spectrum, even in TFA, could not be obtained.

Anal. Calcd for $C_{22}H_{23}N_5O_4$: C, 62.69; H, 5.50; N, 16.62. Found: C, 62.38; H, 5.41; N, 16.33.

2-Acetyl-7,10-methano-5-deazapteroic Acid (17). Method A. Hydrogen chloride was bubbled for 2 min through a suspension of 0.1 g of *tert*-butyl 2-acetyl-7,10-methano-5-deazapteroate in 10 mL of nitromethane at room temperature. A yellow precipitate rapidly separated from the initially homogeneous solution. The mixture was stirred for 2 h and diluted with 10 mL of diethyl ether, and the suspended solid collected by filtration and dried at 100 °C (0.1 mm) to give 80 mg (92%) of **17** as a tan solid: mp >250 °C; NMR (Me_2SO-d_6) 2.2 (s, 3 H), 4.75 (s, 4 H), 6.7 and 7.85 (ABq, 4 H, J = 9 Hz), 8.4 (s, 1 H); LRMS 365 (M^+).

Method B. Hydrogen chloride gas was bubbled for 2 min through a suspension of 2.0 g of *tert*-butyl 4-deoxy-4-amino-7,10-methano-5-deazapteroate (**10**) in 50 mL of nitromethane cooled in an ice bath. The reaction mixture was stirred at room temperature for 3 h and diluted with 30 mL of diethyl ether, and the precipitated solid collected by filtration, dried at 70 °C (0.1 mm), and then suspended in 100 mL of 1 N sodium hydroxide solution. This suspension was heated under reflux for 6 h and acidified to pH 6 with acetic acid, and the resulting gelatinous precipitate collected by filtration to give 1.5 g (88%) of 7,10-methano-5-deazapteroic acid (**2**). A suspension of 0.2 g of **2** in 10 mL of acetic anhydride containing 3 drops of 4-(dimethylamino)pyridine was heated under reflux for 1 h, cooled, and diluted with 10 mL of ether, and the precipitated solid collected by filtration. This material was dissolved in 10 mL of 1 N sodium hydroxide solution. Neutralization with acetic acid resulted in the separation of a solid which was collected by filtration and dried to give 0.18 g (80%) of **17**, identical in every respect with the material prepared by Method A as described above.

Registry No. **1**, 94943-98-3; **2**, 94930-26-4; **3a**, 90030-20-9; **3b**, 94930-27-5; **4**, 94930-28-6; **5**, 5661-00-7; **6**, 65242-18-4; **7a**, 94930-29-7; **7b**, 94930-30-0; **8a**, 94930-31-1; **8b**, 94930-32-2; **9a**, 94930-33-3; **9b**, 94930-34-4; **10**, 94930-35-5; **14**, 94930-36-6; **15**, 94930-37-7; **16**, 94930-38-8; **17**, 94930-39-9; *N*-[4-(methoxycarbonyl)phenyl]-4-(methoxycarbonyl)-3-pyrrolidinone, 23935-80-0; *tert*-butyl 4-fluorobenzoate, 58656-98-7; 2,4-diamino-6-(1*H*)-pyrimidinone, 56-06-4; 6-[*p*-(*tert*-butyloxycarbonyl)phenyl]-6,7-dihydro-5*H*-pyrrolo[3,4-*d*]pyrimidine, 94930-40-2; 3-pyrrolidinol, 40499-83-0; malononitrile, 109-77-3; (chloromethylene)malononitrile, 10472-09-0; *N*,*N*-dimethylguanidine, 6145-42-2; dimethylformamide dimethyl acetal, 4637-24-5; 1,3,5-triazine, 290-87-9.

A Theoretical Analysis of the Interaction of the Phosphonate and Sulfonyl Groups with a Carbocationic Center

Daniel J. Pasto

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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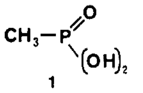
Solvolytic studies on derivatives of the α-hydroxy phosphonate system have indicated that the destabilizing effect of the phosphonate function on the carbocationic center is less than anticipated. An interaction between the p AO of the cationic center with a d AO on phosphorus was suggested to account for this effect. Theoretical calculations have been carried out on methanephosphonic acid and hydrogen methyl sulfone and the corresponding carbocations. Calculations have been carried out with and without a set of d AO's on phosphorus and sulfur in the STO-3G and 4-31G basis sets to assess the effect on charge delocalization and on the relative stability of the substituted cations. Very interestingly, with the parent systems no open cationic structures representing a local minimum were found in these studies; the open structures closed to form three-membered ring structures. The effect of methyl substitution at the cationic center has been briefly investigated.

