New boron isotopic absorptions in radiolysis and photoionization experiments just above the parent ν_3 modes are attributed to the BCl_2 and BBr_2 free radicals owing to the resolved chlorine isotopic splittings and the decrease on sample warming. Calculations based on boron isotopic ν_3 values predict $125 \pm 5°$ valence angles for BCl_2 and BBr_2. Photoionization studies revealed boron isotopic doublets above the parent absorption which are assigned to ν_3 of BCl_3^+ and BBr_3^+; the BCl_3^+ absorptions exhibited multiplet structure appropriate for a doubly degenerate vibration of three equivalent chlorine atoms. These bands are photosensitive as

expected from appearance potential data. Absorption bands at 320 and 357 nm in the ultraviolet are assigned to BCl_3^+ and BBr_3^+, in excellent agreement with the appropriate electronic band spacing in photoelectron spectra. The substantial increase in ν_3 of BCl_3 and BBr_3 on ionization, also characteristic of carbon–halogen systems, is attributed to increased π bonding in the cations.

Ab Initio Calculations and Carbon-13 NMR Study on the Methoxymethyl Cation[1]

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Contribution from Exxon Research and Engineering Company, Corporate Research–Science Laboratories, Linden, New Jersey 07036. Received August 8, 1979

Abstract: The relative energies of several conformations of the title ion (**1**) have been computed by single configuration ab initio calculations with geometry optimization at both STO-3G and 4-31G level. The planar form **3** is the stable conformation, followed by the linear form **4**, which should represent the top of the barrier for the geometrical isomerization of **3**; the perpendicular form **5** is less stable. The high relative energy of the 1,3 hydrogen-bridged structure **7** agrees with experimental estimates for the barrier for 1,3-hydride shift in **1** in the gas phase. The perpendicular conformation **6**, with a C1–O–C3 angle equal to that in **7** is more stable than the latter but still lies far higher in energy than **5**, in which the C1–O–C3 angle was kept the same as in **3**. Both the energy sequencing and the variation of C1–O bond length in the series **3, 4, 5** parallel those calculated by previous authors for protonated formaldehyde (**2**). On the other hand, the response of the O–C3 bond length to the conformational changes in the series **3, 5, 6** parallels that calculated previously for the corresponding conformations of the 1-propyl cation (**8**), while the energy variations in the two series are opposite. From the calculated stabilization energies it is concluded that ion **1** is more stable than the 2-propyl cation, and even the perpendicular form **5** is more stable than the 1-propyl cation. The charge distribution calculated for all conformers suggests that oxygen in formaldehyde acquires an extra negative charge upon coordinating a methyl cation. Most of the positive charge in **1** is distributed among the hydrogen atoms; this is similar to what the calculations predict for ions **2** and **8**. Comparison of calculations on **1** and **2** suggests that replacement of H by CH_3 enhances the π donation from oxygen to carbon but has little effect upon the σ donation from carbon to oxygen. The relative energies, the bond lengths, and the orbital populations all indicate a significant hyperconjugation in **5**. Comparison with **8** suggests that O–C hyperconjugation is more effective than C–C hyperconjugation in stabilization of carbocations. Strong hyperconjugation alone can produce significant alterations of bond lengths. Formation of **1** from methoxyacetyl chloride (**19**) does not involve the corresponding acyl cation (**20**) as an intermediate stable at low temperature as reported in the literature. Instead, ^{13}C NMR supports the intermediacy of a halogen-coordinated complex of **19** with SbF_5 (**21**). The ^{13}C NMR spectrum of **1** has been recorded and is discussed in terms of the calculated charge distribution.

The methoxymethyl cation (**1**) is one of the few primary carbocations stable enough to be studied in super acid solutions,[2] as well as in the gas phase.[3] Yet, theoretical studies of ion **1** are scarce.[4] We have calculated the geometries and energies of various conformations of this cation, comparing the results with the existing experimental data. A comparison with calculations

on protonated formaldehyde (**2**)[5] was also made.

$$CH_2 {=\!=\!=} O\text{-}CH_3 \qquad CH_2 {=\!=\!=} OH$$
$$\quad\;\; \mathbf{1} \qquad\qquad\qquad\;\; \mathbf{2}$$

Calculations were carried out by using the ab initio SCF-MO Gaussian 70 programs.[6] The structures were first optimized at the STO-3G level.[7] The STO-3G geometries were then used as the starting point for a partial geometry optimization (one cycle) at the split-valence basis 4-31G level.[8] One optimization cycle

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(4) (a) Two semiempirical treatments have dealt with the charge distribution in a nonoptimized planar geometry of **1**: Nakano, S.; Iwasaki, K.; Fukutani, H. *J. Polym. Sci., A-1* **1963**, 3277. Eyzner, Yu. E.; Yerusalimskii, B. L. *Vysokomol. Soedin.* **1970**, *A12*, 1614. (b) See also: John, I. G.; Radom, L. *J. Mol. Struct.* **1977**, *36*, 133.

