the results for the cation are at the geometry of the 1^2B_g state of the cation, while the energy spacings between the anion states determined from the energy loss and ETS measurements are at the geometry of the neutral molecule. It would be most constructive to compare the above results with the $1^2B_g \rightarrow 2^2A_u$ transition energy of the cation at the geometry of the neutral molecule. The necessary information could, in principle, be obtained from the photoelectron spectrum. Unfortunately, photoelectron spectroscopic studies do not yield a feature which can be unambiguously assigned to the 2^2A_u cation state.

IV. Conclusions

The energy-loss spectra of butadiene provide evidence for π^* anion states near 0.9 and 2.8 eV and $\pi^{-1}(\pi^*)^2$ anion states near 5.0, 6.7, 8.1, 11.0, and 12.5 eV. The two low-energy features are due to the 1^2A_u and 1^2B_g anion states, which have previously been assigned on the basis of ETS. The 5.0-, 6.7-, and 8.1-eV features are attributed to the 2^2B_g, 2^2A_u, and 3^2A_u anion states, respectively. The 5-eV anion state decays strongly into both the 1^3B_u and 1^1A_g states of the neutral molecule, indicating that it has both 1p and 2p-1h character, consistent with the predictions of CI calculations that both the $1a_u^2 1b_g 2a_u^2$ and $1a_u^2 1b_g^2 2b_g$ configurations make sizable contributions to the 2^2B_g anion state. The 11.0- and 12.5-eV features in the energy loss spectra are each attributed to one or more $\pi^{-1}(\pi^*)^2$ anion states.

There appear to be no assignments of the 1p-2h cation states of butadiene other than the lowest such state, which is paired with the 5-eV anion state studied here. We are also unaware of assignments of the higher lying anion states on the basis of absorption spectra of the radical anion in glasses. Indeed, the states observed in the energy loss spectrum at 6.7 and 8.1 eV would not be expected to be prominent in the absorption spectra, since transitions to these states from the ground-state anion are dipole-forbidden.

The 0.60- and 1.12-eV energy loss spectra both display a very broad feature centered near 8 eV, which is attributed to electron capture into one or more σ^* orbitals. Finally, it is proposed that the series of weak, narrow features observed between 5.5 and 6.9 eV in the 1^3A_g and 1^1B_u excitation functions are due to $\pi^{-1}(3s)^2$ and $\pi^{-1}(3p)^2$ Feshbach resonances.

Acknowledgment. This research was carried out with the support of a grant from the National Science Foundation. The calculations were carried out on the Chemistry Department's FPS Model 500EA computer, funded by a grant from the National Science Foundation. We wish to thank Drs. P. D. Burrow, M. Allan, and T. Bally for helpful discussions, and Drs. L. Ng and B. Veeraraghavan for assistance in the initial construction of the electron energy loss spectrometer.

Registry No. 1,3-Butadiene, 106-99-0.

Single-Crystal Molecular Structure Determinations and Theoretical Calculations on Alkynyl Sulfonate and Carboxylate Esters[†]

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Abstract: The single-crystal X-ray structures of propynyl tosylate, **4**, and of ethynyl benzoate, **5**, were determined. Both esters are essentially linear acetylenes with C≡C—O bond angles of 174.7° and 177.6°, respectively. The C≡C—O acetylenic–oxygen bond length is 1.331 (4) Å in **4** and 1.329 (4) Å in **5**, significantly shorter than the analogous bond length in the corresponding saturated alkyl or vinyl esters. There is a concomitant increase in the S—O or O—C(=O) bond lengths from saturated to vinyl (enol) to alkynyl esters. Ab initio molecular orbital calculations (6-31G*) for several smaller model systems are in excellent agreement with the X-ray geometries including the changes that occur as a function of R (R = alkynyl, vinyl, alkyl). $HC{\equiv}COSO_2R$, **7**, prefers a gauche conformation (∠HSCO = 70° for R = H and 76° for R = Me). The barriers to rotation around the S—O bond are 2.7 kcal mol^{-1} in **7**, R = H, and 4.8 kcal mol^{-1} in **7**, R = Me (6-31G*). The energies of several reactions of these esters have been calculated (MP3/6-31G*//6-31G*, kcal mol^{-1}). The calculated values below are given in the order R = C≡CH → R = CH=CH$_2$ → R = CH$_3$. Hydrolysis energies are −7.7, −4.1, and 3.5 for HSO_2OR and −7.2, −2.9, and 3.0 for ROC(=O)H. The hydrogenation energies of the O—R bonds are −30.7, −17.3, and −21.8 in $ROSO_2H$, −30.3, −16.1, and −22.4 in ROC(=O)H, and −23.0, −13.3, and −25.4 in ROH. The hydrogenation energies of the RO– bond are −2.4, 1.1, and 8.8 in RO—SO$_2$H and 2.8, 7.2, and 12.9 in RO—C(=O)H. Agreement with experimental data is good. The trends in the above energies as a function of R are discussed. The PM3 and AM1 calculations reproduce well the geometries of the alkynyl sulfonate and carboxylate esters but fail to reproduce these reaction energies.

Introduction

Esters of all types play a key role in organic chemistry. They serve as valuable synthetic reagents, have important biological functions, and they have a place in mechanistic investigations. The three major classes of esters, carboxylates, sulfonates, and phosphates, are so ubiquitous that they are often taken for granted.

Recently, we reported the preparation of alkynyl sulfonates[1] **1**, carboxylates[2] **2**, and phosphates[3] **3**, members of the family of previously unknown, unique acetylenic esters that combine two

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[†] Dedicated to Professors Hiroshi Taniguchi and Yuho Tsuno on the occasion of their 60th birthdays.

[‡] University of Utah.

