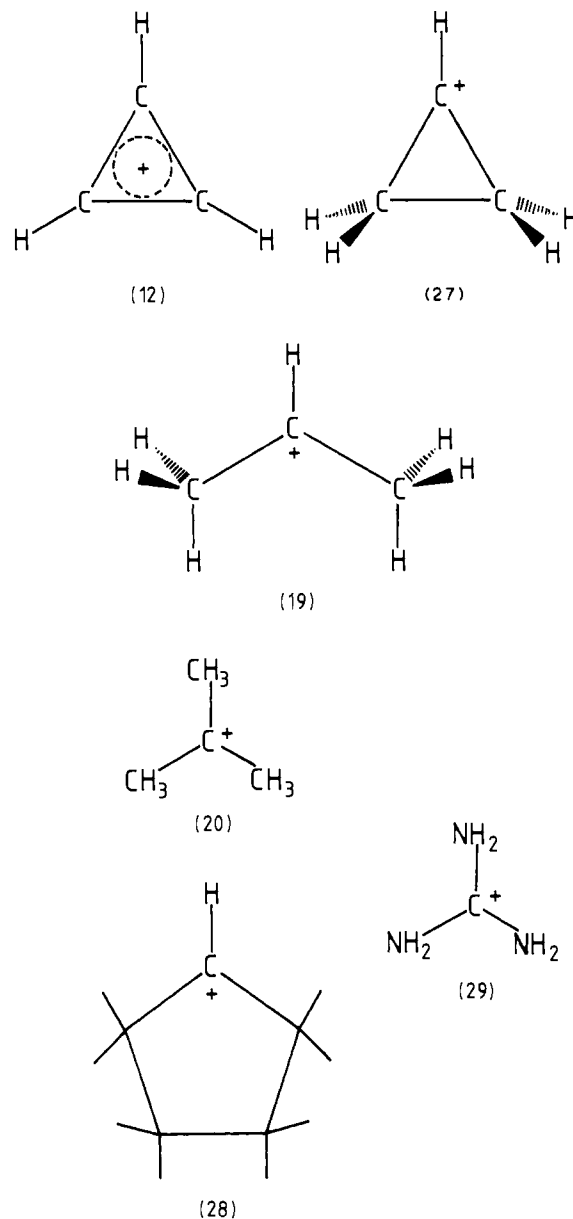


Figure 2. Structures of cyclopropenyl and some classical cations.

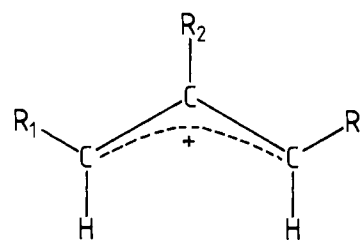


Figure 3. Allylic cations: **13**, $R_1 = H$, $R_2 = H$, $R_3 = H$; **14**, $R_1 = CH_3$, $R_2 = H$, $R_3 = H$; **15**, $R_1 = H$, $R_2 = CH_3$, $R_3 = H$; **16**, $R_1 = C_2H_5$, $R_2 = H$, $R_3 = H$; **17**, $R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$.

For the C_1 and C_2 cations (Figure 1) optimized MP2 6-31G* geometries were taken from ref 17. For CH_3^+ the experimental geometry¹⁸ was used. Geometry references for the larger cations are given in Table II. If a reference is missing, rea-

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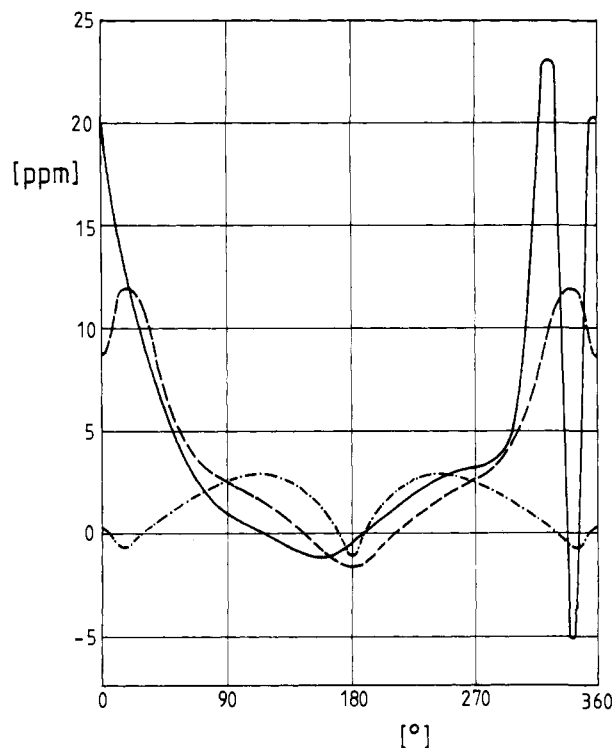


Figure 4. σ in the molecular symmetry plane along a circle with $r = 2$ Å around the central C atom (basis DZ; absolute shielding in ppm, $\sigma > 0$ corresponds to shielding and $\sigma < 0$ to antishielding): (—) cyclobutenyl, (---) cyclopropenyl, and (-·-) allyl. For the orientations of the ions and for the definition of ϑ see Figure 6.

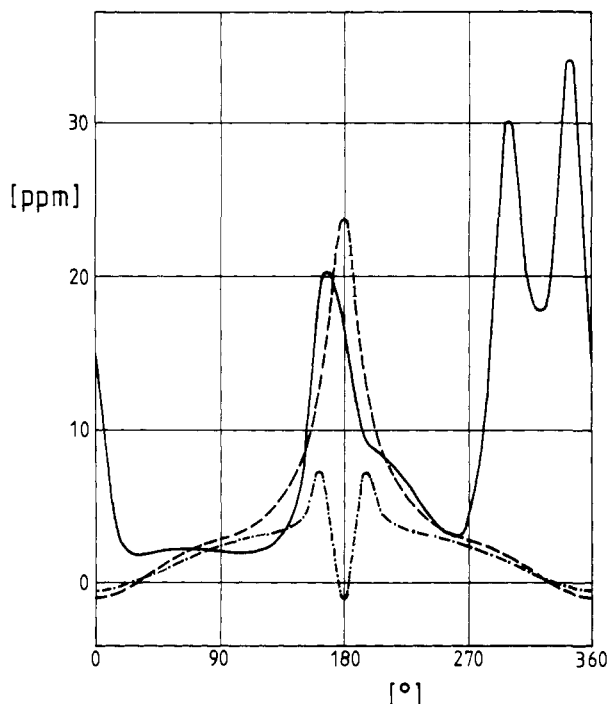


Figure 5. σ in the molecular symmetry plane along a circle with $r = 2$ Å around the the C_2 - C_3 midpoint (see Figures 4 and 6 for explanations).

sonable guesses for the respective structures were made.¹⁹ There exist several different experimentally or theoretically determined

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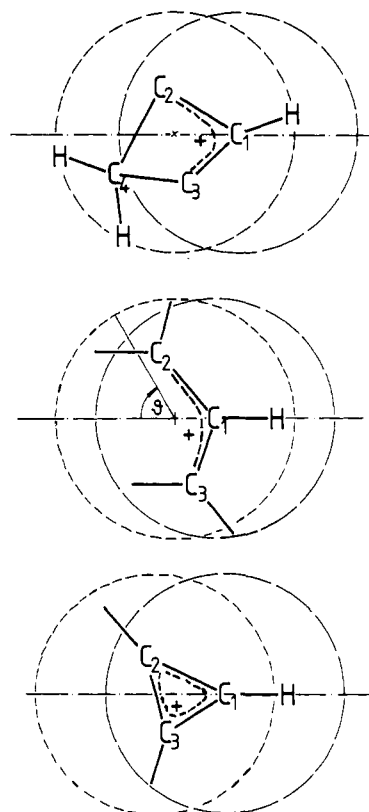


Figure 6. Orientations of the cyclobutenyl (18), cyclopropenyl (12), and allyl (13) cations.