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(7) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

Carbon-13 NMR Study on the Methoxymethyl Cation

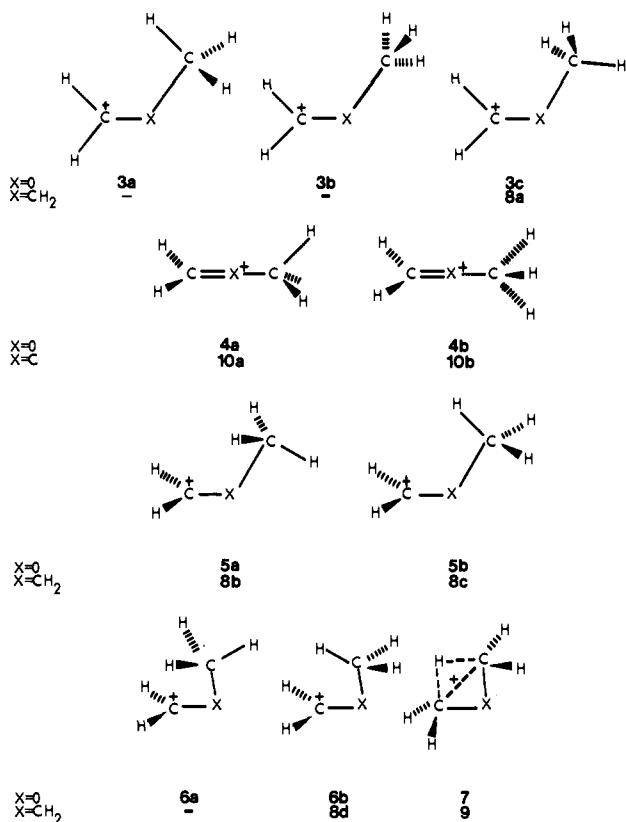*J. Am. Chem. Soc., Vol. 102, No. 15, 1980* 4907

at the 4-31G level led to optimum geometries noticeably different from those predicted by STO-3G calculations, while decreasing the energies by only 2–3 kcal/mol.

Five main conformations (3–7) of ion 1 have been studied. The

first three (3, 4, 5) are similar to the geometries investigated previously for 2;[5] they will be called the planar, linear, and perpendicular conformation, respectively. The hydrogen-bridged structure (7) should occur in the 1,3-hydride shift[9] observed in the gas phase,[3h] while 6 is a perpendicular conformation with a C1–O–C3 angle equal to that in 7. (To facilitate comparison with the 1-propyl cation, we numbered the methyl carbon in 1 C3 throughout the paper.)

In order to test the effect of rotation around the O–C3 bond upon the energy, we tested several rotamers of 3 (3a, 3b, 3c), 4 (4a, 4b), 5 (5a, 5b), and 6 (6a, 6b). Formulas 3c, 5a, and 5b (or 6b) are reminiscent of the conformations of 1-propyl cation (8) calculated by Pople et al.[11] while 7 can be considered an edge-protonated oxirane and therefore analogous to the edge-protonated cyclopropane (9) investigated by the same authors.[11]

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(8) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971,** *54,* 724. (b) Use of STO-3G geometries for calculation of the energy at the 4-31G level can result in serious errors for species containing oxygen or fluorine: L. C. Allen, personal communication, see also ref 5j.

(9) We briefly looked at a model for the 1,3-hydride shift directly from 3 ("lateral" shift). In preliminary calculations at the STO-3G level its energy
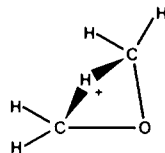
appeared so much higher than that of 7 that no more effort was spent on it.

(10) This represents an application of the "tool of increasing electron demand": (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970,** *92,* 2549. (b) Brown, H. C. "The Nonclassical Ion Problem" (with comments by P. v. R. Schleyer); Plenum Press: New York, 1977; pp 163–186 and references therein.

(11) (a) Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972,** *94,* 311. (b) Hariharan, P. C.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1974,** *96,* 599. (c) Radom, L.; Poppinger, D.; Haddon, R. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. 5, p 2303 and esp p 2341.

Table I. Relative Energies of CH_2^+ XY Ions (kcal/mol)

formula	X = O, Y = CH₃ (1)		X = O, Y = H (2)	X = CH₂, Y = CH₃ (8 and 9)[a]		
	STO-3G	4-31G		STO-3G	4-31G[b]	6-31G*[b]
7	61.92	73.08		7.4[c]	10.2[c]	5.0[c]
6b	54.90	65.62[b]		...	...	...
6a	55.61	62.77[b]		0.8	0	0
5b	34.70	22.08	22,[e] 31.4,[f]	d	d	d
5a	32.80	20.78	23[g]	0	0.5	2.9
4b	25.22	12.01	23,[e] 17.2,[f]	...	...	...
4a	25.21	12.07	13.98[g]	...	..	...
3c	0.71	0.78		1.3	2.5	4.7
3b	0.36	0.36				
3a	0	0	0			

[a] From ref 11. [b] STO-3G geometry. [c] Edge-protonated cyclopropane (9). [d] Closes to the analogue of 6a.[11] [e] CNDO/2 calculations.[5c] [f] Without geometry optimization.[5a] [g] With geometry optimization (4-31G level).[5f]

The study reported by Lossing[3m] of substituent effects on the heats of formation of carbocations and their oxa analogues prompted our examination of the similarities and differences between ions 1 and 8. It had been expected that in the presence of a major stabilization by oxygen, a methyl group should have less of a stabilizing effect in 2 than in the ethyl cation.[10] Actually, the stabilizing effects of α- and β-methyl groups are the same in the two systems.[3m] Therefore, Lossing concluded that there should be little or no contribution from the methyleneoxonium structures in 2 or 1.[3m]

Calculated Relative Energies

The relative energies calculated for the indicated conformations of 1 are given in Table I, together with the literature values for 2 and 8.[5,11] The planar conformation (3) is the energy minimum, as expected. Attempts to optimize the C1–O–C3 bond angle convert the perpendicular forms 5 and 6 to the linear conformation 4. Therefore, the energies of structures 5 were calculated with the use of the C1–O–C3 bond angle found optimum for 3. The bridged structure 7 has the highest energy. Simultaneous variation of geometrical parameters at the STO-3G level indicated that energy decrease during conversion of 7–6 is monotonic.[12] The ordering of structures for 1 is, with one exception, the same at the STO-3G and 4-31G level. Because of the very large difference in energy between 5 and 6, we did not perform a geometry optimization for the latter at the 4-31G level (cf. Table I).