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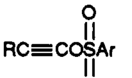
0002-7863/91/1513-7461$02.50/0

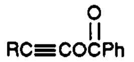
Table I. Summary of Crystallographic Data for Alkynyl Esters **4** and **5**

	4	**5**
molecular formula	$S_1O_3C_{10}H_{10}$	$O_2C_9H_6$
formula wt (g/mol)	210.253	146.147
space group	$P\bar{1}$	*P*212121
space group no.	2	19
crystal system	triclinic	orthorhombic
A (Å)	8.288 (1)	4.2853 (6)
B (Å)	8.262 (1)	10.860 (2)
C (Å)	8.6635 (9)	16.139 (2)
α (deg)	111.82 (1)	90.0000
β (deg)	88.84 (1)	90.0000
γ (deg)	109.71 (1)	90.0000
all volume (Å^3)	514.69	751.13
Z	2.0	4.0
d(calcd) (g/cm^3)	1.357	1.292
crystal size (mm)	0.23 × 0.19 × 0.15	0.21 × 0.19 × 0.15
absorptn coefficient (cm^{-1})	25.857	7.175
radiatn defractometer	Cu (1.540 56 Å)	Cu (1.540 56 Å)
no. of reflectns	CAD4 1843	CAD4 800
no. of unique reflectns	1713	
2θ range (deg)	4.00–130.00	4.00–130.00
scan technique	$\theta/2\theta$ scan	$\theta/2\theta$ scan
scan width	0.8000 + 0.140 tan θ	0.8000 + 0.140 tan θ
data collectn positn	bisecting, with $\omega = 0$	bisecting, with $\omega = 0$
highest peak in final difference Fourier (e/Å^3)	0.199	0.301
max ρ value in final difference Fourier (e/Å^3)	77.764	112.999
weighting scheme	non-Poisson contributn	non-Poisson contributn
ignorance factor	*P* = 0.06	*P* = 0.04
no.of observatns	1413	678
no. of variables	154	119
data to parameter ratio	9.175	5.697
shift to error ratio	0.021	0.001
error in an observatn of unit wt	1.7693	1.7930
R factor	0.0500	0.0412
weighted *R* factor	0.0522	0.0421

of the most interesting, useful, common, and simple functionalities in organic chemistry into a single, novel molecule.


$RC\equiv CO\overset{O}{\underset{O}{S}}Ar$

1


$RC\equiv CO\overset{O}{C}Ph$

2


$RC\equiv CO\overset{O}{P}(OR')_2$

3

Since they were first reported in the mid-1980s, these unique esters have rapidly become the object of numerous investigations. Alkynyl sulfonates serve as precursors to ynolates[4] and novel vinyl 1,1-bis(esters),[5] whereas alkynyl carboxylates are potent serine-based protease inhibitors[6] and both esters undergo cycloadditions resulting in unique Dewar pyridines.[7] All three esters undergo hydrolyses in neutral aqueous media via an unusual mechanism involving cyclic dioxolenylium ions.[8]

Therefore, intrinsic, fundamental properties for this new class of compounds, such as the precise molecular structure, bonding, electron distribution, etc., are of particular interest. Moreover,

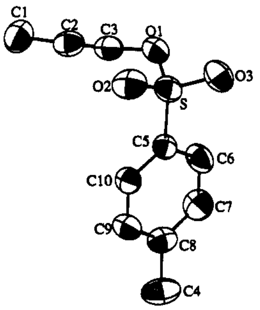


Figure 1. ORTEP of propynyl tosylate, **4**.

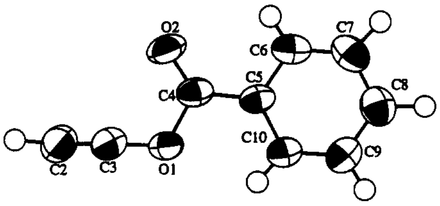


Figure 2. ORTEP of ethynyl benzoate, **5**.

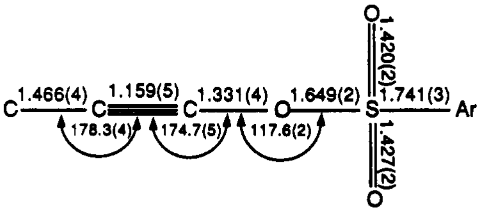


Figure 3. Summary of key structural features (and their esd's) of propynyl tosylates **4**.

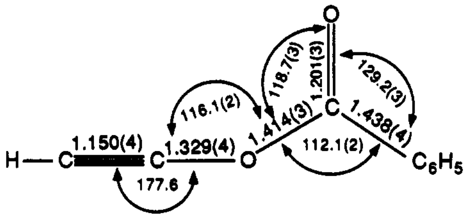


Figure 4. Summary of key structural features (and their esd's) of ethynyl benzoate **5**.

Table II. Bond Distances for Propynyl Tosylate, **4**, in Angstroms[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
S	O1	1.649 (2)	C4	C8	1.504 (4)
S	O2	1.420 (2)	C5	C6	1.382 (4)
S	O3	1.427 (2)	C5	C10	1.380 (6)
S	C5	1.741 (3)	C6	C7	1.379 (4)
O1	C3	1.331 (4)	C7	C8	1.390 (4)
C1	C2	1.466 (4)	C8	C9	1.388 (4)
C2	C3	1.159 (5)	C9	C10	1.379 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

there is considerable current interest and research activity in the relationship between chemical dynamics and reactivity and systematic molecular structure analysis and its relationship to bonding.[9,10] In a previous study,[11] we reported for the first time on these properties for alkynyl carboxylates, **2**. In this paper, we

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Table III. Bond Angles for Propynyl Tosylate, **4**, in Degrees[a]

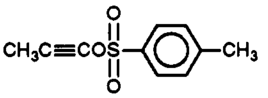
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	S	O2	107.7 (1)	S	C5	C10	119.7 (3)
O1	S	O3	100.9 (1)	C6	C5	C10	121.3 (3)
O1	S	C5	102.4 (1)	C5	C6	C7	119.0 (3)
O2	S	O3	121.8 (2)	C6	C7	C8	120.8 (3)
O2	S	C5	110.6 (1)	C4	C8	C7	120.6 (3)
O3	S	C5	111.1 (2)	C4	C8	C9	120.4 (3)
S	C1	C3	117.6 (2)	C7	C8	C9	118.9 (3)
C1	C2	C3	178.3 (4)	C8	C9	C10	120.9 (3)
O1	C3	C2	174.7 (5)	C5	C10	C9	119.0 (3)
S	C5	C6	119.0 (2)				

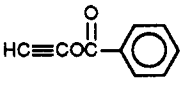
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Torsion Angles for Propynyl Tosylate, **4**, in Degrees

atom 1	atom 2	atom 3	atom 4	angle
C5	S	O1	O3	72.23 (0.31)
S	O1	C3	C2	−179.33 (4.68)
O2	S	O1	C3	−44.44 (0.32)
O3	S	O1	C3	−173.10 (0.30)
O1	S	C5	C6	65.62 (0.31)
O1	S	C5	C10	−115.06 (0.29)
O2	S	C5	C10	−0.79 (0.34)
O3	S	C5	C10	137.67 (0.29)
S	C5	C6	C7	178.14 (0.30)

wish to report our results for the alkynyl sulfonates **1**. Specifically, we present the single-crystal X-ray structure of propynyl tosylate, **4**, as well as of the parent ethynyl benzoate, **5**, the simplest alkynyl benzoate ester, along with theoretical calculations on these species and comparisons with their better known enol and saturated analogues.