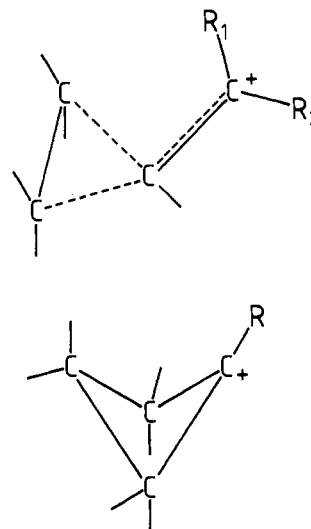


Figure 7. Cyclopropylcarbinyl and bicyclobutonium cations **21**, $R_1 = H$, $R_2 = H$; **22**, $R_1 = CH_3$, $R_2 = H$; **23**, $R_1 = H$, $R_2 = CH_3$; **24**, $R_1 = CH_3$, $R_2 = CH_3$; **25** $R = H$; **26** $R = CH_3$; **35**, $R_1 = OH$, $R_2 = c-C_3H_5$; **36**, $R_1 = c-C_3H_5$, $R_2 = c-C_3H_5$.

geometries of norbornane.²⁷ In order to get more detailed information on C-H bond lengths and CCH bond angles we, too,

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Table II. ^{13}C NMR Shifts of Carbocations^{a,c}

no.	cation	atom	DZ	II	III	experiment	
1	CH_3^+		361.1	373.2	379.2		
2	CH_5^+						
	C_s		-10.6	-7.3	-6.6		
3	C_{2v}		-28.4	-24.5			
4	C_{4v}		-39.5	-33.7			
5	D_{3h}		-44.9	-38.6			
	C_2H_3^+						
6	classical	C^+	405.5	457.8	460.9		
		CH_2	72.5	69.4	71.0		
7	nonclassical		104.3	95.7	95.3		
	C_2H_5^+						
8	C_s	C^+	338.8	347.7	351.6		
		CH_3	52.2	53.1	53.8		
9	C_{2v}		152.4	150.9	153.6		
	C_2H_7^+						
10	C_s	CH_4	7.1	14.3	15.4		
		CH_3	7.4	11.2	11.5		
11	C_1		34.7	40.6			
			35.3	40.9			
12	cyclopropenyl		186.3	179.8	178.7	177.0 ^h	
	C_3H_5^+						
13	allyl	CH	139.5	147.8	148.6		
		CH_2	233.3	242.1	245.7		
27	cyclopropyl	CH	515.9	528.2			
		CH_2	37.2	35.1			
19	isopropyl	CH	358.2	364.7		320.6 ^h	
		CH_3	51.3	51.3		51.5	
20	<i>tert</i> -butyl	C^+	337.8	369.3		335.7 ^h	
		CH_3	46.0	46.4		48.3	
18	<i>c</i> - C_4H_5^+						
	<i>d</i>	$\text{C}_{2,3}$	146.1	146.3		133.5 ⁱ	
		C^+	202.0	198.3		187.6	
		C_4	49.5	50.5		54.0	
	<i>e</i>	$\text{C}_{2,3}$	143.4	143.4			
		C^+	205.6	201.5			
		C_4	49.0	49.7			
	C_4H_7^+						
14	1-methylallyl	CH_2	216.5	222.3		201.5 ^k	
		CH_{centr}	142.2	149.2		149.8	
		CH	269.2	278.7		255.1	
		CH_3	34.9	36.8		36.3	
15	2-methylallyl	C	145.0	159.2			
		CH_2	233.1	240.2			
		CH_3	19.6	23.3			
	C_5H_9^+						
16	<i>trans</i> -ethylallyl	CH_2	216.2	221.2		199.6 ^k	
		CH_{centr}	139.0	146.8		146.5	
		CH	274.4	284.2		258.0	
		CH_2	34.1	41.8		46.4	
		CH_3	8.3	14.7		9.0	
17	1,3-dimethylallyl	CH	249.5	259.3		231.3 ^h	
		CH_{centr}	143.5	148.9		147.0	
		CH_3	31.5	33.7		29.8	
28	cyclopentyl	C^+	401.9	415.4		320 ⁱ	
		CH_2	64.2	68.2		71.0	
		CH_2	18.4	26.9		28.0	
	C_4H_7^+						
21	cyclopropylcarbinyl	$\text{C}_{1,2}$	77.6	75.1			
		CH	60.4	70.0			
		C^+	240.8	244.3			
		$\overline{\text{CH}_2}$	132.0	131.5		47 ± 3 ^m	116 ^b
		CH	60.4	70.0		115 ± 3	76
	bicyclobutonium						
25	<i>f</i>	$\text{C}_{1,2}$	70.5	71.3			
		C^+	168.9	167.0			
		C_4	-15.8	-14.3			
		$\overline{\text{CH}_2}$	41.7	42.8		47 ± 3 ^m	56 ^b
		CH	168.9	167.0		115 ± 3	114
	<i>g</i>	$\text{C}_{1,2}$	72.5	73.2			
		C^+	142.9	140.8			
		C_4	-21.3	-18.2			
		$\overline{\text{CH}_2}$	41.2	42.7			
		CH	142.9	140.8			

Table II (Continued)

no.	cation	atom	DZ	II	III	experiment		
26	$C_5H_9^+$ methylbicyclobutonium	$C_{1,2}$	71.2	71.2		71 ^o	71.3 ⁿ	
		C^+	194.3	192.5		162	162	
		C_4	-8.4	-5.4		-3	-2.8	
		CH_3	33.6	34.4		25	25	
22	<i>cis</i> -1-methylcyclopropylcarbanyl	CH_3	26.2	28.3			26.4 ^k	
		C^+	256.2	262.0			257.5	
		CH_2	72.0	69.9			66.1	
		CH	52.8	58.3			65.3	
		CH_3	35.8	36.1		32.5 ^p	32.7 ^k	32.6 ^q
23	<i>trans</i> -1-methylcyclopropylcarbanyl	C^+	260.1	266.9		251.6	252.2	250.5
		CH_2	70.3	67.4		56.2	59.9	59.9
		CH	51.8	58.2		66.0	66.7	67.4
		CH_c	27.9				29.8 ^p	
		CH_{tr}	37.2				38.5	
24	1,1-dimethylcyclopropylcarbanyl	C^+	271.4				279.3	
		CH	46.7				58.7	
		CH_2	66.0				52.1	
		C^+	296.6				272.0 ^h	271.6 ^u
		CH	29.0				33.4	32.6
35	$C_7H_{11}O^+$ hydroxydicyclopropylmethylum ^f	CH_2	27.0				31.7	30.9
		C^+	261.3					
		C_{α}^1	31.2					
		$C_{\alpha'}$	29.6					
		C_{β}^1	22.8					
29	guanidinium ^r	$C_{\beta'}$	24.3					
		C^+	296.6					
		CH	29.0					
		CH_2	66.0					
		CH	46.7					
			165.5	165.2				

^a Values in ppm; experimental shifts are referenced to Me_4Si , theoretical ones to CH_4 . ^b Estimated in ref 21b for the assumed geometry. ^c A bar indicates an averaged value; subscripts n, x, c, tr, and centr correspond to endo, exo, cis, trans, and central positions. ^d Optimized HF geometry, ref 6e. ^e Optimized MP2 geometry, ref 6e. ^f Reference 23. ^g Dihedral angle changed to 116°. ^h Reference 31. ⁱ Reference 25. ^k Reference 37. ^l Reference 42. ^m Reference 21b. ⁿ Reference 26. ^o Reference 39. ^p Reference 38. ^q Reference 41. ^r Geometry from ref 48. ^s Geometry from ref 49. ^t α , α' , β , and β' correspond to the nonequivalent CH and CH_2 groups of the two cyclopropyl rings. ^u Reference 1.

have optimized its geometry on the Hartree-Fock DZ level by means of the Columbus program package with several additional features, which we adapted to the Cyber 205 computer recently.²⁸ We find consistently larger CC bonds than in ref 27c and slightly different bond angles: $C_1C_2 = 1.553 \text{ \AA}$, $C_1C_7 = 1.558 \text{ \AA}$, $C_2C_3 = 1.576 \text{ \AA}$, $C_1C_7C_4 = 94.4^\circ$, and $C_6C_4C_1C_2 = 112.4^\circ$. This geometry was used to set up the structures of the classical $C_7H_{11}^+$ ions 31-33, since these conformations do not correspond to local minima of the potential hypersurface of $C_7H_{11}^+$. The geometry of the bridged ion 34 was taken from ref 6c.