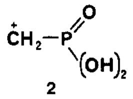
Considerable interest has been shown recently in the effect of electron-withdrawing groups on the stability of carbocationic centers. Experimental results have been reported describing the effects of the carbonyl,[1] cyano,[2] phosphonate,[3] and trifluoromethyl[4] groups on the stability of carbocations. The carbonyl and cyano groups destabilize the carbocationic center to a lesser degree than would have been expected on the basis of their σ values. This attenuated destabilization has been attributed to delocalization of the π-orbitals of the carbonyl and cyano groups to the carbocationic center. The results of theoretical studies have supported this view.[5] The phosphonate group similarly destabilizes the cationic center to a lesser degree than anticipated,[3] and an interaction between the p AO of the cationic center with a d AO on phosphorus was suggested to account for this attenuated destabilization. Calculations have now been carried out on model phosphonate and sulfonyl systems in order to gain a more thorough understanding of this type of interaction.

Results and Discussion

Methanephosphonic Acid and Related Cations. Complete geometry optimization calculations on methanephosphonic acid (1) have been carried out at the



1



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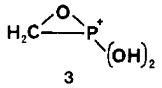

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[1] Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1983**, *105*, 7123; **1982**, *104*, 4151. Creary, X. *J. Am. Chem. Soc.* **1981**, *103*, 2463; *J. Org. Chem.* **1979**, *44*, 3938.

[2] Gassman, P. G.; Guggenheim, T. L. *J. Org. Chem.* **1982**, *47*, 3023. Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1628. Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1981**, *22*, 5233. Gassman, P. G.; Saito, K. *Ibid.* **1981**, *22*, 1311. Gassman, P. G.; Saito, K.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 7613. Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Ibid.* **1980**, *102*, 6640. Gassman, P. G.; Talley, J. J. *Ibid.* **1980**, *102*, 1214, 4138.

[3] Creary, X.; Geiger, C. C.; Hilton, K. *J. Am. Chem. Soc.* **1983**, *105*, 2851.

[4] Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216.

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Table I. STO-3G and STO-3G* Orbitals and Orbital Energies (eV) of 1, 4, and 5

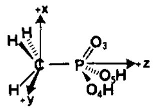
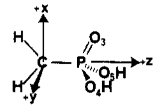
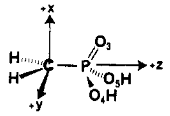
MO	STO-3G	STO-3G*	orbital character
			
17a′	−7.08	−9.11	$O_3\ (x - z) + P(xz - z^2)\ (\pi)$
8a″	−7.09	−9.16	$O_3(y) - O_4(y) + O_5(y)$
16a′	−9.22	−11.06	$O_3(s + x + z)$ (n)
7a″	−10.70	−11.11	$O_4(x + y - z) - O_5(x - y - z)$
15a′	−11.13	−11.98	$O_4(x + y - z) + O_5(x - y - z)$
			
8a″	−4.77	−5.24	$C(y) + P(yz)$
17a′	−13.84	−15.73	$O_3(x - z) + P(xz - z^2)\ (\pi)$
7a″	−13.88	−15.25	$O_3(y) - O_4(y) + O_5(y)$
16a′	−15.53	−17.21	$O_3(s + x + z)$ (n)
6a″	−16.69	−17.17	$O_4(x + y - z) - O_5(x - y - z)$
15a′	−17.81	−18.87	$O_4(x + y - z) + O_5(x - y - z)$
			
17a′	−5.10	−5.27	$C(x) + P(xy)$
16a′	−13.96	−15.94	$O_3(x - z) + P(xz - z^2)\ (\pi)$
8a″	−14.07	−15.57	$O_3(y) - O_4(y) + O_5(y)$
15a′	−15.57	−17.39	$O_3(s + x + z)$ (n)
7a″	−16.69	−15.94	$O_4(x + y - z) - O_5(x - y - z)$
14a′	−17.84	−18.94	$O_4(x + y - z) + O_5(x - y - z)$

Table II. Total Energies (au) of 1, 3, 4, and 5

structure	STO-3G	STO-3G*	4-31G + d's on P
1	−598.65924	−598.98921	−605.34452
3	−597.98373	−598.15780	−604.37486
4	−597.71960	−598.06413	−604.31011
5	−597.72471	−598.06732	−604.31117

Table III. Reaction Energies (kcal/mol) for (1)

cation	STO-3G	STO-3G*	4-31 + d's on P[a]
3	114.1	49.6	−0.8
4	4.9	14.0	−41.4
5	8.1	16.0	−40.7

[a] 4-31G + d's on S calculations are carried out on STO-3G* optimized structures.