4


5

Results and Discussion

X-ray Structure Data. A summary of the crystallographic data for **4** and **5** is given in Table I. ORTEP structures for **4** and **5** are shown in Figures 1 and 2, respectively. Key structural data are given in Tables II–VII and summarized in Figures 3 and 4, respectively. Since this is the first time that reliable X-ray data are available[12] on these key, novel alkynyl esters, positional parameters (and their estimated standard deviations) are also reported in Tables VII and VIII.

The data reveal a number of interesting structural features of these unique alkynyl esters. In particular, as expected, both esters are essentially linear acetylenes with C≡C—O bond angles of 174.7° and 177.6°, respectively, and **5** is essentially planar, with all atoms lying in the same plane. Moreover, like all known acyclic carboxylic esters,[13] ethynyl benzoate, **5**, adopts the antiperiplanar (syn) or *Z* conformation around the O—C(=O) carbonyl moiety.

Table V. Bond Distances for Ethynyl Benzoate, **5**, in Angstroms[a]

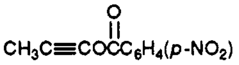
atom 1	atom 2	distance	atom 1	atom 2	distance
O1	C3	1.329 (4)	C5	C10	1.388 (3)
O1	C4	1.414 (3)	C6	C7	1.370 (4)
O2	C4	1.201 (3)	C7	C8	1.381 (4)
C2	C3	1.150 (4)	C8	C9	1.379 (4)
C4	C5	1.438 (4)	C9	C10	1.375 (4)
C5	C6	1.397 (4)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Especially interesting are the structural features of the sulfonyl ester moiety of **4** and their comparison to saturated and enol (vinyl) tolylates.[14] A search of the Cambridge Crystallographic Data File reveals numerous single-crystal structure determinations for saturated sulfonate esters and a few determinations for enol (vinyl) sulfonates.

The structural features of seven saturated *primary*[15] alkyl tosylates and the three known[16] enol (vinyl) tosylate esters are summarized in Table IX. It is evident from the data that, as intuitively expected, the S=O, and S—C(Ar) bond lengths, as well as the C—O—S bond angles, are essentially independent of the nature of the tosylate ester from alkyl to alkynyl ester. In contrast, both the C—O and S—O bond lengths are considerably affected by the nature of the ester. Particularly noteworthy is the C≡C—O acetylenic-oxygen bond length of 1.331 (4) Å, to our knowledge the first experimentally determined C_{sp}—O bond distance for a sulfonate ester. There is a clear and significant shortening of this bond from the saturated alkyl C(sp^3)—O of 1.465 Å through the enol C(sp^2)—O bond length of 1.431 Å to the alkynyl C(sp)—O bond length of 1.331 Å. There is a concomitant *increase* in the S—O bond length from the 1.575 Å of the saturated tosylates to 1.613 Å for enol tosylates and 1.649 Å for the alkynyl tosylate **4**. The significance and reasons for these trends are discussed in the subsequent section on theoretical calculations.

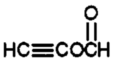
Theoretical Calculations. Calculations for **4–6**, the molecules for which we have carried out X-ray determinations, were performed with the semiempirical AM1[17a] and PM3[17b] methods.[17c] As ab initio calculations for these large molecules are still impractical, we have carried out such calculations for the smaller alkynyl sulfonate esters **7–9**. Ab initio calculations for the alkynyl carboxylate esters **10–12** as well as the X-ray structure of **6** were reported in our previous paper.[11] In addition, for the sake of completion and comparison, the vinyl and methyl sulfonate esters, **13** and **14**, were also calculated.

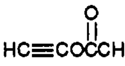

$CH_3C{\equiv}COC(=O)C_6H_4(p\text{-}NO_2)$
6

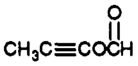
$HC{\equiv}COSO_2H$
7

$HC{\equiv}COSO_2CH_3$
8

$CH_3C{\equiv}COSO_2H$
9


$HC{\equiv}COC(=O)H$
10


$HC{\equiv}COC(=O)CH_3$
11


$CH_3C{\equiv}COC(=O)H$
12

$H_2C{\equiv}HCOSO_2H$
13

H_3COSO_2H
14

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(12) The previously reported[11] structure of propynyl *p*-nitrobenzoate, **6** was complicated by the fact that the unit cell of the only suitable sample contained two crystallographically independent molecules in the asymmetric unit. Moreover, **5**, the simplest alkynyl carboxylate ester likely to be a solid and hence suitable for single crystal structure determination, is also more ameanable to meaningful theoretical calculations and comparisons than the substituted ester **6**.

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Table VI. Bond Angles for Ethynyl Benzoate, **5**, in Degrees[a,b]

atom 1	atom 2	atom 3	angle
C3	O1	C4	116.1 (2)
O1	C3	C2	177.6 (4)
O1	C4	O2	118.7 (3)
O1	C4	C5	112.1 (2)
O2	C4	C5	129.2 (3)
C4	C5	C6	118.1 (2)
C4	C5	C10	122.9 (3)
C6	C5	C10	119.1 (3)
C5	C6	C7	120.2 (3)
C6	C7	C8	121.1 (3)
C7	C8	C9	118.2 (3)
C8	C9	C10	121.9 (3)
C5	C10	C9	119.4 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] The molecule is essentially planar, with all atoms lying approximately in the same plane; e.g., the C5–C4–O1–C3 and the C6–C5–C4–O2 dihedral angles are 179.63 (0.32) and 0.57 (0.60), respectively.