III. Results and Discussion

The IGLO results for χ (Table I) are discussed in section III.1. ^{13}C and 1H NMR chemical shifts and orbital contributions to $\sigma(C)$ for various types of cations (Figures 1-7) are given in Tables II-IV. Our relative shifts δ are referenced to methane, as we cannot afford to calculate the NMR parameters of the experimental standard reference Me_4Si with all basis sets. (For basis II the absolute shielding values, i.e., referenced to the naked nuclei, in Me_4Si are $\sigma(Si) = 375.1 \text{ ppm}$, $\sigma(C) = 192.7 \text{ ppm}$, and $\sigma(H)$

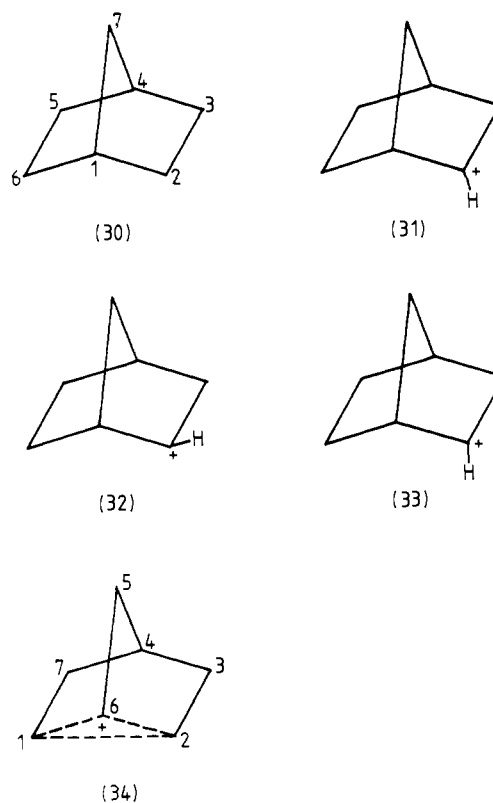


Figure 8. Structures of norbornane and of the 2-norbornyl cations.

= 31.03 ppm, to be compared with $\sigma(C) = 198.4 \text{ ppm}$ and $\sigma(H) = 31.06 \text{ ppm}$ in CH_4 .)

In order to get a feeling for the reliability of the IGLO method for carbocations in general we first applied it to a number of small to medium sized cations, where we could afford basis saturation tests. For a few of the calculated ions the geometries are well-

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Table III. ¹H NMR Shifts of Carbocations^a

no.	cation	atom	DZ	II	III	experiment
1	CH ₃ ⁺		16.43	14.61	14.85	
2	CH ₅ ⁺	CH ₃	4.55	4.76	5.03	
	C _s	H ₂	2.85	2.66	3.05	
6	C ₂ H ₃ ⁺					
	classical	CH	23.2	22.4	21.6	
		CH ₂	10.2	9.3	9.8	
7	nonclassical	CHC	-2.6	0.7	1.5	
		CH	8.0	5.9	5.7	
8	C ₂ H ₅ ⁺					
	C _s	CH ₃	5.2	4.4	4.8	
		CH ₂ ⁺	15.7	13.6	13.6	
9	C _{2v}	CHC	-3.0	-1.8	-1.7	
		CH ₂	9.2	7.6	7.9	
10	C ₂ H ₇ ⁺					
	C _s	CH ₄	3.4	4.0		
		CH ₃	2.1	2.2		
11	C ₁	CH ₃	4.0	3.8		
		CHC	-6.0	-3.7		
12	cyclopropenyl		13.5	11.0	10.8	11.1 ^f
27	cyclopropyl	CH	29.0	26.4		
		CH ₂	4.6	3.5		
13	allyl	CH	9.5	7.7	8.25	9.64 ^f
		CH _{2x}	10.9	9.9	10.15	8.97
		CH _{2n}	12.4	10.5	10.55	8.97
19	isopropyl	CH	16.6	13.9		13 ^f 13.50 ^g
		CH ₃	4.6	3.8		4.5 5.06
20	tert-butyl	CH ₃	4.1	3.2		4.15 ^f 4.35 ^g
25	C ₄ H ₇ ⁺					
	bicyclobutonium	CH	9.16	7.38		6.5 ^h
	c	CH _{2c}	1.42	0.62		
		CH _{2tr}	3.71	3.44		
		C _{1,2} H _c	5.64	4.59		
		C _{1,2} H _{tr}	4.65	3.85		
		CH _{2c}		3.27		4.21
		CH _{2tr}		3.71		4.64
	b	CH	8.56	6.85		
		CH _{2c}		2.76		
		CH _{2tr}		4.64		
21	cyclopropylcarbinyl	CH	3.93	4.19		
		CH _{2c}	11.64	10.91		
		CH _{2tr}	10.27	10.04		
		C _{2,3} H _c	5.80	5.89		
		C _{2,3} H _{tr}	4.96	5.62		
		CH _{2c}	7.75	7.54		
		CH _{2tr}	6.73	7.09		
14	C ₄ H ₇ ⁺					
	1-methylallyl	CH _{2x}	11.20	8.46		
		CH _{2n}	10.5	8.19		
		CH _{centr}	9.0	7.81		
		CH	12.6	10.14		8 - 9 ^t
		CH ₃	4.3	3.45		3
15	2-methylallyl	CH ₃	2.1	2.16		3.85 ^f
		CH _x	12.2	10.34		8.95
		CH _n	10.8	9.52		8.95
16	C ₅ H ₉ ⁺					
	trans-ethylallyl	CH _{2x}	12.07	9.80		8.46 ^k
		CH _{2n}	10.43	9.00		8.19
		CH _{centr}	9.51	7.84		7.81
		CH	12.58	11.29		10.14
		CH ₂	3.28	2.73		3.45
		CH ₃	0.83	1.07		1.07
17	1,3-dimethylallyl	CH ₃	2.97	2.48		3.45 ^f
		CH _{centr}	9.07	7.49		8.30
		CH	11.75	10.31		10.10
18	C ₄ H ₅ ⁺					
	cyclobutenyl	CH _{centr}	12.2	9.92		9.72 ^m
	d	CH	9.8	7.44		7.95
		CH _n	4.26	3.81		4.12
		CH _x	3.78	2.91		4.91
	e	CH _{centr}	12.48	9.94		
		CH	9.87	7.78		
		CH _n	4.22	3.76		4.12
		CH _x	3.72	2.92		4.91

Table III (Continued)

no.	cation	atom	DZ	II	III	experiment
26	C ₅ H ₉ ⁺ methylbicyclobutonium	CH ₃		2.30		2.87 ^l
		C ₄ H _n		0.09		2.70
		C ₄ H _x		3.32		
		C _{1,2} H _x		3.70		
		C _{1,2} H _n		4.38		4.59
22	<i>cis</i> -1-methylcyclopropylcarbinyl	CH _{2c}	3.34	3.88		3.75 ^k
		CH _{2tr}	4.46	3.93		3.87
		CH	5.00	2.00		3.75
		C ⁺	13.10	10.43		10.07
		CH ₃	1.80	1.71		2.23
23	<i>trans</i> -1-methylcyclopropylcarbinyl	CH _{2c}	4.41	3.62	4.32 ^h	3.51 ^k
		CH _{2tr}	4.91	3.85	4.45	3.73
		CH	3.40	2.29	4.58	3.75
		C ⁺	11.48	9.50	9.60	8.78
		CH ₃	2.79	2.29	3.34	2.57
24	C ₆ H ₁₁ ⁺ 1,2-dimethylcyclopropylcarbinyl	CH _{3c}	1.78		2.70 ^h	
		CH _{3tr}	2.94		3.18	
		CH	3.14		3.83	
		CH _{2c}	3.85		3.57	
		CH _{2tr}	4.30		3.68	

^a See footnotes *a* and *c* of Table II. ^b See footnote *g* of Table II. ^c Cis and trans with respect to the methine H. ^d Optimized HF geometry. ^e Optimized MP2 geometry. ^f Reference 1. ^g Reference 44. ^h Reference 38. ⁱ Reference 43. ^k Reference 37. ^l Reference 39. ^m Reference 25.

known, and experimental data are available (section III.2-4).

For some other rather small cations such as C₄H₇⁺ reliable geometries are missing, and only NMR data are known. By calculating NMR chemical shifts for different proposed structures of C₄H₇⁺ and for a number of methyl- and cyclopropyl-substituted cyclopropylcarbinyl cations, the structures of which are known, we can decide that a cyclopropylcarbinyl geometry must be ruled out for the present C₄H₇⁺ cation (section III.5).

One of the oldest questions in carbocation chemistry concerns the structure of the 2-norbornyl cation (Figure 8) in the context of the so-called 'classical' - 'nonclassical' ion controversy^{14,15} and references therein. Our calculations for several classical and a nonclassical geometry strongly support the nonclassical geometry (section III.6).

In order to allow for a comparison of the performance of the IGLO method with other programs, we give some representative CPU times in section III.7.

1. Magnetic Susceptibilities. In Table I molecular susceptibilities (in 'ppm cgs' per mole) are tabulated for two basis sets. The sign convention is such that diamagnetic contributions to χ are positive and paramagnetic ones negative. The results obtained with the larger basis II are divided into diamagnetic, paramagnetic, and nonlocal contributions. The diamagnetic part of the susceptibility dominates, followed by the much smaller, usually negative paramagnetic and the nonlocal contributions. None of the three contributions to χ is physically relevant within the IGLO formalism, only their sum should be compared with experimental data.