The relative energy calculated for 7 is within the range estimated experimentally for the activation energy of the 1,3-hydride shift in 1 (58–83 kcal/mol).[3h] This high value was interpreted in terms of "forbiddenness" of the 1,3-hydride shift.[3h] Our calculations suggest a more complex sequence for this process,[9] in which it is the rotation around the C1–O bond (3 → 5) and chiefly the decrease in the C1–O–C3 bond angle to a geometry prone to the migration (5 → 6) which require a large amount of energy in 1. The actual hydride shift (6 → 7 → 6′) involves an energy barrier[12] similar to that calculated[11] for the same transformation in 8 (8d → 9 → 8d′),[13a] in which the migration takes place directly from a stable conformation (8d).[13b]

Among the three rotamers of the planar form 3 investigated, the most stable, 3a, has a syn coplanar arrangement of atoms H–C1–O–C3–H; the analogous form of the 1-propyl cation has

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(12) While evaluating the energy difference between these structures, one should keep in mind the warning that "the split-level basis generally gives excessively lower energy for more symmetrical structures": Pople, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1976,** *19,* 89.

(13) (a) NMR evidence for fast tertiary–tertiary 1,3-hydride shifts in carbocations has been published: Brouwer D. M.; Van Doorn, J. A. *Recl. Trav. Chim. Pays-Bas* **1969,** *88,* 573. (b) The activation energy for such shifts was reported to increase from 2,4-dimethyl-2-pentyl cation (E_a = 8.5 kcal/mol: Saunders, M.; Stofko, J. J. *J. Am. Chem. Soc.* **1973,** *95,* 252) to 1,3-dimethylcyclohexyl and 1,3-dimethylcyclopentyl cation (E_a = 10.7 and 11.4 kcal/mol, respectively: Hewett, A. P. W. Ph.D. Thesis, Yale University, 1975.)

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not been computed in the study on **8**.[11] The same arrangement in the 2-propyl cation (syn coplanar H–C1–C2–C3–H, **11a**) has

11a (X=CH⁺)
12a (X=O)

11b (X=CH⁺)
12b (X=O)
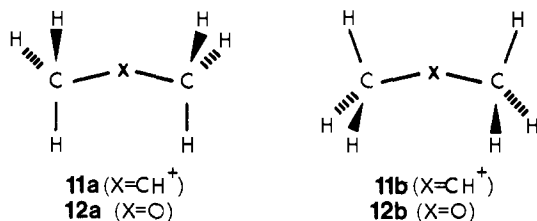
been predicted to be preferred over rotamer **11b**, while for dimethyl ether form **12b** is more stable than **12a**.[14] A π-type interaction between the methyl groups was postulated, stabilizing **12b**, ("aromatic") but destabilizing **11b** ("antiaromatic").[14] A similar argument for **3** would involve an interaction between the π-like orbital of CH_3 and the empty p orbital of C1.

The two rotamers of the linear form, **4a** and **4b**, are about equal in energy. Similarly, no barrier for the rotation of the methyl group has been predicted for the 2-propenyl cation (**10**).[15]

The calculated (4-31G) energy difference between **3** and **4** suggests that **1** should undergo a geometric isomerization (**3** ⇌ **4**) easily. This prediction has been experimentally checked. The energy barrier measured for this process ($\Delta H^{\ddagger} = 11.9 \pm 1$ kcal mol⁻¹, $\Delta S^{\ddagger} = -4 \pm 3$ cal mol⁻¹ K⁻¹) is in very good agreement with the calculations (Table I).[16]

Of the perpendicular forms, **5a** and **5b**, the former (1,3 eclipsed) appears more stable at both the STO-3G and 4-31G level. At the STO-3G level the analogous form of the 1-propyl cation, **8b**, is also more stable than the other rotamer (**8c**).[11] The latter is not an equilibrium geometry, however, but closes its C1–C2–C3 angle to **8d** which at the 4-31G level becomes more stable than **8b**.[11a,b] **8d** can be considered a distorted corner-protonated cyclopropane.[11] At the 6-31G* level[11c] **8d** rearranges to the symmetrical, corner-protonated cyclopropane (**13**).[12]

The perpendicular forms with small C1–O–C3 angle (**6a**, **6b**) could be considered corner-protonated oxiranes, akin to **13**. The

13a   **13b**
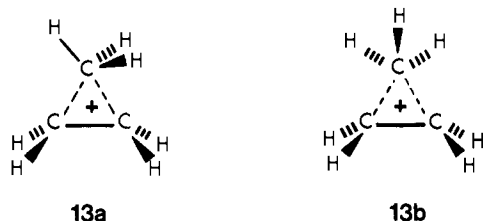
latter was predicted by calculations to be either very close (4-31G) in energy to or (6-31G*) more stable than **8d**.[11] By contrast, **6a** and **6b** have much higher energies than the forms with a larger C1–O–C3 angle. Also, the rotation of the methyl group (**6a** → **6b**) is computed to change the energy of the system by almost 3 kcal/mol (4-31G) while the same process in **13** (**13a** → **13b**) was predicted to require little or no energy.[11]

From the comparison above it appears that the energy variations produced by conformational changes are generally different, and usually opposite for **1** and **8**.