Table VII. Positional Parameters for Propynyl Tosylate, **4** (Standard Deviations Are Given in Parentheses)[a]

atom	*X*	*Y*	*Z*	*B* (Å^2)
S	0.4053 (1)	0.2992 (1)	0.2617 (1)	4.21 (2)
O1	0.3017 (3)	0.0873 (3)	0.1221 (3)	4.61 (7)
O2	0.5705 (3)	0.3665 (4)	0.2114 (4)	5.43 (8)
O3	0.3853 (4)	0.2675 (4)	0.4132 (3)	6.22 (8)
C1	0.3083 (6)	−0.0310 (6)	−0.3634 (5)	5.9 (1)
C2	0.3081 (5)	0.0217 (5)	−0.1820 (5)	4.5 (1)
C3	0.3094 (5)	0.0598 (5)	−0.0389 (5)	4.13 (9)
C4	−0.0280 (5)	0.7367 (6)	0.2138 (6)	6.0 (1)
C5	0.2781 (4)	0.4221 (4)	0.2418 (4)	3.35 (8)
C6	0.1121 (5)	0.3762 (5)	0.2853 (5)	4.8 (1)
C7	0.0130 (5)	0.4771 (6)	0.2741 (5)	5.1 (1)
C8	0.0789 (4)	0.6241 (5)	0.2218 (5)	4.10 (9)
C9	0.2448 (5)	0.6648 (5)	0.1759 (5)	4.35 (9)
C10	0.3450 (4)	0.5644 (5)	0.1853 (5)	3.86 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined s $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VIII. Positional Parameters for Ethynyl Benzoate, **5** (Standard Deviations Are Given in Parentheses)[a]

atom	*X*	*Y*	*Z*	*B* (Å^2)
O1	0.0632 (6)	0.1049 (2)	0.3332 (1)	4.87 (5)
O2	−0.0243 (7)	0.3092 (2)	0.3387 (1)	6.19 (6)
C2	0.384 (1)	0.1213 (4)	0.4607 (2)	6.3 (1)
C3	0.234 (1)	0.1160 (3)	0.4016 (2)	5.08 (8)
C4	−0.0724 (9)	0.2145 (3)	0.3026 (2)	4.58 (7)
C5	−0.2505 (8)	0.1935 (3)	0.2283 (2)	4.07 (7)
C6	−0.3900 (9)	0.2948 (3)	0.1901 (2)	5.10 (8)
C7	−0.559 (1)	0.2796 (3)	0.1187 (2)	5.91 (9)
C8	−0.597 (1)	0.1647 (4)	0.0835 (2)	5.9 (1)
C9	−0.458 (1)	0.0652 (3)	0.1217 (2)	5.51 (9)
C10	−0.2863 (9)	0.0777 (3)	0.1932 (2)	4.50 (7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

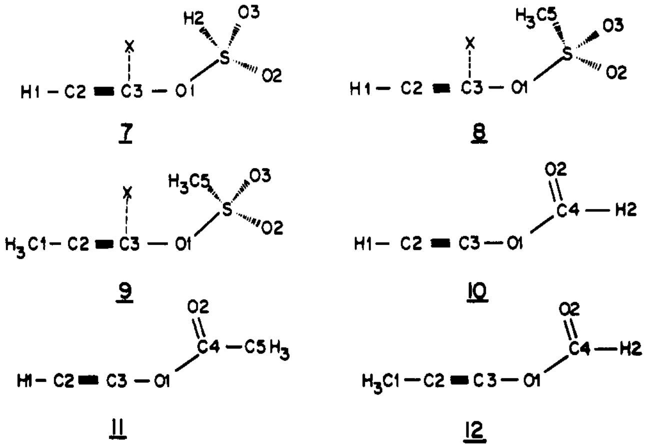

Figure 5. Atom numbering for alkynyl sulfonate esters **7–9** and for alkynyl carboxylate esters **10–12**. X is a dummy atom placed in the C2–C3–O1 plane with a C2–C3–X angle of 90°.

Calculations used standard molecular orbital theory, and they were carried out with the Gaussian 86 series of programs,[18] using gradient optimization techniques for geometry optimizations.[19]

The molecular geometries of all the sulfonates were optimized by using three basis sets: (a) the split-valence 3-21G basis set,[20] (b) the partially polarized 3-21G(*) basis set, which includes a set of d functions on sulfur,[21a] and (c) the fully polarized 6-31G* basis set, which includes a set of d functions on all non-hydrogen atoms.[21b,c] In general, several conformations were considered for each ester to ensure that the global minimum had been located. For the parent alkynyl carboxylate ester **10**, geometry optimizations were carried out also at the correlated MP2/6-31G* level.[22] Energy comparisons were generally made at the MP3/6-31G*//6-31G* level.[22] The optimized geometries and the calculated total energies of the most stable conformers of the alkynyl sulfonates are given in Table X and those of the alkynyl benzoates in Table XI, and the corresponding atom numberings are presented in Figure 5.

A. Alkynyl Sulfonate Esters. 1. Geometries. Geometry optimizations for the simple sulfonate esters **7–9** were carried out at 3-21G, 3-21G(*), and 6-31G*. As could have been expected,[11,23] the calculated structure of the C≡C—O subunit is relatively insensitive to the basis set or to the conformation adopted by the sulfonate group, while larger differences between the basis sets were found in the geometrical parameters around the sulfur atom (Table X). Specifically, the S—O bonds are much longer at 3-21G than at 3-21G(*) or at 6-31G*. For example, the calculated S—O bond distances in **7** (Å) are 1.703, 1.613, and 1.617 at 3-21G, 3-21G(*), and 6-31G*, respectively. Similarly, with the same basis sets, the calculated S═O bond distances (Å) in **7** (average of two values) are 1.561, 1.415, and 1.409, respectively. Methyl substitution at the acetylenic carbon shortens the S—O bond by 0.006 Å, while methyl substitution at sulfur lengthens this bond by 0.017 Å (Table X). The effects of methyl substitution on the S═O bond lengths are small. The 6-31G* calculated S—O and S═O bond distances in **8** (1.634 and 1.415 Å, respectively; Table X) are in excellent agreement with the experimental values in **4** of 1.649 and 1.423 Å (average of two values), respectively. Agreement for the bond angles around the sulfonate unit is also good. We conclude (as did previous studies of hypervalent molecules[23]) that the inclusion of polarization

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(18) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Borowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleudor, E. M.; Pople, J. A. Carnegie Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

(19) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem., Symp.* **1979**, *13*, 225; Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(20) (a) First row atoms: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939; (b) Second row atoms: Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Wehre, W. J. *Ibid.* **1982**, *104*, 2797.

(21) (a) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213; (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(22) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 1618; (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(23) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

Table IX. Summary of Structural Features of Primary Alkyl and Enol (Vinyl) Tosylates

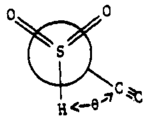
	C—O		O—S		S=O		S—C(Ar)		C—O—S	
	range	av	range	av	range	av	range	av	range	av
primary alkyl tosylates	1.454–1.484	1.465 ± 7	1.565–1.584	1.575 ± 5	1.422–1.429	1.425 ± 2	1.749–1.757	1.751 ± 2	114.7–119.8	118.0 ± 1.3
enol (vinyl) triflates	1.424–1.434	1.429 ± 5	1.609–1.620	1.615 ± 5	1.421–1.422	1.422 ± 1	1.741		117.9–119.6	118.8 ± 1.1
propynyl tosylate **4**	1.331		1.649		1.423		1.741		117.6	

functions on sulfur is essential for a realistic description of sulfonate esters.