Improvement of the basis generally leads to a lowering of the magnetic susceptibility, the only exceptions being CH₅⁺ and the almost paramagnetic CH₃⁺ cation.

In addition the principal values of the symmetric χ tensor are given in Table I, in order to allow for comparisons with experimental anisotropies. It is rather difficult to obtain magnetic susceptibilities of cations by conventional experimental methods. Under experimental conditions cations build an extremely dilute solution in strongly polar solvents, the latter contributing almost all of the total measurable susceptibility. Recently, however, susceptibility anisotropies of cations became available by using NMR techniques.²⁴ So it should be possible to compare our calculated anisotropies with experimental ones in the near future.

2. Chemical Shifts of C₁ and C₂ Cations. CH₃⁺ (1) and CH₅⁺ (2-5) are the simplest examples for classical and "nonclassical" carbocations. A typical nonclassical cation has one two-electron three-center bond as in CH₅⁺, although in all experimentally studied cases at least two carbon atoms are involved in this type

of bond. Despite this, both the ¹³C shifts of CH₃⁺ (ca. 370 ppm) and those of the formally pentacoordinated C in CH₅⁺ (ca. -10 ppm) and the corresponding orbital contributions fit into the pattern found for these types of cations (Tables II and IV). Of the several calculated CH₅⁺ structures the one with C_s geometry **2**, which is energetically preferable, shows the least shielded ¹³C resonance.

For the cations C₂H₃⁺ (**6**, **7**), C₂H₅⁺ (**8**, **9**) and C₂H₇⁺ (**10**, **11**) (Figure 1) one still does not know from experiment, whether their classical or nonclassical structures, i.e. C-H or C-C protonated, are more stable. Ab initio calculations^{5d,17} predict the nonclassical geometries to be lower in energy. The question of which structures are realized experimentally could be decided, if the NMR spectra were known. Classical and H-bridged structures of C₂H₃⁺ and C₂H₅⁺ differ markedly in their shift positions.

The C₁-H orbital contributions (Table IV) to σ (C) in CH₃⁺, the CH-protonated form **8** of C₂H₅⁺ and in the classical isopropyl (**19**) and cyclopentyl (**28**) carbenium ions, are of similar magnitude, and so are the C₁-C₂ contributions in **8**, **19**, **20**, and **28**.

The C-C-protonated structure **9** of C₂H₅⁺ shows ¹³C and methylene ¹H shifts comparable to those of the central C and H atoms of the allylic cations **13-17**.

The C-H protonated ethane **10** is very similar to the C_s form of CH₅⁺. The corresponding two-electron three-center orbital contributions to σ (C) are almost identical. The more stable C-C protonated form **11** of C₂H₇⁺ has two nonequivalent carbon atoms, whose NMR shifts can hardly be distinguished. Orbital contributions from the CHC bond and from the C₂-H bonds are identical for each of the C atoms, only the C₁-H contributions differing slightly. For this reason averaged values are shown in Table IV.

3. Aromatic, Homoaromatic, and Allylic Cations. The smallest cation, whose experimental proton- and carbon-shift data are available, is the aromatic cyclopropenyl cation **12** (Figure 1). IGLO results and experimental shifts agree surprisingly well. Because of the molecular D_{3h} symmetry large basis sets could be used in a conventional CHF calculation.^{7b} As expected, CHF and IGLO converge to the same results in the limit of large basis sets.

To our knowledge no ¹³C but only proton NMR shifts have been measured for the allyl cation **13**, and the exo- and endo-protons H_x and H_n could not be distinguished by the NMR experiment. We find H_n more shielded by approximately 0.5 ppm than H_x.

As far as the ¹³C data are concerned, we can draw some conclusions from the comparison between IGLO calculations and experiment for the 1-methylallyl-, 2-methylallyl-, 1-ethylallyl-, and 1,3-dimethylallyl cations **14-17** (Figure 3). The agreement

Table IV. Orbital Contributions to ^{13}C NMR Shifts of Carbocations•C⁺ Atoms^{a,b}

no.	cation	C ₁ C ₂	C ₁ H	C ₂ C ₃	C ₂ H	2e3c ^c	C ₃ H	C ₃ C ₄
1	CH ₃ ⁺		-125.3					
2	CH ₅ ⁺		-4.1			9.5 ^d		
	C _s		-4.1					
			3.5					
7	C ₂ H ₃ ⁺							
	n.cl. ⁱ	-21.3	-33.2		-10.8	4.7		
		-21.3						
6	cl. ⁱ	-187.5	-81.9		-1.7			
		-187.5						
9	C ₂ H ₅ ⁺							
	C _{2v}		-44.0		-3.3	-8.2		
8	C _s	-134.0	-105.6		-2.1 H _{op}			
					-0.9 H _{ip}			
10	C ₂ H ₇ ⁺							
	C _s							
	CH ₄	-7.5	-8.5 H _{op}		-0.7 H _{op}	9.4 ^d		
					-0.3 H _{ip}			
	CH ₃	0.5	-5.5 H _{op}		-0.0	-0.2		
			-3.1 H _{ip}					
11	C ₁							
			-19.1		0.3	4.5 ^e		
			-15.9		0.9			
			-14.0		0.0			
19	isopropyl	-129.3	-99.4		-2.1 H _{op}			
					-0.5 H _{ip}			
27	cyclopropyl	-217.2	-87.1	4.1 ^k	-3.4 H _{op}			
20	tert-butyl	-119.9			-1.7 H _{op}			
					-0.6 H _{ip}			
28	cyclopentyl	-152.1	-97.7	-0.9	-3.1 H _{op}			-1.4 ^l
29	guanidinium	-26.8 ^f			-1.2 ^f			
13	allyl	-91.7	-72.6 H _n	-2.0	-1.6 H _{ip}	-6.9	-1.0 H _n	
			-69.2 H _x				0.4 H _x	
15	2-methylallyl	-90.5	-71.7 H _n	-2.2		-7.2	-1.1 H _n	
			-60.7 H _x	-2.3 ^m			0.4 H _x	
14	1-methylallyl							
	CH ₂	-61.7	-65.7 H _n	-2.9	-2.2 H _{ip}	-30.9	-1.1 H _n	
			-60.7 H _x					
	CHCH ₃	-96.2	-76.8 H _n	-2.9	-0.5 CH _{3ip}	-4.1	-1.2 H _n	
		-95.2 ^m			-1.3 CH _{3op}			
					-1.4 CH			
17	1,3-dimethylallyl	-90.2	-70.7 H _n	-1.8	-0.5 CH _{3ip}	-6.9	-1.0 H _n	
		-87.0 ^m			-1.3 CH _{3op}			
					-1.4 CH			
16	trans-ethylallyl							
	CH ₂	-44.2	-65.4 H _c	-3.1	-2.2		-1.1	0.2
		-47.6	-60.5 H _{tr}					
	CHC ₂ H ₅	-96.9 ⁿ	-77.2	-1.0 ^p	-1.5 CH ₂		-0.8 H _{ip}	
		-98.2 ^o		-3.5 ^q	-1.4		-0.2 H _{op}	
				-3.4 ^q			-1.2 CH _{2c}	
							0.2 CH _{2tr}	
21	cyclopropylcarbinyl	-50.7	-64.4 H _c ^x		-1.4	-6.5	-0.7 H _c ^y	-0.2 ⁱ
		-50.7	-72.3 H _{tr}				0.4 H _{tr}	
22	cis-methyl-	-19.1	-70.1 H _{tr}		-1.1	-4.9	-0.4 H _c ^y	+0.0 ⁱ
		-82.6			-1.2 CH _{3tr} ^x		0.3 H _{tr}	
		-83.7 ^m			-0.3 CH _{3c}			
23	trans-methyl-	-18.0	-63.9 H _c		-0.7	-5.3	-0.6 H _c ^y	-0.0 ⁱ
		-85.1			-1.4 CH _{3c}		0.3 H _{tr}	
		-92.6 ^m			-0.4 CH _{3tr}			
25	bicyclobutonium							
	g	-54.4	-50.2	-2.9	-1.4 H _c ^z		-0.1 H _c ^z	
					-2.1 H _{tr}		2.4 H _{tr}	
25	h	-44.6	-41.7	-4.2	-1.6 H _c ^z		0.1 H _c ^z	
					-1.8 H _{tr}		2.7 H _{tr}	
26	methyl-	-57.7		-2.2	-1.2 H _c ^z		0.1 H _c ^z	
		-68.6 ^m			-2.3 H _{tr}		2.4 H _{tr}	
					-1.0 CH _{3tr} ^z			
					-0.9 CH _{3c}			

^a Absolute shielding in ppm (basis II). Contributions less than 0.1 ppm and the constant Is(C) contribution are omitted. ^b See footnote c of Table II. ^c Two-electron three-center bond. ^d HCH bond. ^e CHC bond. ^f C-N and N-H bonds. ^g Partially optimized geometry, ref 23. ^h Dihedral angle 116°. ⁱ cl. and n.cl. mean classical and non-classical structure. ^k C₂-C₂ bond. ^l C₃-C₃ bond. ^m C-CH₃ bond. ⁿ C-CH bond. ^o C-CH₂ bond. ^p CH₂-CH₃ bond. ^q CH-CH₂ bond. ^x With respect to the cyclopropyl ring. ^y With respect to C⁺. ^z With respect to the ring.

between calculated and observed data is excellent, the only exception being the NMR data of the positively charged carbon atoms, whose calculated shifts are too far downfield by approximately 25 ppm as compared to experiment. Taking this sys-

tematic deviation into account we predict the experimental ^{13}C data of the allyl cation to be 149 and 225 ppm, respectively.