Methyl Stabilization Energies

In order to compare cation **1** with other related species, the stabilization relative to the methyl cation has been calculated. This procedure[17] was reported to cancel systematic errors and has been employed in other theoretical studies on carbocations.[17,18] The

Table II. Stabilization Energies for R⁺ Relative to $CH_3^{+\ a}$

| R | ΔE, kcal/mol | | |
	calcd[b]	exptl[c]	diff
HCH₂	0	0	
FCH₂	−5[d]	4[d]	9
CH₃CH₂	27,[d] 29.9[e]	31–42,[d] 40[e]	10.1[e]
CH₃CH₂CH₂	35.0[e]	46[e]	11
CH₃OCH₂ (5a)	42.2[f,g]	...	...
HOCH₂	45,[d] 46.1[g]	32–57,[d] 63[h]	16.9[g,h]
CH₃OCH₂ (4b)	50.9[f,g]	...	...
(CH₃)₂CH	52.4[e]	62[e]	9.6
CH₃OCH₂ (3a)	62.9[f,g]	76[h,i]	13.1
H₂NCH₂	89.0[d]	96.5,[d] 97.1[h]	8.1[d,h]

[a] Energy changes for the reaction: $R^+ + CH_4 \rightarrow RH + CH_3^+$. *[b]* All values obtained from extended basis set calculations. *[c]* Obtained from the measured heats of formation of the four species involved, at 298 K, without vibrational or temperature corrections. *[d]* Reference 18. *[e]* Reference 11a. *[f]* This work. *[g]* Total energy for CH_3OCH_3 from 17b, for CH_3OH from ref 17c, for CH_2OH^+ from ref 5f, and for CH_4 and CH_3^+ from: Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1971, 93, 808. *[h]* ΔH_f for CH_3^+ (261 kcal/mol) from ref 20, for CH_2OH^+ (169 kcal/mol) from ref 3m, for $CH_2NH_2^+$ (178 kcal/mol) from ref 3j, for CH_4 (−15.97), CH_3OH (−45.355), and CH_3NH_2 (−1.91 kcal/mol) quoted in ref 17b, and for CH_3OCH_3 (−44.0 kcal/mol) quoted in ref 3h. *[i]* ΔH_f reported for **1** varies from 41[3c] to 170 kcal/mol.[3b] The value listed was calculated by using $\Delta H_f = 157$ kcal/mol[3m] which being the most recent and obtained reproducibly by several procedures should be the most reliable; if we use ΔH_f CH_3OCH_3 quoted in ref 17b (−39.745 kcal/mol) the figure becomes 80.

results are given in Table II, together with experimental values for the same quantity.

The calculated values are consistently lower. This deviation (8–17 kcal/mol) is disturbing when contrasted with the agreement achieved for neutral molecules (deviation ±3.5 kcal/mol).[17] The reason could be a systematic error, either in the calculations on carbocations[19] or in an experimental value which affects the results in all cases such as $\Delta H_f CH_3^{+}$.[20] Nevertheless, the calculated and experimental sequence of stabilities is the same. It can be seen that **1** is more stable than the 2-propyl cation and that even perpendicular form **5a** is predicted to be more stable than the 1-propyl cation. An important source for this stabilization is the overlap of the occupied hybrid orbital on oxygen (n_σ) with the vacant p orbital at C1.[51] However, this orbital interaction exists also for protonated formaldehyde (**2**) in the perpendicular conformation, which is predicted to be less stable than the ethyl cation.[5f] As the stabilization energies (below) show, the re-

27–29.9 kcal/mol   23.1 kcal/mol

35.0 kcal/mol   42.2 kcal/mol

Δ: 5.1 – 8 kcal/mol   19.1 kcal/mol

(14) Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 6900.

(15) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531.

(16) Fărcaşiu, D.; O'Donnell, J. J.; Wiberg, K. B.; Matturro, M. *J. Chem. Soc., Chem. Commun.* **1979**, 1124.

(17) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A.; Radom, L. *Chem. Phys. Lett.* **1970**, *5*, 13. (b) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (c) Radom, L.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *93*, 289.

(18) Kollman, P. A.; Trager, W. F.; Rothenberg, S.; Williams, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 458.

(19) Use of the single determinantal approach is a possible source of deviation. It must be noted that a limited configuration interaction study on the conformation of CH_2SH^+ related to **5** undertaken in ref 5f failed to change the energy of that species from the value computed by the single determinantal approach.

(20) Lossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955.

placement of hydrogen in this conformtion of **2** by methyl has a dramatic effect, much higher than for the pair ethyl–propyl cations. On the assumption that hyperconjugation is the chief mechanism of stabilization of a carbocation by β bonds coplanar with the empty orbital, this indicates that O–C hyperconjugation is more effective than C–C hyperconjugation. The latter had in turn been predicted to be more effective than C–H hyperconjugation.[21]

Equilibrium Geometries

Some geometrical parameters obtained for **3**, **4**, and **5** at the 4-31G level are compared below with the values calculated for protonated formaldehyde (**2**)[5f] in the same conformations.