The AM1 and the PM3 calculated geometries of the sulfonate esters are very similar, except for the S=O bond lengths, which are very much longer and closer to experimental at PM3 than at AM1 (see data for **4** in Table X). This observation is interesting in connection with a recent controversy on the usefulness of the PM3 method.[24]

The overall agreement between the 6-31G* calculated structures of the model sulfonate esters **7**–**9** or of the PM3 (or AM1 except for the S=O bond) calculated structure of **4** and the X-ray experimental geometry of **4** is very good. We note, in particular, the excellent agreement for the C(sp)—O bond length, which is calculated to be 1.319 Å (6-31G*) in **9**, compared with the experimental bond length in **4** of 1.331 Å. Substitution at sulfur is not expected to affect much this bond distance (compare **7** and **8**, Table I). This excellent computational–experimental agreement (inclusion of electron correlation is expected to lengthen the calculated C—O bond by 0.01–0.02 Å,[11,23] improving the agreement) contrasts with the relatively large difference that was found[11] between the calculated and experimental C(sp)—O bond distance in the alkynyl carboxylate ester **6** (see also discussion below). The experimental C≡C bond distance in **4** of 1.159 Å is somewhat shorter than the 6-31G* value in **9** of 1.180 Å. A similar experimental–computational difference was found for this bond length also in the alkynyl carboxylate esters **5** and **6** (see below).

The simple sulfonate esters **7**–**9** are most stable, according to 6-31G* ab initio calculations, in a nearly gauche conformation, as shown in the general Newman projection **15**, with $\theta = 69.6°$, 76.4°, and 67.8° in **7**, **8**, and **9**, respectively (Table X). However,



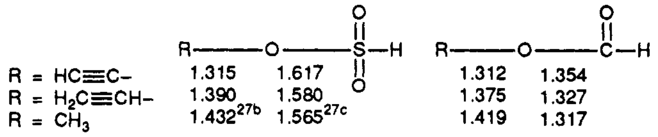
15

the energy difference between the gauche ($\theta = 70°$) and the anti ($\theta = 180°$) conformations is small (e.g., in **7**, 0.5 kcal mol^{-1} at 6-31G*), and it is therefore not surprising that, at 3-21G and 3-21G* (and also with PM3 and AM1), the anti conformation is the ground state of **7**–**9** (Table X).

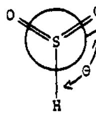
In the solid state, the sulfonate ester **4** adopts the gauche conformation ($\theta = 72°$), in line with the 6-31G* calculations for **7**–**9**. The semiempirical calculations for **4** find the anti conformation of **4** to be the most stable, but the gauche conformation ($\theta = 75°$) is only 0.4 kcal mol^{-1} (PM3) higher in energy.

The calculated barriers to rotation around the S–O bonds[25] are 2.7 and 4.8 kcal mol^{-1} (6-31G*) in **7** and **8**, respectively, the highest point along the rotational path[25] being the syn conformation ($\theta = 0°$). These relatively small rotational barriers suggest that, in other alkynyl sulfonate esters, specific interactions between substituents or crystal forces in the solid state may result in other conformations being the most stable.

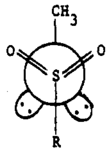
Chart I. Comparison of the Calculated (6-31G*) R–O and O–S (or O–C) Bond Distances (Å) in the Parent Sulfonate and Carboxylate Esters as a Function of R



It is interesting to compare the rotation barriers in the alkynyl sulfonate esters **7** and **8** with these barriers in $HOSO_2H$, in methyl sulfonate, CH_3OSO_2H, and in methyl methanesulfonate, $CH_3OSO_2CH_3$.[26] As with **7** and **8**, also in these cases the rotational potential surface is relatively flat in the range $\theta = 70$–$180°$ and the eclipsed conformation ($\theta = 0$) is the highest point along the rotational coordinate. At 6-31G*, $HOSO_2H$ adopts conformation **16** ($\theta = 111°$), while with the bulkier methyl group the anti conformation is preferred in both CH_3OSO_2H (**17**, R = H) and $CH_3OSO_2CH_3$ (**17**, R = CH_3).



16



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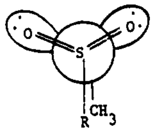

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Interestingly, the rotational barriers in $HOSO_2H$ and CH_3OSO_2H are significantly higher than in **7** or in **8**. The barrier to rotation around the S–O bond is 7.6 kcal mol^{-1} (6-31G*; 7.4 kcal mol^{-1}, at MP3/6-31G*) in $HOSO_2H$, 6.7 kcal mol^{-1} (6-31G*; 6.5 kcal mol^{-1} at MP3/6-31G*) in CH_3OSO_2H, and 10.1 kcal mol^{-1} (6-31G*) in $CH_3OSO_2CH_3$,[26] compared with 2.7 and 4.8 kcal mol^{-1} in **7** and **8**, respectively.

The major contributor to the rotation barriers in all these sulfonates is probably electronic not steric, as the eclipsing interactions between the two hydrogens in, e.g., **16**, would require barriers consisting of only ca. 1 kcal mol^{-1}.[23] We attribute the relatively high energy of the syn-eclipsed conformations to electrostatic repulsions between the lone pair electrons on the sp^3 oxygen and the negatively charged oxygens of the S=O bonds, which are maximized when $\theta = 0°$ (see **18**). The calculated dipole moments (6-31G*) of $HOSO_2H$ of 2.61 D for $\theta = 180°$ and 5.17 D for $\theta = 0°$ support this interpretation. When R is the strongly electron withdrawing ethynyl group, these electron–electron repulsions (as well as the steric repulsions relative to R = CH_3) diminish and the rotation barrier drops considerably (as does the difference between the dipole moments of the syn and anti conformations, e.g., in **8** 4.17 and 2.24 D, respectively). Naturally, steric eclipsing effects also play their role, the rotation barrier in $CH_3OSO_2CH_3$ being higher by 3.4 kcal mol^{-1} than in CH_3OSO_2H, and in **8** it is 2.1 kcal mol^{-1} higher than in **7**.