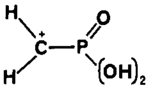
Table IV. STO-3G* Total Energies of Methyl-Substituted 3 and 5

substituent	3	5	ΔE
(none)	−598.15780	−598.06732	56.8
monomethyl	−636.74880	−636.68634	39.2
dimethyl	−675.33822	−675.29645	26.2

STO-3G[6] and STO-3G*[7] (containing 3d AO's on phosphorus and sulfur) levels using the GAUSSIAN 80 package of programs. The optimized structures are shown in Figure 1, along with the calculated structural parameters and total atomic charges. It is interesting to note that the C–P bond lengths are similar using the two basis sets; however, the P–O bond lengths are considerably shorter when calculated at the STO-3G* level, consistent with the expected oxygen lone pair interactions with the vacant d AO's on phosphorus. This lone-pair donation reduces substantially the charge density on the phosphorus atom and also lowers the energies of the predominantly lone-pair orbitals (see Table I). The energy of 1 was also calculated at 4-31G + d's level[8] at the STO-3G* optimized geometry (see Table II).

Attempts to carry out complete geometry optimization calculations on the methylenephosphonic acid cation (2) resulted in optimization to the cyclic structure 3, regardless of the initial conformation about the C–P bond, for example, as in 4 or 5. Attempted optimization from the C_s structure 4 resulted in rotation about the C–P bond and subsequent collapse to 3. An open form of the cation 2 does not appear to represent a local minimum on the energy surface of the cation at the STO-3G and STO-3G* levels.[9] The geometrical parameters and total charges for 3 are shown in Figure 1, while the total energies are given in Table II. In 3 most of the positive charge resides on the phosphorus atom and is considerably lower when calculated at the STO-3G* level.

In order to derive an estimate of the relative energies of the open cationic structures 4 and 5, the C–P–O bond angles and the C–P–O–H dihedral angles were held constant to maintain C_s symmetry at the values calculated for 1 while all of the other parameters were optimized (see Figure 1). It should be pointed out that the calculated C–P bond lengths in 4 and 5 are considerably longer (1.89–1.92 Å) than that calculated for 1 (~1.82 Å) at both the STO-3G and STO-3G* levels. Optimization of only the C–P bond length at the 4-31 + d's on phosphorus level resulted in only a slight shortening of the C–P bond length (1.89 Å) with only a very slight decrease in energy (0.01 kcal/mol). The lowest unoccupied vacant p orbitals 8a″ in 4 and 17a′ in 5 contain significant C_{2p}–P_{3d} bonding interactions (illustrated in Figure 2), which results in a significant lowering in energy of these MO's (Table I) and delocalization of the positive charge (see charge distributions in Figure 1) at the STO-3G* level.



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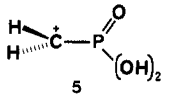

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A comparison of the relative energies of 1 and the three cations 3, 4, and 5 (Figure 3) shows that the incorporation of 3d AO's on phosphorus stabilizes 1 and the open cations 4 and 5 (207, 215, 216 kcal/mol), respectively) to a greater extent than the cyclic cation 3 (166 kcal/mol).

The effect of the $PO(OH)_2$ group on the stability of the cation relative to hydrogen can be estimated from the heats of reaction calculated for the isodesmic reactions calculated

$$[H_2CPO(OH)_2]^+ + CH_4 \rightarrow CH_3^+ + H_3CPO(OH)_2 \qquad (1)$$

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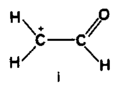
(6) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *Ibid.* **1970**, *52*, 2769.

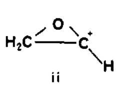
(7) Collins, J. B.; Schleyer, P. v. R.; Brinkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(8) The 4-31G basis set (Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724) was augmented with the five 3d AO's having the same coefficients and exponents as in the STO-3G* basis set.