3

4

5

12
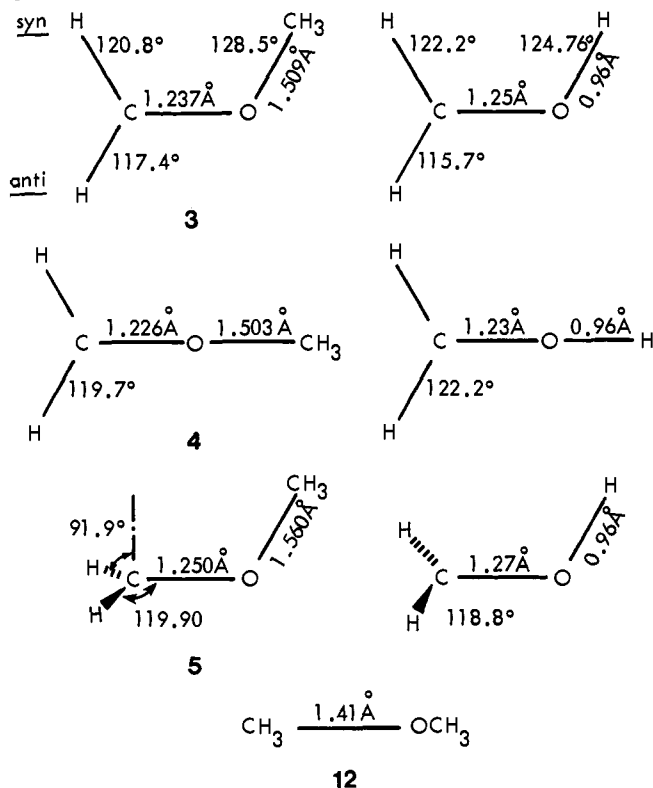
It appears that the C=O bond in formaldehyde (length 1.21 Å)[5f] is weakened less upon the addition of a CH_3^+ than upon the addition of a proton. Also, while the O–H bond length is unaffected by conformational changes in **2**, the O–CH_3 bond length in **1** is quite sensitive to such changes.

Based on Lossing's[3m] representation of **1** and **2** discussed above, it is also interesting to compare the bond length variations produced by conformational changes in **1** with those predicted by similar calculations on the 1-propyl cation (**8**).[11] For the planar form **3**, the calculations indicate a strong contribution from the methyleneoxonium form (methylated formaldehyde): the C1–O bond contracts by 12.3% on hydride abstraction from dimethyl ether (**12**) to form **3**, not far from the 14.2% shorter bond found in formaldehyde compared to that of **12**.[22] The O–C3 bond length increases by 7.0% on going from **12** to **3**. By contrast, C1–C2 bond contracts by only 3.2% and C2–C3 does not change on going from propane to **8a**. Thus, our results contradict the conclusions[3m] based on the application of the "tool of increasing electron demand"[10] and point out the limitations of that approach.

On the other hand, the perpendicular form **5** could be indeed considered an oxa carbocation rather than a formaldehyde de-

rivative. Nonetheless, the calculated C1–O bond length is almost as short in **5** as in **3** (11.3% shorter than a single C–O bond in **12**); this is a result of electron donation from the n_σ orbital on oxygen and from the O–CH_3 bond (O–C hyperconjugation), as discussed above in connection with the relative stabilization energies. In line with this interpretation the O–C3 bond in **5** is considerably lengthened: 10.7% over the C–O bond lengths in **12**. Again by contrast, calculations predict that the C2–C3 bond length increases by only 3.3% in **8b** and 5.9% in **8d**, over the C–C bond length in propane. For **8d**, this bond lengthening and the angle distortion from **8c** were assigned to incipient bridging.[11] This is not the case for **5** with its large C1–O–C3 angle (128.5°) and the opposite tendency of angle distortion, going to linear form **4**. Thus, the bond length criterion corroborates the stabilization energy prediction that O–C hyperconjugation should be more effective than C–C hyperconjugation.

Dramatic lengthening of β bonds in a carbocation has been predicted for the cyclopropylcarbinyl system in the bisected form **14**.[23] In that case, the computed bond length change is still only
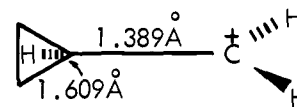
14

7.1% over the normal carbon–carbon bond in cyclopropane (1.502 Å). We find that bond length changes at least as important are predicted by calculations for a species like **5**, with very strong hyperconjugation.

The calculated geometry of the methyl group in **3–5** exhibits the asymmetry evidenced in CH_3X compounds.[24] The methyl C–H bond lengths in **3** decrease with the increase of the dihedral angle H–C3–O–C1; the same feature appears in **5** but only for bonds in the same rotamer.[25]

For the two rotamers of **6**, the C1–C3 distance (1.875 Å for **6a**, 1.830 Å for **6b**, at the STO-3G level) is similar to the H_2-C···CH_3 distance in **13** (1.803 Å).[11] This supports the representation of corner-protonated oxirane for **6**. (Note, however, that the C1–O–C3 angle was fixed at 77.9°, since no perpendicular conformation of **1** is a local energy minimum.) The geometry and energy of **13** showed little sensitivity to the rotation of the methyl group (**13a** ⇌ **13b**).[11] Rotation of the methyl group from **6b** to **6a**, around an axis perpendicular to the C1–O bonds, leads to an energy increase of 5.14 kcal/mol at the STO-3G level; rotation around the O–C3 bond in **6b** leads to a geometry for **6a** which is 12.6 kcal/mol less stable than **6b**. Geometry optimization for **6a** resulted in significant changes in bond lengths from the values in **6b**,[25a] while the energy difference between **6a** and **6b** decreased to 0.71 kcal/mol (STO-3G, Table I). The relative stabilities of **6a** and **6b** were reversed at the 4-13G level (Table I); no geometry optimization of either was undertaken at this level, but the STO-3G optimum geometries were used.