An explanation of the deviations found for the positively charged C atoms will be given at the end of section III.4.

Table V. Orbital Contributions to $\sigma(\text{C})$ of the Central Carbon Atom^{a,b}

no.	cation	C ₁ C ₂	C ₁ H	2e3c ^c	C ₂ H _c	C ₂ H _{ir}	C ₂ C ₃
13	allyl	-48.8	-28.0	-12.7	-3.0	-2.9	
14	1-methylallyl	-39.4 ^d	-28.4	-24.3	-3.7 ^e	-3.1	-4.2
		-44.9 ^f			-3.2 ^g		
15	2-methylallyl	-48.9 ^d		-13.4	-3.0	-2.8	
		-37.9 ^h					
16	1-ethylallyl	-30.6 ^d	-28.4	-32.2	-3.9	-3.1 ^e	-3.9
		-43.4 ⁱ			-3.2 ^k		
17	1,3-dimethylallyl	-48.9	-27.8	-11.1	-2.9		-3.9
18	cyclobutenyl	-57.4	-42.5	-34.5		-3.3	-2.1
12	cyclopropenyl	-64.1	-41.9	-2.3		-4.4	-1.2

^a Basis II; contributions of carbon 1s orbitals (200.9 ppm) and contributions smaller than 1 ppm are omitted. ^b Numbering of the atoms: 1, C-atom under consideration 2, 3, ..., next neighbors, 2nd next neighbors etc. ^c Two-electron three-center bond. ^d C-CH₂ bond. ^e C-H bond. ^f C-CHCH₃ bond. ^g C-H bond of CH₃-substituted C atom. ^h C-CH₃ bond. ⁱ C-CHC₂H₅ bond. ^k C-H bond of C₂H₅-substituted C atom.

The cyclobutenyl or homocyclopropenyl cation **18** does not show the ¹H and ¹³C spectra characteristic for allyl cations, indicating that the central C atom bears most of the positive charge, which is distributed over the adjacent carbon atoms in allylic systems. This can be seen in more detail from the orbital contributions to $\sigma(\text{C})$ of the "central" C atom in several unsaturated cations (Table V). The allylic C atoms are considerably less deshielded by adjacent CC and CH bonds and by the two-electron three-center bond than the central C atom of homocyclopropenyl cation.

Despite these differences, all orbital contributions to $\sigma(\text{C})$ of the central C atoms are much smaller than those shown in Table IV for the carbon atoms bearing most of the positive charge.

By recording ¹H spectra at temperatures where the conformations of C₄H₅⁺ are frozen, Olah et al.²⁵ were able to observe different signals for the two methylene protons. They assigned the high field signal to the endo and the low field signal to the exo proton. In our calculation, however, the positions of these signals are reversed, the other resonances being in agreement with the experimental ones. Experimentally the assignments for the methylene protons could be checked, in principle, via an observation of the intramolecular NOE. To clarify these discrepancies theoretically we made two more calculations with dihedral angles changed by 10° in each direction. Although the absolute NMR signals varied considerably, we could not find a change of the relative positions of H_x and H_n.

In addition, by positioning phantom nuclei with nuclear charges of zero in the molecular plane of symmetry in circles with radius $r = 2 \text{ \AA}$ around the central C atom C₁ and around the C₂-C₃ midpoint we probed the shielding effect due to the electronic motion caused by the external magnetic field. These effects are shown in Figures 4 and 5 together with those for the allyl and the cyclopropenyl cations. The orientations of the molecules and the definition of the angle ϑ are given in Figure 6.

Contrary to common assumptions but in agreement with the findings of Childs et al.²⁰ no deshielding effect can be seen in the C₂C₃C₄ plane of C₄H₅⁺, and no extra shielding perpendicular to it. Instead, we find at the "open" side of C₄H₅⁺, i.e., at angles ϑ from 0 to 180° in Figure 4, a behavior almost identical with that of C₃H₃⁺, only the deshielding dip of C₃H₃⁺ in the molecular plane at $\vartheta = 0$ is missing. On the "bridged" side of C₄H₅⁺ we see large amplitude oscillations of the shielding when passing through the C₁C₂C₄ plane. These are caused mainly by the strongly varying contributions of the two CH₂-C bonds. Coming from the "open" side of C₄H₅⁺ they are increasingly shielding, reaching their maximum of 9 ppm each at an angle of 5° below the C₂C₃C₄ plane ($\vartheta = 355$) and then becoming deshielding up to -2.4 ppm each near the C₁C₂C₄ plane. The large shielding effect at the other side of this plane is due to the contribution of the CH_n bond (16 ppm).

In Figure 5, as in Figure 4, below the C₁C₂C₃ plane, i.e., at angles $270^\circ \leq \vartheta \leq 360^\circ$, the similarity of C₄H₅⁺ and C₃H₃⁺ is obscured by the influence of the additional methylene group of C₄H₅⁺. While the shielding effects due to the C₁-H bonds almost coincide, shielding maxima of increasing height are found for H_n and H_x. It is interesting to note that in C₃H₃⁺ at angles corresponding to H_n and H_x we have shielding (2 ppm) and deshielding

(-1 ppm) effects, respectively. In despite of these findings, in C₄H₅⁺ H_n is less shielded than H_x.

Although it cannot be ruled out that the calculated geometry is very different from the exact one, it might be that the experimental assignments of the two methylene ¹H resonances of the homocyclopropenyl cation are not correct and should be interchanged.

The allyl cation is quite different. We do not find as large variations of the shielding as in the two other cations, and near the molecular plane deshielding effects dominate. The deshielding hole at $\vartheta = 180^\circ$ in Figure 5 results mainly from the C₁-H bond. Due to the large CCC angle in C₃H₅⁺ the circle around the midpoint of C₂-C₃ cuts the molecular plane relatively far outside the molecule, at a distance where the CH bond is deshielding, unlike C₃H₃⁺ and C₄H₅⁺, whose respective CH contributions to $\sigma(\text{C})$ are strongly shielding.

4. Classical Cations with Localized Charge. The classical isopropyl (**19**), *tert*-butyl (**20**), and cyclopentyl cations (**28**) (Figure 2) exhibit a similar behavior. The NMR shifts of the methyl and methylene carbons agree well, whereas the positively charged carbon atoms are deshielded by approximately 30 ppm as compared to the experimental data. The differences between calculated and measured data increase when we employ larger basis sets.

At first glance this is rather surprising since in general one expects an improvement of the calculations with enlargement of the basis sets.

The reason for this assumption is quite clear: The quality of the first-order wave function is not as good as the quality of the unperturbed one. So the calculated paramagnetic contribution to a second-order property will be too small in absolute value and this property appears too diamagnetic when a small basis set is used. Enlargement of the basis improves the first-order wave function more than the "almost complete" zeroth-order one, and this leads to a better description of the respective property.

Although in our IGLO method the qualities of zeroth- and first-order zeroth-wave functions do not differ as much as in conventional schemes, these arguments are valid in our case, too, and our experiences with neutral molecules support this. So there should be another source for the lack of agreement between theory and experiment, namely the different surroundings of the molecules under study. We calculate the properties of a single molecule in space. Interactions either with counterions or with solvent molecules are hence not present. This situation is rather different from that found experimentally under long-lived stable ion conditions. Of course, solute-solvent interactions and ion-pairing effects are the more important the less distributed the molecular charge is.

This hypothesis explains the increasing differences between calculated and measured data when going from perfectly delocalized systems like C₃H₃⁺ to typical localized ones like (CH₃)₃C⁺, and it is not surprising that the calculated ¹³C NMR shifts for guanidinium **29** agree with those found experimentally for the corresponding *N*-methyl-substituted ions.