(9) Extensive calculations have been carried out on the C_2H_3O cation.[10] The eclipsed and cyclic structures i and ii represent local minimum structures at the STO-3G and 4-31G levels. At the STO-3G level ii is lower in energy (17.9 kcal/mol) than i, whereas at the 4-31G level i is lower in energy (7.5 kcal/mol). Calculations at the 6-31G** and MP2- and MP3/6-31G** levels indicate that the cyclic ion is lower in energy.



i



ii

(10) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309.

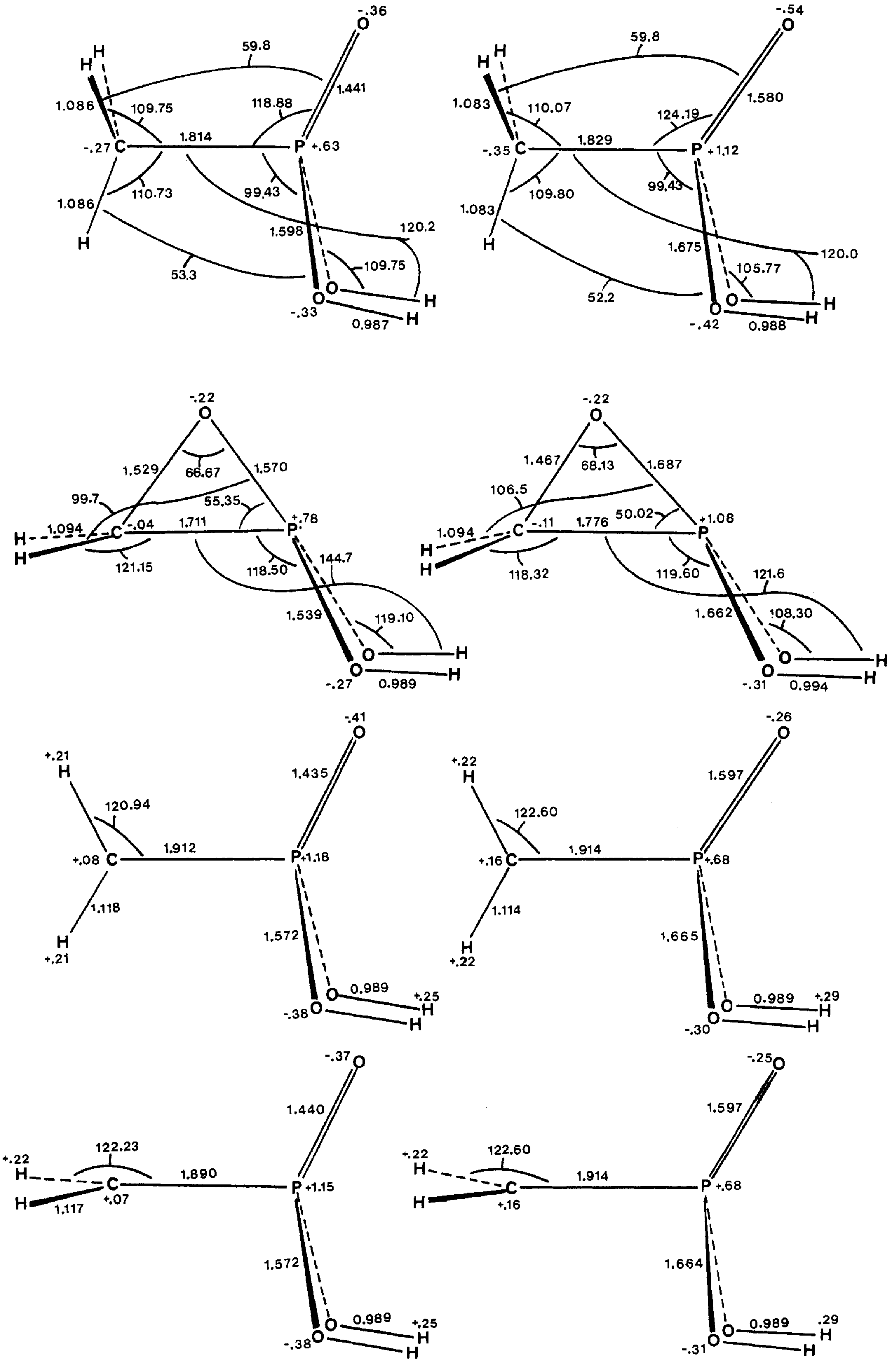


Figure 1. Calculated structural parameters and total atomic charges for **1**, **3**, **4**, and **5**. Structures on the right are derived from geometry optimization calculations at the STO-3G level and those on the left from the STO-3G* level calculations. Dihedral angles are indicated by the lines connecting 1,3-related bonds.