Finally, the geometry of **7** is similar in all respects to that of edge-protonated cyclopropane (**9**).[11]

Calculated Charge Distribution

The charge distribution and the gross orbital population of the formally unoccupied p orbital at C1 for the various conformations of **1** are compared in Table III with the values calculated for a number of model structures.

The calculations suggest that in the most stable conformation there is as much charge at C1 in **3** as in the protonated formaldehyde (**2**), while the total charge of the methylene group is lower in **3** by 0.07 units. On the other hand, the orbital population

(21) (a) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935. (b) See also: Radom, L. *Aust. J. Chem.* **1974**, *27*, 231.

(22) (a) The C–O bond length (1.41 Å) in dimethyl ether (**12**) was taken from: Blukis, U.; Kasai, P. H.; Meyers, R. J. *J. Chem. Phys.* **1963**, *38*, 2753. (b) Use of the value of 1.43 Å given in: "Handbook of Chemistry and Physics", 57th ed. Weast, R. C., Ed. CRC Press: Cleveland, OH, 1976; p F218 does not change the conclusions. (c) The C–O bond length for CH_2O (1.21 Å) is quoted in ref 5f.

(23) (a) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5917; *Ibid.* **1974**, *96*, 302. (b) Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369. (c) Reference 10b, pp 69–78. (d) *Ibid.* pp 79–82.

(24) Flood, E.; Pulay, P.; Boggs, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 5570.

(25) The supplementary material contains (a) complete lists of calculated geometric parameters and (b) tables with C3–H bond lengths and charge densities at the hydrogen atoms of the CH_3 groups.

Table III. Net Atomic Charges and Gross Orbital Populations[a]

formula	atomic charge, q						orbital pop $2p_x$ (C1)
	C1	syn H[b]	anti H[b]	O	C3	CH$_3$	
Me$_2$O (13)[c]	−0.11	...	...	−0.69	−0.11	+0.35	
CH$_2$=O[d]	+0.17	+0.16	+0.16	−0.49	...	...	0.73
CH$_2$OH$^+$ (2)[d]	+0.31	+0.33	+0.35	−0.53	...	(+0.54[e])	0.37
3[f]	+0.31	+0.29	+0.32	−0.55	−0.18[g]	+0.63	0.45[h]
4[f]	+0.38	+0.29	+0.29	−0.69	−0.08	+0.74	0.46
5[f]	+0.37	+0.29	+0.29	−0.63	−0.15	+0.67	0.36
6a[i]	+0.23	+0.33	+0.33	−0.42	−0.46	+0.44	0.36
6b[i]	+0.14	+0.34	+0.34	−0.44	−0.35	+0.61[j]	0.39
7	−0.10	+0.35	+0.35	−0.47	−0.10	k	0.62
8a[l]	+0.05	+0.33	+0.32	(+0.10[m])	−0.46	+0.20	0.13
8b[l]	+0.04	+0.32	+0.32	(+0.09[m])	−0.50	+0.23	0.18
8d[l]	−0.11	+0.32	+0.32	(+0.20[m])	−0.58	+0.26	0.38

[a] Calculated at the 4-31G level. The C1–O bond is along the z axis. The hydrogens bonded to C1 are symmetrically placed about the XZ plane. [b] Hydrogens bonded to C1. [c] All-staggered conformation (see ref 14 and 17c); geometrical parameters from ref 21a. [d] From ref 5f. [e] Value for the hydrogen bonded to oxygen. [f] The values do not change upon rotation around the O–C3 bond, unless states otherwise. [g] −0.19 in 3c. [h] 0.44 in 3c. [i] STO-3G geometry. [j] H$_{bridging}$: +0.29. [k] H$_{bridging}$: +0.28. [l] See ref 26. [m] Value for the C2H$_2$ group; the charge at C2 is −0.50 in 8a, −0.48 in 8b, and −0.38 in 8d.

in the formally unoccupied orbital of C1 (2p$_x$) is higher by 0.08 units for 3 than for 2. It appears as if replacement of H by CH$_3$ enhances the π donation from oxygen to carbon but has little effect upon the σ donation from carbon to oxygen. Also, coordination of a methyl cation on formaldehyde *increases* the negative charge at oxygen; this is the same effect as for protonation,[5f] albeit a little more pronounced. (Semiempirical calculations gave the opposite result.[4a])

Most of the positive charge is distributed among the hydrogen atoms. The methylene hydrogens carry only slightly more charge than the methyl hydrogens, while in the methyl group of 3, 5, and 6, the hydrogen atoms pointing away from the C1–O bond are more positive than those pointing toward it.[25b] In 4 the charge at a methyl hydrogen increases slightly as the C–H bond becomes closer to coplanar with the symmetry axis of the nominally empty orbital at C1.[25b] The carbon atom of the methyl group is negative in all cases. In fact, loss of a hydride ion from a methyl group of dimethyl ether (13) is predicted to render the carbon atom of the other methyl group more negative. Whether all these results have physical reality we cannot say. In any event, the same type of charge distribution is calculated for the 1-propyl cation[11,26] (Table III).

The changes in the charge distribution during the inversion process of 1 (3 → 4) are as expected. Also expected, on the basis of the differences in energy and geometry, is the significant difference in charge distribution between 6a and 6b.

The calculated electron densities at the bridging hydrogen and in the 2p$_x$ orbital of C1 in 7 are consistent with the existence of a one-electron bond between these two atoms.
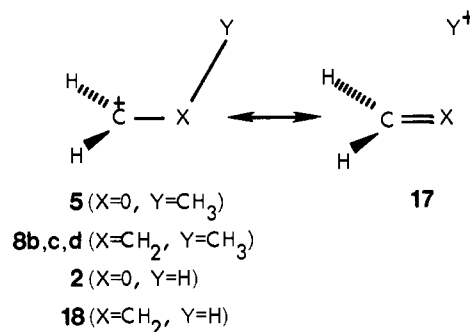
Finally, the data in Table III are consistent with a significant hyperconjugation in the perpendicular form 5.