The deviation for the ¹³C shifts of the positively charged C atom in **28** is too large for this explanation to hold. Probably our

Table VI. Norbornane and the 2-Norbornyl Cations^a

no.	$-(E_{SCF} + 270)$	basis	χ	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	sum ^b
30 ^d	1.69947	DZ	101.9	27.1	27.7	27.7	27.1	27.7	27.7	37.8	202.8
k	1.70730	DZ	98.8	27.5	24.2	24.2	27.5	24.2	24.2	35.1	186.9
	1.82080	DZ+d	98.4	29.4	24.4	24.4	29.4	24.4	24.4	33.7	190.1
	1.82239	I	92.1	31.7	24.8	24.8	31.7	24.8	24.8	33.1	195.7
	expt ^e			36.4	29.7	29.7	36.4	29.7	29.7	38.4	230.2
	expt ^f			36.7	30.0	30.0	36.7	30.0	30.0	38.6	232.0
	expt ^g			36.3	29.6	29.6	36.3	29.6	29.6	38.3	229.3
	expt ^h			37.3	30.6	30.6	37.3	30.6	30.6	39.2	236.2
31 ^k	0.82218	DZ	78.0	78.2	423.2	72.6	32.4	22.8	22.6	42.9	694.7
	0.93803	DZ+d	76.2	72.7	393.1	65.8	32.5	23.1	20.3	39.4	646.9
	0.93962	I	73.8	71.0	391.0	64.5	33.1	23.3	19.5	38.2	640.6
32 ^k	0.76398	DZ	75.2	96.6	495.2	110.7	47.2	27.5	37.8	42.2	857.2
33 ^k	0.75962	DZ	68.7	106.0	533.3	89.8	41.7	30.1	20.2	52.4	873.5
34 ^c	0.83677	DZ	92.2	142.5	142.5	35.7	33.3	19.8	37.3	35.7	446.8
	0.95228	DZ+d	88.5	131.9	131.9	33.0	32.3	19.5	34.0	33.0	415.6
	0.95442	I	86.5	128.0	128.0	32.1	33.7	19.1	32.9	32.1	405.9
	expt ⁱ			124.5	124.5	36.3	37.7	20.4	21.2	36.3	400.9

^a See footnotes a of Tables I and II. ^b Sum of all ¹³C NMR shifts. ^c Geometry from ref 6c. ^d Geometry from ref 27c. ^e Reference 45. ^f Reference 32. ^g Reference 33. ^h Reference 34. ⁱ Reference 35. ^k Geometry optimization using the program package described in ref 28.

assumed geometry for **28** needs improvement.

5. Bicyclobutonium and Cyclopropylcarbinyl Cations. The structure of C₄H₇⁺—cyclopropylcarbinyl (**21**) or bicyclobutonium (**25**) (Figure 7) static or equilibrium of different structures—is not known despite numerous theoretical and experimental investigations.^{6,21,22} According to ab initio calculations,^{6a} the bisected cyclopropylcarbinyl geometry should be energetically favored, a slightly different structure with C₁ symmetry (geometry V of ref 6a) being only 0.5 kcal higher in energy. Our calculations using either geometry, however, give CH and averaged CH₂ carbon shifts of 70 vic. 130 ppm for the bisected structure and 69 vic. 112 ppm for the unsymmetrical one, whereas the extrapolated experimental ones are 115 ± 3 and 47 ± 3, respectively.

These differences between calculated and measured ¹³C shifts are so large (45 and 80 ppm) that we must rule out the cyclopropylcarbinyl geometries.

Replacing the *cis*- and *trans*-hydrogen by methyl groups we can compare IGLO calculations with NMR measurements of *cis*- and *trans*-1-methylcyclopropylcarbinyl and 1,1-dimethylcyclopropylcarbinyl cations **22–24**.^{37,38} The agreement is much better, especially the shielding effect due to the cyclopropane ring experienced by the *cis*- and *trans*-methyl groups is reproduced in the calculations quite well. This indicates that the assumed structures are similar to the actual ones of the substituted cyclopropylcarbinyl cations. In this context the disagreement of the experimental ¹H shifts for the *trans*-1-methylcyclopropylcarbinyl cation between different groups^{37,38} is surprisingly large (ca. 0.8 ppm).

Very recently the structure of the hydroxydicyclopropylmethyl cation (**35**) ion has been determined by single-crystal X-ray diffraction techniques.⁴⁹ Using the experimental carbon skeleton together with CH distances and CCH angles—from ref 6a we have

performed DZ-IGLO calculations for **35**. As far as we know, no ¹³C data have been published so far. Our calculated shifts (Table II) seem to be in the expected ranges.

In order to have one more cyclopropylcarbinyl cation with known geometry, the computed NMR parameters of which can be compared with the experimental ones, we have chosen the tricyclopropylmethyl cation **36**. Assuming the carbon skeleton of **36** to be similar to that of **35**, we derived its geometry from ref 49 and 6a as was done for **35**. Our calculated ¹³C parameters for **36** are in good agreement with the experimental findings.

Obviously IGLO is able to reproduce the experimental NMR shifts with a reasonable accuracy when the proposed geometries are close to the experimental ones. This means that electron correlation directly affects the calculation of σ only to a minor extent. Therefore both our calculations for methyl-substituted cyclopropylcarbinyls **22–24** based on the optimized SCF geometry **21** of C₄H₇⁺ and the calculations for the hydroxydicyclopropylmethyl cation **35** using the experimental structure and for tricyclopropylmethyl cation **36**, confirm our doubts concerning the bisected cyclopropylcarbinyl geometry for the unsubstituted C₄H₇⁺ ion.

A much better, though not quite satisfactory, agreement for the ¹³C shifts of C₄H₇⁺ is reached when we use a partially optimized bicyclobutonium-like geometry²³ where 167 and 43 ppm have to be compared with 115 and 47 ppm. The calculated ¹H shifts for this structure, too, fit better to the observed ones (cf. Table III) than do those for the cyclopropylcarbinyl geometry. (The bicyclobutonium-like puckered cyclobutyl geometry of ref 6a gives 177 and 41 ppm for the CH and CH₂ ¹³C shifts and 7.4, 2.4, and 3.1 ppm for the ¹H shifts of the methine and the *cis*- and *trans*-methylene protons, respectively.)

One DZ-level, however, the bicyclobutonium geometry **25** is higher in energy by 19 kcal/mol than is the optimized cyclopropylcarbinyl geometry **21** of ref 6a (puckered cyclobutyl: 16 kcal/mol). The difference is reduced to 6.8 kcal/mol (5.1 kcal/mol) for basis II. This indicates that it is necessary to investigate the C₄H₇⁺ potential hypersurface including electron correlation together with large basis sets.

By varying the dihedral angle C₄C₁C₂C₃ from 124 to 116°, thus letting the C₄—CH distance become almost equal to the C₁—CH and C₂—CH distances, the agreement can be improved considerably not only for ¹³C (141 ppm for CH and 43 ppm for CH₂, basis II) but also for the ¹H results. While the averaged shifts of the methylene carbons remain almost unchanged, the methine carbon becomes more shielded by about 26 ppm. The latter geometry again does not correspond to a minimum of the potential hypersurface of C₄H₇⁺ (9.4 kcal/mol above the minimum; basis II). It is interesting to compare the orbital contributions to $\sigma(C)$ for these two geometries. Due to the smaller dihedral angle the C⁺—C

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Table VII. ^1H NMR Shifts of the 2-Norbornyl cations^a

atom	31, classical				34, nonclassical			expt ^d
	DZ ^c	DZ ^e	DZ+d ^e	I ^e	DZ	DZ+d	I	
H ₁ , H ₂ ^b	13.38	13.40	12.09	11.88	8.14	7.24	7.13	6.75
H ₃ , H ₇ ^b	3.44	2.59	2.36	2.06	1.55	1.37	1.43	2.13
					1.95 H _x	1.74	1.79	
					1.15 H _n	0.99	1.06	
H ₆	2.24	1.90	1.74	1.27	2.42	2.27	2.35	3.17
H ₅		1.57	1.55	1.16	0.57	0.51	0.61	1.37
H ₄	4.07	3.55	3.38	2.87	2.31	2.15	2.16	2.82

^a See footnote a of Table II. ^b Averaged. ^c Geometry from ref 27c. ^d Reference 35. ^e See footnote k of Table VI.

as well as the C⁺-H bond contributions are less shielding by approximately 10 ppm each, the other contributions remaining almost unaffected.