Comparing the calculated geometries of the parent alkynyl (**7**), alkenyl (**13**), and alkyl (**14**) sulfonate esters (Chart I), we find geometrical trends that are similar to those which were observed and discussed for the corresponding carboxylate esters.[11] Furthermore, the trends that we find computationally for the parent sulfonates are similar to those found experimentally (Table IX, see also ref 27a). In both series, the R—O bond length increases

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[24] (a) Dewar, M. J. S.; Healy, E. F.; Holder, A. J.; Yuan, Y.-C. *J. Comput. Chem.* **1990**, *11*, 541. (b) Stewart, J. J. P. *Ibid.* **1990**, *11*, 543.

[25] The calculations used the "flexible rotor" approximation; i.e., the R-S-O-C dihedral angle θ was fixed at the desired value (e.g., 60° in **15**), and all other structural parameters were fully optimized.

[26] Bindal, R. D.; Golab, J. T.; Katzenellenbogen *J. Am. Chem. Soc.* **1990**, *112*, 7861.

Table X. Optimized Geometries,[a] Total Energies,[a,b] and Heats of Formation[c] for Structures 4 and 7–9

geometric parameters[d]	7				8				9				4[e]		
	6-31G*	3-21G(*)	3-21G	PM3	6-31G*	3-21G*	3-21G(*)	PM3	6-31G*	3-21G(*)	3-21G	PM3	PM3	AM1	exptl
Bond Lengths (Å)															
C2–C3	1.180	1.181	1.181	1.192	1.180	1.181	1.182	1.192	1.181	1.180	1.181	1.193	1.193	1.196	1.159
C3–O1	1.313	1.326	1.321	1.316	1.310	1.325	1.320	1.316	1.319	1.334	1.327	1.316	1.315	1.310	1.331
O1–S	1.617	1.613	1.703	1.735	1.634	1.624	1.709	1.735	1.611	1.607	1.699	1.735	1.738	1.737	1.643
O2–S	1.408	1.415	1.561	1.424	1.414	1.421	1.561	1.427	1.410	1.416	1.562	1.425	1.430	1.375	1.420
O3–S	1.410	1.415	1.561	1.424	1.416	1.421	1.561	1.427	1.412	1.416	1.562	1.425	1.430	1.375	1.427
H1–C2	1.056	1.049	1.049	1.063	1.056	1.049	1.049	1.063	1.469[f]	1.465[f]	1.464[f]	1.431[f]	1.431[f]	1.423[f]	1.466[f]
S–H2	1.322	1.310	1.334	1.235	1.765[g]	1.737[g]	1.815[g]	1.780	1.322	1.311	1.334	1.235	1.763[g]	1.651[g]	1.741[g]
Bond Angles (deg)															
H1–C2–C3	181.4	179.8	179.9	179.3	180.1	149.8	179.9	179.4	180.2[h]	179.7[h]	179.8[h]	179.2[h]	179.2[h]	180.0[h]	178.3[h]
C2–C3–O1	180.1	181.3	180.9	184.7	181.7	181.1	180.8	184.8	181.4	181.6	181.1	185.0	185.1	185.3	174.7
C3–O1–S	119.0	124.7	123.7	119.9	119.8	124.4	123.3	119.4	118.6	124.0	122.4	119.6	118.8	117.3	117.6
H2–S–O1	98.1	92.00	90.1	93.8	100.5[i]	95.0[i]	92.6[i]	95.8[i]	98.3	92.2	90.4	93.8	95.6[i]	98.9[i]	102.4[i]
O1–S–O2	104.4	108.8	109.7	107.4	103.6	108.0	107.7	107.3	104.6	109.1	110.1	107.5	104.7	104.7	
O2–S–O3	123.6[j]	121.5	120.7	119.4	122.2[j]	120.3	119.1	120.5	123.3[j]	121.3	120.5	119.2	120.0	119.7	121.8
Dihedral Angles (deg)															
H2–S–O1–C3	69.6	179.9	180.0	180.0	76.4[k]	179.9[k]	180.0[k]	179.4[k]	67.8	180.0	180.0	180.1	180.0[k]	179.9[k]	72.2[k]
S–O1–C3–X	0.0	–0.5	–0.5	0.0	2.1	6.6	1.2	0.0	–0.1	0.0	0.0	0.0	0.0	0.0	0.0
O2–S–O1–H2	112.7	112.9	112.6	115.2	113.8[l]	114.2[l]	114.4[l]	114.6[l]	112.8	112.7	112.6	115.2	115.1[l]	116.7[l]	116.7[l]
O3–S–O1–H2	246.7	247.4	247.4	244.8	244.9[m]	245.6[m]	245.6[m]	245.4[m]	246.7	217.3	247.4	244.8	244.9[m]	243.3[m]	245.3[m]
total energies[b]	–698.797 38 –699.710 27[p]	–695.319 07	–695.021 17	–50.0[n]	–737.853 85	–734.167 44	–733.878 18	–55.2[n]	–737.843 95	–734.149 68	–733.851 79	–60.1[n]	–40.0[n]	–30.9[n]	

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[a] For the most stable conformation. Structures are fully optimized; only selected parameters are given. [b] In hartrees. [c] In kilocalories per mole. [d] Atom numbering according to Figure 5. [e] The plane of the phenyl ring is rotated by 90° relative to the plane of the acetylenic skeleton except for AM1 where it is in this plane. [f] The C1–C2 bond length. [g] The S–C5 bond length. [h] The C1–C2–C3 bond angle. [i] The C5–S–O1 bond angle. [j] The O1–S–O3 bond angle in 7, 8, and 9 is 109.2, 108.2, and 109.5, respectively. [k] The C5–S–O1–C3 dihedral angle. [l] The O2–S–O1–C3 dihedral angle. [m] The O3–S–O1–C3 dihedral angle. [n] Heat of formation (kcal mol^{-1}). [p] MP3/6-31G*//6-31G*.