Hyperconjugation in carbocations has been so far discussed for β C–H bonds[27] and β C–C bonds.[21,28] Such an electron donation from β bonds involving heteroatoms α to the carbocationic center has not, to our knowledge, been considered before. A major conclusion of the present calculations is that hyperconjugation involving single bonds to heteroatoms situated α to the positive charge can occur and that O–C hyperconjugation is more effective than C–C hyperconjugation. Admittedly, this prediction is not very easy to test experimentally, since the perpendicular form (5) of 1 is not a stable conformation or even the intermediate or transition state in the inversion of 1. We can, however, imagine

crowded or rigid, polycyclic structures, the cations of which would be constrained to the perpendicular conformation. Based on our calculations, one could predict that ionization of species like 15 is easier than that of the carbocyclic analogue.[16,29–32]

15 (X=O)
16 (X=CH$_2$)
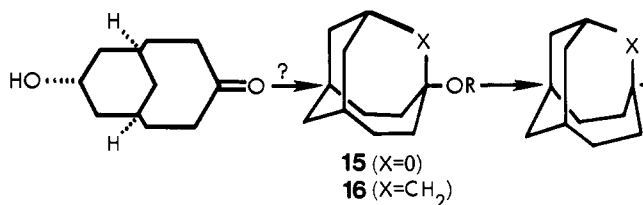
A rationalization of these results can be offered in terms of the VB representation of hyperconjugation.[33] The C=O double bond is stronger than the C=C double bond, while the C—O single bond is weaker than the C—C single bond.[34] Therefore, there should be a higher contribution from the limiting structure 17 for X = O, Y = CH$_3$ (5) than for X = CH$_2$, Y = CH$_3$ (8b–d).

5 (X=O, Y=CH$_3$)   17
8b,c,d (X=CH$_2$, Y=CH$_3$)
2 (X=O, Y=H)
18 (X=CH$_2$, Y=H)

(26) This was checked at both the STO-3G and 4-31G level by using the optimum STO-3G geometry given in ref 11.

(27) (a) Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41. (b) See the discussion in ref 21.

(28) (a) The C–X hyperconjugation in $^+$CH$_2$–CH$_2$–X (X = Li, BeH, BH$_2$, NH$_2$) has also been investigated by ab initio calculations: Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901. (b) See also the discussion in: Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *Ibid.* **1972**, *94*, 6221.

(29) The related 9-oxabicyclo[3.3.1]nonyl-1[30] and 2-oxa-1-adamantyl substrates[31] solvolyzed faster than expected on the basis of "inductive" effect of oxygen,[51] yet slower than the carbon analogues by factors of 3 and 7–370, respectively. Possible reasons are as follows: (a) In those systems[30,31] the carbocation is pyramidal and less prone to hyperconjugation with the O–C β bond. (b) Hyperconjugation is diminished in tertiary ions. (c) The calculations are approximate. Since 15 should form a more nearly planar carbocation with the O-Cβ bond still in the perpendicular conformation, a study on 16 could answer hypothesis a.

(30) Krabbenhoft, H. O.; Wiseman, J. R.; Quinn, C. B. *J. Am. Chem. Soc.* **1974**, *96*, 258.

(31) (a) Stetter, H.; Tacke, P.; Gärtner, J. *Chem. Ber.* **1964**, *97*, 3480. (b) Meyer, W. P.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1231.

(32) The increased reactivity of 15 would actually represent the combined effect of electron donation from the n$_\sigma$ orbital on oxygen and O–C hyperconjugation.

(33) Coulson, C. A. "Valence"; Oxford University Press: London, 1961; pp 360–5.

(34) The bond strengths were taken from or calculated by using the termochemical data of ref 22b, pp D276, D279, F230-3, F238, F239; for ΔH_f Me$_2$O, see Table II, footnote h.

Table IV. Carbon-13 Spectra of Carbocations and Related Species

compd	solvent	chem shift, ppm^a (J (C-H), Hz)		
		CH$_3$	CH$_2$	CO
CH$_3$OCH$_2$$^+$ (1)	FSO$_2$Cl	82.3 (159)	219.8 (b)	
HOCH$_2$$^+$ (2)	FSO$_3$H-SbF$_5$-SO$_2$		222.9^c (d)	
CH$_3$OCH$_3$ (12)	e	59.4^f (140^g)		
FCH$_2$COF^h	SO$_2$		75.4	159.7
FCH$_2$C(F)=O→SbF$_5$^{h}	SO$_2$		75.9	162.1
FCH$_2$C(=O)F→SbF$_5$^{h}	SO$_2$		77.1	180.3
FCH$_2$-CO$^+$ ^{h}	SO$_2$		75.4	145.1
MeOCH$_2$COCl^i	CDCl$_3$	59.6^j	77.6^j	171.9^j
MeOCH$_2$C(=O)Cl→SbF$_5$	FSO$_2$Cl	73.2^j	77.7^j	209.9^j

^{a} From external Me$_4$Si, at -60 °C. ^{b} Only the sum J(C-H$_{syn}$) + J(C-H$_{anti}$) = 407 Hz and the fact that J(C-H$_{syn}$) ≠ J(C-H$_{anti}$) could be ascertained from the fully decoupled spectrum at 25.2 MHz. (lit. values: J(C-H$_{syn}$) = 197 Hz; J(C-H$_{anti}$) = 212 Hz^{2b}). ^{c} From ref 2b, converted by using δ(CS$_2$) = 193.7; in ref 35a the conversion term was δ 194.6. ^{d} J(C-H$_{syn}$) = 198.4 Hz; J(C-H$_{anti}$) = 209.8 Hz.^{2b} ^{e} Solvent and temperature unknown. ^{f} Reference 35b. ^{g} Reference 36. ^{h} Reference 41. ^{i} At +35 °C. ^{j} Assignment checked by off-resonance decoupling.