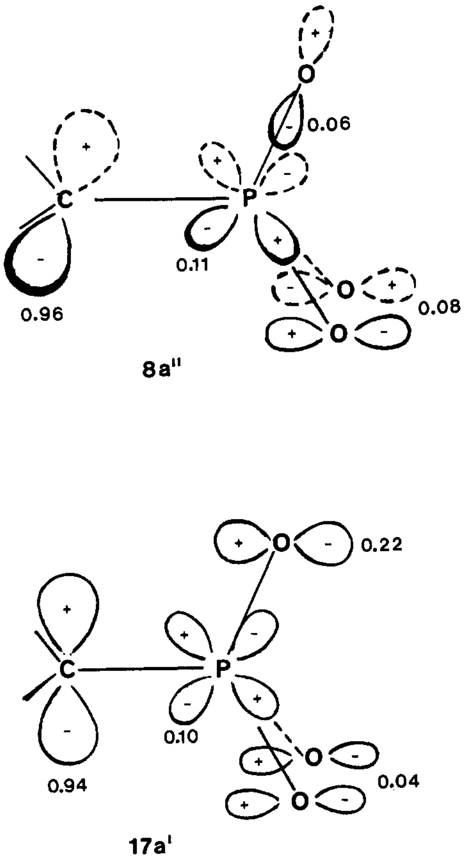
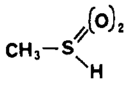


Figure 2. AO contributions to the 8a'' MO of 4 and the 17a' MO of 5.

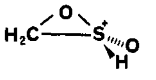
at the STO-3G, STO-3G*, and 4-31G + d's on phosphorus level.[11] These heats of reaction are given in Table III. It must be recognized that the heats of reactions for the open cationic structures are too positive in that the energies do not represent fully geometry optimized structures.

Effect of Methyl Substitution. Calculations have also been carried out on the monomethyl- and dimethyl-substituted cyclic and open cations 3 and 5 at the STO-3G* level. The bond lengths and angles used were those calculated for 3 and 5 with the C–C and C–H bond lengths assigned as 1.53 and 1.06 Å. The conformation about the methyl–C bond in 5 was chosen to attain the maximum overlap of the π-type methylene group orbital with the vacant p orbital. The total energies are given in Table IV. As expected, methyl substitution lowers the energy of the open cation 5 to a greater extent than in the cyclic cation 3.

Hydrogen Methyl Sulfone and Related Cations. Complete geometry optimization calculations on hydrogen methyl sulfone (6) and the related cations were carried out only at the STO-3G* level. The optimized structural parameters for 6 and the atomic charge densities are shown in Figure 4.


$CH_3-S(O)_2H$

6



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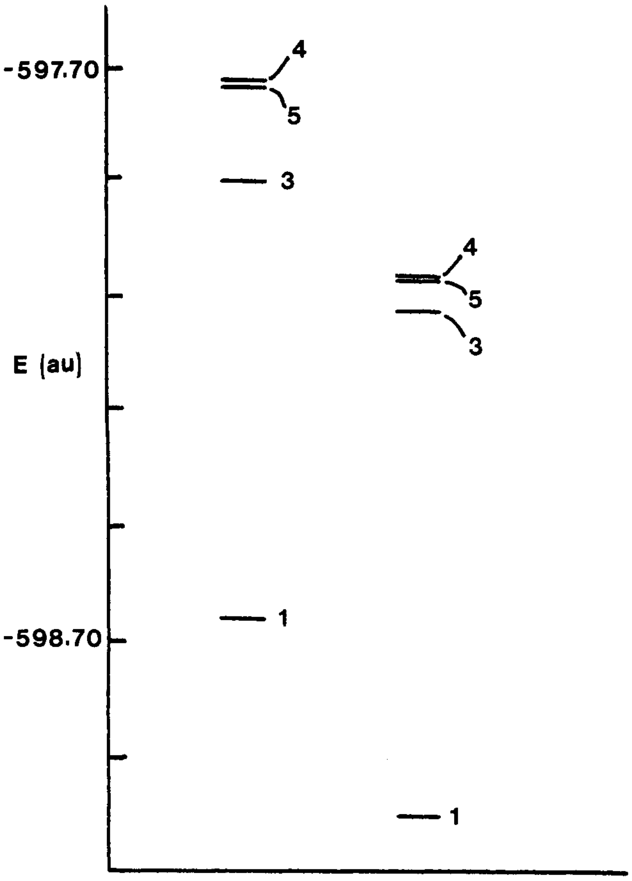


Figure 3. Relative energies of 1, 3, 4, and 5 at the STO-3G (left) and STO-3G* (right) level.