Substituting the methine hydrogen of bicyclobutonium by a CH₃ group we find rather good agreement with the experimental work of Kirchen and Sorensen³⁹ for both ¹³C and ¹H. So our calculations support the conclusions from EIE NMR investigations²⁶ that the C₄H₆CH₃⁺ cation has indeed the structure of a methylbicyclobutonium ion **26**.

6. The 2-Norbornyl Cation. Energies, molar diamagnetic susceptibilities, and NMR chemical shifts relative to CH₄ are shown in Tables VI and VII for norbornane **30** and for several conformations of the 2-norbornyl cation **31-34** (Figure 8) together with experimental data.^{29-35,45}

Taking the C₇H₁₂ geometry of ref 27c we find the wrong order of ¹³C resonances for C₁ and C₂, whereas our optimized geometry gives the correct one, although the DZ basis is not flexible enough to describe the tertiary carbon atoms properly. The wrong order found with ref 27c is mainly due to the different C₁-H contributions as compared to our optimized geometry, and this in turn is due to the fact that we took the averaged C-H distances and CCH angles tabulated in ref 27 c.

To achieve a better description of the tertiary carbon atoms we first augmented the DZ basis set for all C's with one set of d-functions (basis DZ+d), and then we relaxed the contraction of the p-set (basis I). The results of the corresponding calculations show significant improvements as far as the relative positions of the NMR signals within the molecules and their absolute values are concerned.

To improve the overall agreement between theory and experiment further, we should have used even larger basis sets, i.e., basis sets II or III, but unfortunately for molecules of this size this is still prohibitive. As is well-known, comparisons of relative energies between "classical" and "nonclassical" ions computed on DZ-SCF level are rather meaningless. So one should not pay too much attention to the calculated energy difference between ions **31** and **34**; instead one should look at the dramatic changes of the NMR chemical shifts in going from the classical to the bridged structure.

For the classical sp²-hybridized cation **31** the deviation of the C₁,C₂ averaged C⁺ resonance from experiment is approximately 105 ppm, and the averaged C₃,C₇ resonance is wrong by about 15 ppm. As expected, the situation is even worse for the exo and endo cations showing errors for C⁺ or roughly 170 and 190 ppm.

In the case of the bridged geometry **34**, however, not only the differences are only 3.5 and 4 ppm, respectively, which might be explained by the still insufficient basis set flexibility, but also the agreement with the experimental shifts of the remaining carbon atoms is satisfactory.

Taking the experimental total ¹³C chemical shift difference of -168 ppm³⁵ between norbornane and its cation as a measure for the nonclassical nature of the latter,³⁶ this value compares rather well with the theoretical one of -210 ppm for the bridged ion **34** but not at all with -445 ppm for the most reasonable classical structure **31** (basis I).

Thus, independently of the basis sets used, our calculations strongly support a symmetrically bridged geometry of the 2-norbornyl cation.

¹³C Shift Tensors for the Nonclassical 2-Norbornyl Cation. In Table VIII we list the principal values of the ¹³C shift tensors for the nonclassical C₇H₁₁⁺ cation. Only the C atoms involved in the

Table VIII. The Nonclassical Norbornyl Cation C₇H₁₁⁺. ¹³C Chemical Shift Tensors^{a,b}

	C ₆	C ₅	C ₄	C _{3,7}	C _{1,2}
δ _{av}	32.9	19.1	33.7	32.1	128.0
δ ₁₁	-17.9	2.3	23.9	17.9	16.5
δ ₂₂	12.3	21.8	36.1	26.6	163.9
δ ₃₃	104.5	33.1	41.2	51.8	203.7
α ^c	131	9	89	118	10
β ^c	90	90	90	119	84

^a Referenced to CH₄; basis I. ^b The x-y plane is the molecular symmetry plane. ^c α and β are the angles (in degrees) between δ₃₃ and the x and z axes, respectively.

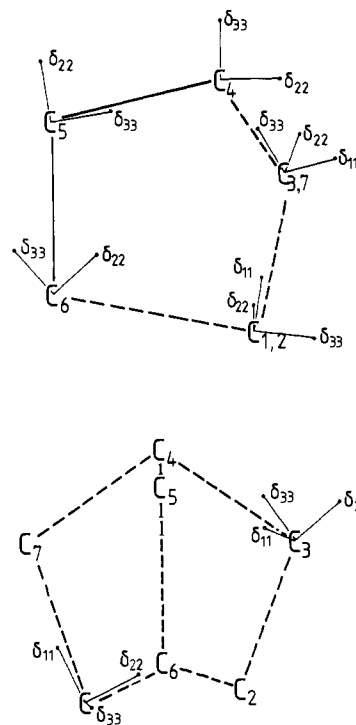


Figure 9. Principal axes for ¹³C shift tensors in the nonclassical 2-norbornyl cation. The upper figure shows the projection onto the molecular x-y symmetry plane. The lower figure shows the projection onto the y-z plane.

two-electron three-center bond show large anisotropies. Symmetry requires one principal axis of any C atom in the molecular symmetry plane to be perpendicular to it. For these C atoms of C₇H₁₁⁺ this direction always corresponds to the least shielding principal value δ₁₁. The remaining axes are given in Figure 9. No symmetry restriction is imposed to the directions of the principal axes system of C₁,C₂ and C₃,C₇, whose calculated principal axes are shown, projected to the symmetry plane and viewed from the top of the molecule.

Orbital Contributions to σ(C) for C₇H₁₁⁺. The largest orbital contribution to σ(C) of norbornane (Figure 10) is due to the carbon 1s-AO (200.9 ppm). It is a constant for almost all molecules that we have studied so far, nearly independent of the

Table IX. Representative CPU Times^a

molecule (symmetry)	basis functions	2e integrals		SCF cycles		1st order operators		IGLO cycles	
		no. [10 ⁶]	CPU time	no.	CPU time	2e CPU time	1e CPU time	no.	CPU time
C ₇ H ₁₂	150	12	586	12	292	967	200	10	284
C ₇ H ₁₁ ⁺	148	24	1114	12	515	953	285	14	818
C ₇ H ₁₁ ⁺	148	45	2105	12	933	1043	448	14	1598

^aCPU times in seconds; calculations performed on the Bochum Cyber 205 vectorcomputer with 0.5 mW core storage.

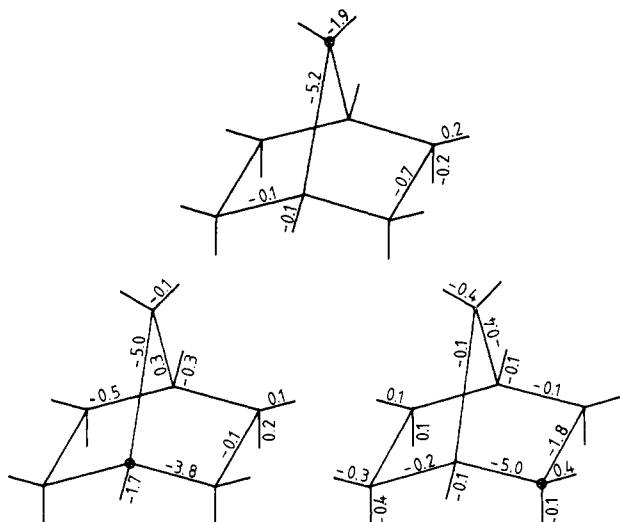


Figure 10. $\sigma(C)$ orbital contributions in norbornane:^{a,b} (a) absolute shielding in ppm, basis I, $\sigma > 0$ corresponds to shielding and $\sigma < 0$ to antishielding; (b) those C atoms, the $\sigma(C)$ -orbital contributions to which are listed, are encircled.

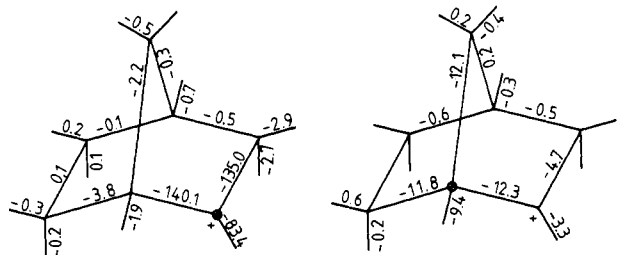


Figure 11. $\sigma(C)$ orbital contributions in the classical 2-norbornyl cation (see a and b in the caption of figure 10).

basis sets used, and therefore it is not shown in the figures. Almost all remaining terms are deshielding and decrease with increasing distances from C atom under consideration. Next neighbor contributions range from -1.7 to -5.2 ppm for C-C bonds and from +0.4 to -1.9 ppm for C-H bonds. Magnitudes of the more distant bonds cannot be classified according to this scheme. Their influence varies between +0.3 ppm (shielding) and -0.2 ppm (deshielding).