Table XI. Optimized Geometries,[a] Total Energies,[b] and Heats of Formation[c] for Alkynyl Benzoates **5**, **6**, and **10–12**

	10				**11**		**12**		**5**			**6**		
geometric parameters[d]	MP2/6-31G*	6-31G*	3-21G	PM3	3-21G	PM3	3-21G	PM3	PM3	AM1	exptl	PM3	AM1	exptl
					Bond Lengths (Å)									
C2–C3	1.213	1.179	1.182	1.190	1.182	1.191	1.187	1.191	1.191	1.193	1.150	1.191	1.194	1.155
C3–O1	1.331	1.312	1.321	1.335	1.319	1.333	1.328	1.335	1.335	1.332	1.329	1.334	1.332	1.366
O1–C4	1.390	1.354	1.382	1.377	1.403	1.393	1.383	1.377	1.393	1.403	1.414	1.391	1.399	1.349
C4–O2	1.201	1.170	1.186	1.201	1.189	1.208	1.187	1.202	1.209	1.227	1.201	1.207	1.226	1.201
C4–H2	1.094	1.071	1.080	1.097	1.493[e]	1.500[e]	1.071	1.097	1.484[e]	1.466[e]	1.438[e]	1.490[e]	1.472[e]	1.48[e]
H1–C2	1.065	1.056	1.049	1.064	1.049	1.064	1.465[f]	1.431[f]	1.064	1.058		1.431[f]	1.424[f]	1.44[f]
					Bond Angles (deg)									
H1–C2–C3	179.6	180.0	180.2	179.9	180.2	179.9	180.4[g]	180.0[g]	179.9	180.6		180.1[g]	180.9	178.5
C2–C3–O1	183.3	183.0	180.8	184.7	180.7	184.9	181.0	184.6	185.0	184.9	177.6	184.9	184.5	178.0
C3–O1–C4	116.0	118.9	122.6	118.7	122.4	117.6	122.4	118.7	117.3	117.6	116.1	117.2	117.5	115.0
O1–C4–O2	125.4	124.5	125.4	121.4	121.8	119.6	124.7	121.5	119.4	117.9	118.7	120.6	118.7	123.2
O1–C4–H2	127.5	108.1	107.1	107.5	107.8	111.3	107.3[f]	107.5[h]	111.9[h]	112.6	112.1	111.2[h]	112.4[h]	111.5[h]
total energies[b]	−265.141 04	−264.398 93 −265.117 99[i]	−262.925 37	−16.1[c]	−301.760 62	−23.0[c]	−301.754 74	−26.3[c]	13.0[c]	21.4[c]		−3.7[c]	16.9[c]	

[a] For the most stable conformation. Structures are fully optimized. [b] In hartrees. [c] In kilocalories per mole. [d] Atom numbering according to Figure 5. (Figure 2 for **5** and **6**). [e] The C4–C5 bond length. [f] The C1–C2 bond length. [g] The C1–C2–C3 bond angle. [h] The O1–C4–C5 bond angle. [i] MP3/6-31G*//6-31G*, −265.114 34 at MP2/6-31G*//6-31G*.

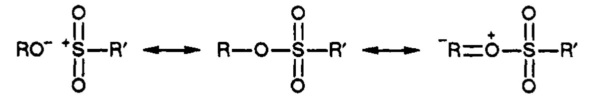
Table XII. Calculated Energies (kcal mol^{-1}) of Equations 1–7 at MP3/6-31G*, PM3, and AM1 (Experimental Values Are Given in Parentheses)[a]

	R								
	$-C{\equiv}CH$			$-CH{=}CH_2$			CH_3		
eq	MP3/6-31G*	PM3	AM1	MP3/6-31G*	PM3	AM1	MP3/6-31G*	PM3	AM1
1	−7.7	0.0	−0.4	−4.1	−7.6	−7.3	3.5	−5.8	−2.8
2	−7.2	−1.4	−4.5	−2.9 (0.0)[b]	−8.3	−9.3	3.0 (4.1)[c]	−5.9	−4.1
3	−2.4	18.4	14.2	1.1	10.8	7.3	8.8	12.6	11.8
4	2.8	18.9	6.9	7.2 (5.9)	12.0	2.6	12.9 (10.9)	14.4	7.8
5	−30.7	−12.5	−24.1	−17.3	−2.3	−11.4	−21.8	−6.9	−8.6
6	−30.3	−13.9	−28.7	−16.1 (−15.6)	−3.0	−13.4	−22.4 (−23.3)	−7.0	−9.9
7	−23.0	−12.5	−23.7	−13.3 (−14.6)[d]	5.7	−4.1	−25.4 (−27.5)	−1.1	−5.8

[a] Experimental heats of formation (in the gaseous phase) of the molecules that appear in the isodesmic equations were taken from ref 34. [b] For $CH_3COOCH{=}CH_2$. [c] 4.6 kcal mol^{-1} for CH_3COOCH_3. [d] Using $\Delta H_f°$ of −30.6 kcal mol^{-1} for $CH_2{=}CHOH$; see: Guthrie, J. P. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 2.

(the range is 0.117 Å for the sulfonate esters and 0.107 Å for the carboxylate esters) and the O—SO_2R' (or O—C(=O)R′) bond length decreases (the range is 0.056 Å for the sulfonates and 0.037 Å for the carboxylates) as the hybridization of the carbon atom in R is changed from sp (R = CH≡C) to sp^2 (R = $CH{=}CH_2$) to sp^3 (R = CH_3). In both ester groups, the changes in the R—O distances as a function of R are larger than in the O—S (or O—C) bonds. Yet the changes in the more remote O—S (or O—C) bonds are significant and somewhat unusual.[28]

These changes in the bond distances are best understood in terms of the hybridization of the C atom forming the R—O bond and in the effect of the electronegativity of the R substituent on the hybridization at oxygen. Thus, on going along the series $CH_3 \rightarrow H_2C{=}CH \rightarrow HC{\equiv}C$, the hybrid orbital used by carbon to form the C—O bond acquires a higher s character and consequently the bond shortens.[28] Very similar changes have been observed in the C—X bond distance in the analogous series $CH_3CH_2X \rightarrow H_2C{=}CHX \rightarrow HC{\equiv}CX$.[29] The changes in the more remote O—S or O—C(=O) bonds result from the fact that the ethynyl group is significantly more electron withdrawing than the vinyl group, which in turn is more electron withdrawing than methyl (the corresponding σ_I and $\sigma_R°$ values are 0.30, 0.08, and 0.02, respectively, and 0.07, −0.05, and −0.10, respectively[30]). As electron withdrawal by R increases, the oxygen becomes more electronegative and according to Bent's rule[31] its bonds acquire a higher p character and the O—S (or O—C(=O) bond lengthens. This substituent effect can be described also in terms of increased weight of the ionic resonance structure **19B** when



$$RO^- \; {}^+S(=O)_2-R' \longleftrightarrow R-O-S(=O)_2-R' \longleftrightarrow {}^-R{=}O^+-S(=O)_2-R'$$

19B **19A** **19C**

the electron-withdrawing ability of R increases, making RO$^-$ a more stable species.[10b] Analysis of the C—O bond lengths of 2367 ethers and esters of type R—O—X have also shown R—O bond lengthening with increasing electronegativity of X.[32] For R = CH_3, the bond length range is from 1.418 Å where X is alkyl to 1.450 Å where X is COR (1.450–1.475 Å for R = *t*-Bu).[32] We note that rationalization of these bond lengths changes in terms of resonance structures **19A** and **19C** (see ref 11 for such a discussion of the carboxylate esters) is less satisfactory.