Table V. Total Energies (au) of 6–9

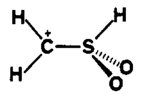
structure	STO-3G*	4-31G + d's on S[a]
6	–580.60204	–586.44874
7	–579.75393	–585.47131
8	–579.65852	–585.38530
9	–579.65223	–585.37507

[a] 4-31G + d's on S calculation on STO-3G* optimized structures.

Table VI. Reaction Energies (kcal/mol) for (1)

cation	STO-3G	4-31G + d's on S
7	62.3	–6.3
8	2.4	–60.3
9	–1.5	–66.7

As in the case of cation 2 derived from 1, full geometry optimization calculations on the cation 7 led only to the cyclic cation 8. No open cationic structure appears to represent a local minimum structure. Geometry optimization calculations were carried out on the two open cationic conformations 8 and 9 at the STO-3G* level with the C–S–O and C–S–H bond angles constrained to those calculated for 6. The resulting structures and charge densities are shown in Figure 4. As in the case of the phosphonate system, the calculated C–S bond lengths in the open cations are significantly longer than that in 6 (~0.1 Å). Optimization of the C–S bond lengths using the 4-31G + d's on the sulfur basis set[8] resulted in shortening of the C–S bond lengths to 1.811 Å in 8 and 1.882 Å in 9! However, these decreases in the C–S bond lengths resulted in only slight lowerings in the total energies at the 4-31G + d's on sulfur level, being 1.6 kcal/mol in the case of 8



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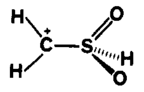

9

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[11] The STO-3G and 4-31G energies for methane and the methyl cation are taken from: Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808.

[12] Private communication from Prof. Creary.