In case of the classical 2-norbornyl cation **31** one observes three strongly deshielding contributions to $\sigma(C_2)$ (Figure 11), namely -83 ppm (CH) and -140 vic. -135 ppm (CC bonds), bonds between 2nd and 3rd next neighbors are deshielding with -0.5 to -2.9 ppm, and the effect of the remaining ones is almost as in the neutral hydrocarbon.

The situation is somewhat different for C₂ of the nonclassical cation **34** (Figure 12). First of all, the deshielding next-neighbor effects are reduced by a factor of 3 to 4 as compared to the classical counterpart, and secondly, contributions originating from bonds of the formally pentacoordinated carbon C₆ to 2nd next neighbors are shielding by about 1 ppm each.

Next neighbor orbital contributions to C₆ are deshielding when "normal" two-electron two-center bonds are involved; the two-

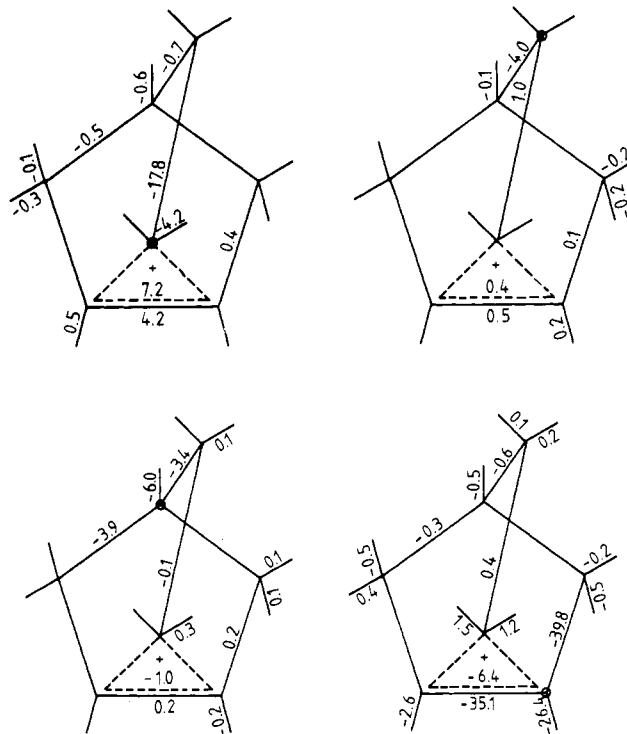


Figure 12. $\sigma(C)$ orbital contributions in the nonclassical 2-norbornyl cation (see a and b in the caption of Figure 10).

electron three-center C₁-C₆-C₂ bond, however, shields C₆ by 7.2 ppm. The C₁-C₂ single bond, too, is shielding by 4.2 ppm.

7. Representative CPU Times. In order to facilitate comparisons of the computational effort between different methods for the calculation of second-order properties, we give CPU times for some representative calculations in Table IX. Our calculations have been performed on a Cyber 205 computer with a rather small core memory of 0.5 MW. This prevents effective vectorization of one of the most time-consuming parts of the program, namely the construction of the first-order Fock operators (three for each occupied MO). The calculation of the two-electron integrals has been vectorized to a large extent⁴⁶ and will be described elsewhere.⁴⁷ As we used localized MOs, we cannot take into account molecular symmetry in the IGLO part as it might be desirable. Anyway, even in the "worst" case, i.e., for molecules with high symmetry, the IGLO program takes less than twice the CPU time needed for an SCF calculation.

IV. Conclusions

Taking into account our experience with smaller cations and larger basis sets, we can summarize the results of our calculations as follows.

IGLO calculations on carbocations reproduce experimental data in cases where the cation geometries are known with sufficient accuracy. The agreement is not perfect because of the following two reasons: (1) The calculations describe single molecules at their equilibrium geometries, whereas spectra are recorded under stable ion conditions. To simulate the influence of counter ions and solvent molecules by ab initio calculations is almost as impossible as to avoid these effects in the experiments. (2) For most

of the experimentally accessible molecules, the basis sets that we can afford are rather small.

Electron correlation can influence second-order properties in two ways, either directly in cases of near-degeneracy or indirectly via the theoretical determination of molecular geometries. For the cations investigated in this study, direct correlation effects have been found to play only a minor role. The situation is quite different for molecules containing multiple bonds between second-row atoms like phosphorus or silicon.⁵⁰

The IGLO method has been shown to be a powerful tool for the determination of molecular structures. Providing the complete information about the molecular χ tensor and the shielding tensors of all atoms in a molecule at the expense of at most two additional SCF calculations, an IGLO calculation constitutes a sensitive test for the quality of a theoretically determined structure, if there are no experimental geometries available.

This has been demonstrated for the $C_7H_{11}^+$ and $C_4H_7^+$ cations. Even on the double- ζ SCF level it is possible to decide that nonclassical structure of the 2-norbornyl cation is the correct one.

For $C_4H_7^+$ the disagreement between our calculations for optimized SCF geometries and the experimental data indicates that a reliable equilibrium geometry can be supplied only by using methods that include electron correlation together with a large basis set. Hence indirect correlation effects are important for the

determination of $\sigma(C)$, at least in this case.

This does not automatically imply, however, that direct correlation effects play an important role for the calculation of magnetic properties like χ and σ in general.

Note Added in Proof. Very recently an MP2/6-31G* ab initio investigation of the potential hypersurface of $C_4H_7^+$ revealed that the bicyclobutonium ion is more stable than the cyclopropylcarbinyl cation (0.7 kcal/mol at the MP4SDQ/6-31G**//MP2/6-31G* level).⁵¹ This supports our conclusion drawn from the IGLO calculations.

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Registry No. 1, 14531-53-4; 2, 15135-49-6; 6, 14604-48-9; 8, 14936-94-8; 10, 24669-33-8; 12, 26810-74-2; 13, 1724-44-3; 14, 17171-49-2; 15, 17542-17-5; 16, 58175-90-9; 17, 22537-04-8; 18, 12316-90-4; 19, 19252-53-0; 20, 14804-25-2; 21, 2154-76-9; 22, 27861-45-6; 24, 25681-56-5; 25, 53032-28-3; 28, 25076-72-6; 29, 43531-41-5; 35, 17104-55-1; 36, 25940-78-7; cyclopropylum, 1724-43-2; 1-methylcyclobutonium, 19394-14-0.

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The Effects of Various Substituents upon the Properties of the Bond between the Bridgehead Carbons in Bicyclobutane

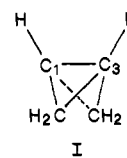
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Abstract: We have used a computational approach to investigate the properties of bicyclobutane and various of its derivatives in which one or more of the groups NH_2 , NCO , NO , and NO_2 are substituted on its bridgehead positions. Our primary focus has been upon the bond between the bridgehead carbons. An ab initio self-consistent-field molecular orbital procedure (GAUSSIAN 82) was used to compute optimized structures for these molecules and then to calculate three key properties: molecular electrostatic potentials, bond deviation indices, and bond orders. We find the two three-membered rings in bicyclobutane to show some definite similarities to cyclopropane, but both the reactivity of the molecule toward electrophiles and also its degree of strain are greater than would be expected in terms of an analogy to cyclopropane. All of the substituents except NH_2 are found to diminish the reactivity of the carbon framework toward electrophiles. The bond between the bridgehead carbons is weakened by the presence of either NO or NO_2 as a substituent at these positions. The greatest degree of weakening of this bond occurs for the combination of NH_2 and NO_2 as substituents; the effect is less for NCO and NO_2 . These observations can be interpreted in terms of electronic rearrangements and resonance arguments. Thus it appears that isocyanate precursors are to be preferred to amines, in this respect, in the stepwise polynitration of strained C-C bonds.

Bicyclo[1.1.0]butane (I) is a strained cyclic hydrocarbon, containing two types of C-C bonds. Our present focus is upon the one between the two bridgehead positions, C_1 and C_3 , as an example of a strained linkage between two tertiary carbons. We wish to determine how the stability and other reactive properties of this bond are affected by the presence of various substituents on the bridgehead carbons. The substituting groups that will be considered, alone or in combination, are NH_2 , NO , NCO , and NO_2 . Derivatives involving the first three of these are possible precursors in nitration processes; thus the results of this work will

be of direct relevance to synthetic approaches to the polynitration of strained hydrocarbons.



A question of particular interest is whether the combination of NH_2 and NO_2 will weaken the C_1 - C_3 bond. Equation 1 shows a mechanism by which, in the extreme case, rupture of this bond would occur.

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