By contrast, the O—H bond is much stronger than the C—H bond,^{34} and this offsets the difference in strength between C=O and C=C. Therefore, the limiting structure **18** might contribute less for protonated formaldehyde (**2**) than for the ethyl cation (**18**), in agreement with the energy comparisons discussed above.

We also consider important the large bond length variations calculated for **5** and associated there with the strong hyperconjugation existing in that conformer. A viewpoint was expressed that hyperconjugation alone cannot produce significant bond length alterations.^{23d} The conclusion reached from our calculations is different.

Carbon-13 NMR Spectra

In the previously published study of cation **1**, only the C-H coupling constants for C1 were reported. We recorded the ^{13}C NMR spectrum of **1** in FSO$_2$Cl, at -60 °C. The spectral parameters are recorded in Table IV, together with those of **1** and **12** taken from literature.^{2b,35a,b,36} It can be seen that the chemical shift of C1 is smaller for **1** than for **2**. The same pattern has been observed in a comparison of tertiary hydroxy and methoxy carbocations.^{35a} Of the factors that determine the ^{13}C chemical shift,^{35c} the π-electron density was said to be the most important in aromatic hydrocarbons and ions^{37} and also in acyclic systems, both anionic^{38} and cationic.^{39} Taken together with the 2p$_x$ orbital populations at C1 (Table III), the experimental values for **1** and **2** are in qualitative agreement with this representation, but the difference is much smaller than that calculated by various equations proposed.$^{37-39}$ As for the methyl carbon, it resonates 23 ppm downfield from the signal of the methyl carbon in dimethyl ether (**12**). It is unlikely that much of this shift could be due to the anisotropy of the partial double bond of **1**; for comparison, the methyl carbon signal moves downfield by only 3.1 ppm from propane to propene and 1 ppm *upfield* from isobutane to iso-

butene.^{35d} Since the net charge of the methyl carbon is more *negative* in **1** than in **12**, a more refined treatment is needed to rationalize the difference.^{35c,40}

Carbon-13 NMR spectra, also shown in Table IV, helped us clarify the mechanism of the reaction employed by us to prepare the ion **1**. This was generated from the methoxyacetyl chloride (**19**) and antimony pentafluoride in SO$_2$ClF solution. This reaction was reported to give the methoxyacetyl cation (**20**), which is stable in solution at low temperature but decarbonylates around -20 °C.^{2a} We found, however, that the ^{13}C NMR spectrum of the species stable at low temperature is not compatible with the acyl cation. By comparison with the fluoroacetyl fluoride, for which two types of acyl-SbF$_5$ complexes as well as an acyl cation have been reported,^{41} we assigned structure **21** to the species formed from **19** at low temperature.^{42} The acyl cation **20** then has to be only a transient intermediate, which is formed at -20 °C and decarbonylates immediately.

$$CH_3OCH_2COCl + SbF_5 \xrightarrow{-60\ °C} CH_3OCH_2C(=O)Cl \to SbF_5$$
$$\textbf{19} \qquad\qquad\qquad\qquad \textbf{21}$$

$$\textbf{21} \xrightarrow{-20\ °C} [CH_3OCH_2C\equiv O^+] \xrightarrow{-CO} CH_3OCH_2^+$$
$$\qquad\qquad\qquad \textbf{20} \qquad\qquad\qquad \textbf{1}$$

Experimental Section

Supplementary Material Available: Tables with the geometric parameters calculated for various conformations of **1** and the variation of C3-H bond lengths and of charge densities at the hydrogen atoms of the CH$_3$ groups (5 pages). Ordering information is given on any current masthead page.

(35) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 218-230; (b) *Ibid.*, p 144; (c) *Ibid.*, pp 102-127; (d) *Ibid.* pp 81 and 82.

(36) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists": Wiley-Interscience: New York, 1972, p 28.

(37) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

(38) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

(39) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 1884.

(40) (a) The reverse approach of assessing the variation of net charges at α-C upon ionization or protonation of amino acids from Δδ ^{13}C (Horsley, W.; Sternlicht, H. *J. Am. Chem. Soc.* **1968**, *90*, 3738. Horsley, W.; Sternlicht, H.; Cohen, J. *Ibid.* **1970**, *92*, 680) might not be free of errors. (b) Alternatively, the net atomic charges as derived from a Mulliken population analysis might be incorrect. (c) See the discussions on charge distribution and ^{13}C chemical shifts in saturated systems in: Morishima, I.; Yoshikawa, K.; Okada, K.; Yonezawa, T.; Goto, K. *J. Am. Chem. Soc.* **1973**, *95*, 165. Kean, G.; Gravel, D.; Fliszar, S. *Ibid.* **1976**, *98*, 4749 and references therein.

(41) Olah, G. A.; Germain, A.; Lin, H. C. *J. Am. Chem. Soc.* **1975**, *97*, 5481.

(42) It is also possible that a halogen exchange takes place in these conditions and the complex is actually MeOCH$_2$-CO-F→SbF$_5$.