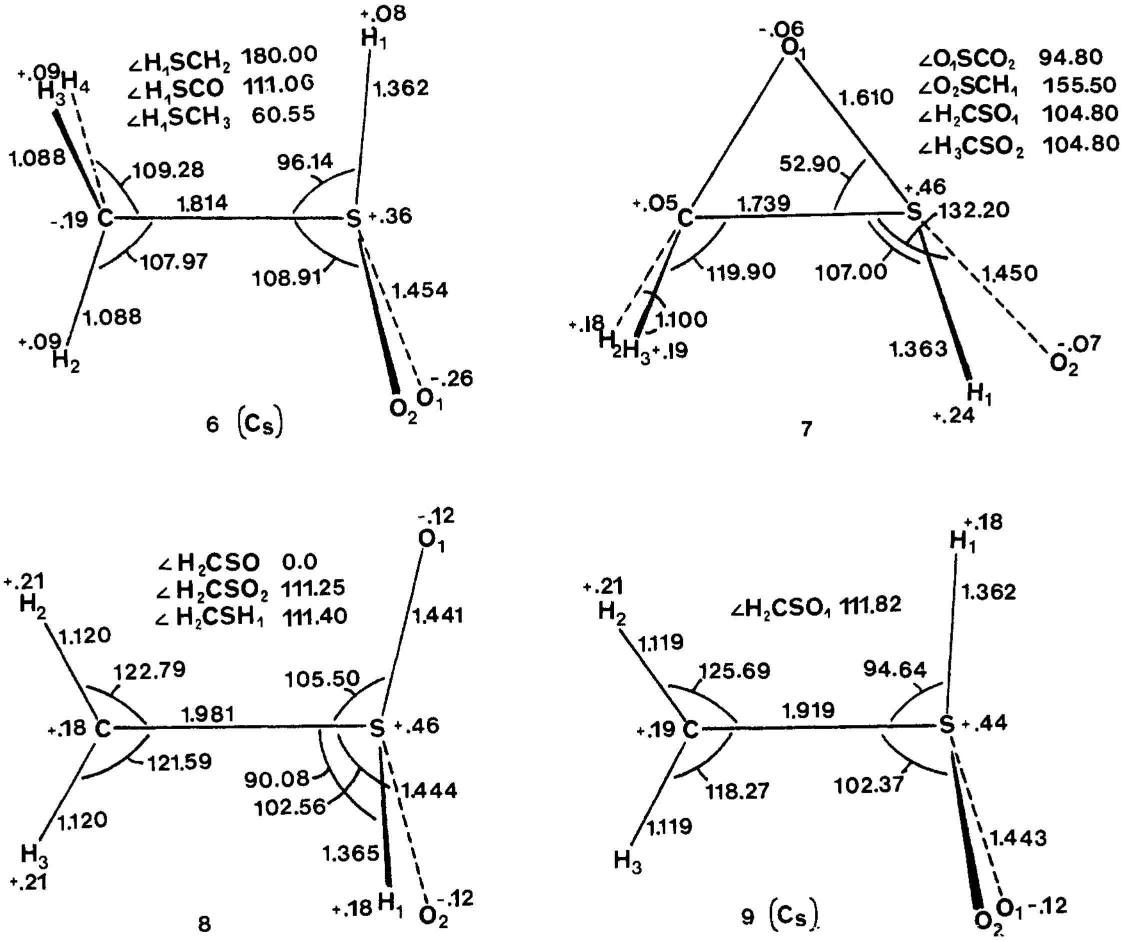

Figure 4. Calculated structural parameters and total energies of 6, 7, 8, and 9 at the STO-3G* level. Dihedral angles are indicated as ∠ABCD where A, B, C, and D represent the atoms in the two planes.

and 1.2 kcal/mol with 9, indicating that the energy surface is relatively flat with respect to stretching of the C–S bond. Of the three cationic structures, the cyclic form is significantly lower in energy (see Table V), although again the energies of 8 and 9 do not represent minima.

The changes in total energy for the reactions have been calculated at the STO-3G* and 4-31G + d's on sulfur levels and appear in Table VI.

$$[H_2CSO_2(H)]^+ + CH_4 \rightarrow CH_3^+ + H_3CSO_2(H) \qquad (2)$$

Comparison of the Results of Calculations and Solvolytic Data. Table VII lists the calculated changes in energy for reaction 3 derived in this study and the earlier

$$H_2C^+{-}X + CH_4 \rightarrow CH_3^+ + H_3C{-}X \qquad (3)$$

study by Paddon-Row, Santiago, and Houk[5] and observed and estimated rates of solvolysis of secondary and tertiary sulfonates in highly fluorinated solvents taken from the various experimental papers cited earlier.

The calculated reaction energies for the open cationic structures indicate that the phosphonate and sulfonyl groups destabilize a cationic center to a greater extent than does the cyano group. These reaction energies are admittedly too large in that calculations on the fully geometry optimized structures could not be achieved. It is doubtful, however, that if such calculations could have been achieved, the reaction energies would be reduced to below that for the cyano substituent. The relative reactivity of the phosphonate-substituted system correlates best with the formation of the cyclic cation. Stereochemical studies, however, have not provided any support for the formation of a cyclic cationic intermediate.

Table VII. Calculated 4-31G (+d's) Reaction Energies for (3) and Relative Solvolytic Reactivities

cation	ΔE	relative reactivity[a]
8, 9	−60.3, −66.7	[b]
4, 5	−41.4, −40.7	(1–5) × 10^{-3} [c]
$^+CH_2CN$	−9.9[5]	(1.6–3) × 10^{-4} [d]
7	−6.3	[b]
3	−0.8	(1–5) × 10^{-3} [c]
ii (ref 9)	+12.1	20–55[e]
$^+CH_2CHO$	+18.9[5]	20–55[e]

[a] Estimated from the rate ranges reported in the literature. [b] Not yet reported. [c] Reference 3. [d] Reference 2. [e] Reference 1.

It is obvious from the present study that the degree of substitution at the cationic center significantly affects the stability of the open cationic center (17.6 and 30.6 kcal/mol more by one and two methyl groups). Recognizing that the energies of the open cationic species are artificially high, methyl substitution might conceivably lower the energy of the open cation to below that of the cyclic cation.

A factor that cannot conveniently be treated theoretically is the effect of the solvent on the relative energies of the starting state, transition state, and the final cation. In these highly polar systems these energy contributions must be substantial.

Studies on the effect of the sulfonyl group on the stability of a cationic center are currently in progress in Prof. Creary's laboratories.

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