The C(sp)—O bond lengths (and also the C≡C distances) are almost identical in the analogous sulfonate and the carboxylate esters; (e.g., compare these bond lengths in **4** and **5** (experimental) or in **7** and **10** (calculated)), although a sulfone group is a stronger electron withdrawing substituent than an acyl group (e.g., the corresponding σ_I and $\sigma_R°$ values are[30] 0.64 and 0.07, respectively, for SO_2CH_3 and 0.29 and 0.22, respectively, for $C(=O)CH_3$).

In Figure 6, we present the electron distribution in the alkynyl, vinyl, and methyl sulfonate esters as calculated at the 6-31G* level by using the Mulliken population analysis method.[18,33] Comparison of the charge distribution in the sulfonate esters shows

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(27) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Bramner, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19. (b) 1.433 Å in $CH_3OSO_2CH_3$.[26] (c) 1.579 Å in $CH_3OSO_2CH_3$.[26]

(28) Smaller substituent effects on remote bond lengths are usually found. See, for example: (a) Topsom. *Prog. Phys. Org. Chem.* **1987**, *16*, 86; (b) Krygowski, T. M. *Ibid.* **1990**, *17*, 239.

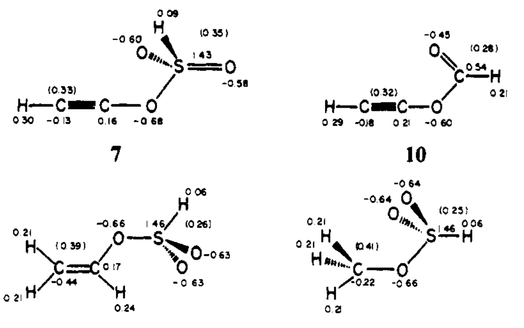
(29) Legon, A. C.; Millen, D. J.; Samson-Baktiari, A. *J. Mol. Struct.* **1979**, *52*, 71.

(30) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1978; Chapter 10. Similar values based on a statistical triparameter relationship were more recently reported: Charton, M. *Prog. Phys. Org. Chem.* **1987**, *16*, 287.

(31) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(32) Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197.

(33) We are aware of the many pitfalls of the Mulliken population analysis, but we choose to include this information because the trends observed for closely related compounds such as **7**, **13**, and **14** are probably meaningful.[23]



7 **10** **13** **14**

Figure 6. Calculated total charges (6-31G*) in sulfonate esters **7**, **13**, and **14** and in ethynyl formate (**10**). Values in parenthesis are the net total charges on the SO_2H group or on the R groups (R = CH_3, $CH{=}CH_2$, $C{\equiv}CH$).

that the positive charge on the substituent decreases on going from methyl to vinyl to ethynyl while the positive charge on the SO_2H group increases along this series, as expected on the basis of the σ values of R.[30]

2. Thermodynamic Stabilities. At present, experimental data on the thermodynamic stabilities of alkynyl esters are not available, and therefore, theory was used to obtain this information. The computational results for eqs 1–7 and the related (limited) available experimental data[34] (for vinyl and alkyl carboxylate esters) are given in Table XII. Table XII shows that the ab initio and the semiempirical predictions are very different, and we base the discussion below on the ab initio results that we believe to be the more reliable (see discussions below).

Equation 1 gives the energy changes involved in the hydrolysis of the parent alkynyl, alkenyl, and alkyl sulfonate esters. Similarly, eq 2 gives the energy changes for the hydrolysis of the corresponding carboxylate esters.

$$HSO_2\text{–}OR + H_2O \rightarrow HSO_2OH + ROH \qquad (1)$$

$$HCO\text{–}OR + H_2O \rightarrow HCOOH + ROH \qquad (2)$$

The sulfonate and carboxylate esters behave similarly. The hydrolysis energies become more exothermic on going from the alkyl (where it is moderately endothermic), to alkenyl, to the alkynyl esters. This suggests that, as the hybridization of the alkyl carbon changes from sp^3, to sp^2, to sp, the thermodynamic stability of the ester toward hydrolysis decreases. The acetylenic ester is the least stable, in accord with experimental observations.[8,33] Thus, alkynyl, and to a lesser extent, alkenyl esters are destabilized by the interaction of R with the electronegative ester group. Note that the exothermicities of the hydrolysis reactions parallel the trends observed in the RO—S and RO—C bond distances (Chart I). We note that the MP3/6-31G* calculated hydrolysis energies of $HCOOCH_3$ and of $HCOOCH{=}CH_2$ are in good agreement with the available thermochemical data (Table XII).[34] The hydrolysis energies of the parent alkynyl sulfonate and alkynyl carboxylate esters are very similar, also in accord with experimental observations.[8,35]

The hydrogenation eqs 3 and 4 compare the RO—S and RO—C bond energies, respectively, with the corresponding RO—H and S—H (eq 3) or C—H (eq 4) bonds. These reactions are less exothermic (in fact, these equations are endothermic except for eq 3; R = $C{\equiv}CH$) than the corresponding hydrolysis reactions (eqs 1 and 2). Note, however, that the hydrogenation equations give essentially the same information as the corresponding hydrolysis reactions on the effect of R on the strengths of the S—OR and C—OR bonds.[36]

$$HSO_2\text{—}OR + H_2 \rightarrow HSO_2\text{—}H + H\text{—}OR \qquad (3)$$

$$HCO\text{—}OR + H_2 \rightarrow H(O{=})CH + H\text{—}OR \qquad (4)$$

The hydrogenation reactions 5–7 compare the strength of the R–O bond in the various sulfonate (eq 5) and carboxylate (eq 6) esters and in the corresponding alcohols (eq 7) with the strength of the corresponding R–H bonds. Equations 3–7 are not isodesmic, but the comparisons between the different R substituents (e.g., the relative hydrogenation energies of **7** and **13**) are isodesmic, so that the calculated relative energies of these equations (Table XII) are expected to be reliable, in particular with the correlated MP3/6-31G*//6-31G* level of theory.[23] The limited experimental gas-phase thermochemical data that are available (values in parenthesis in Table XII) are in good agreement with the theoretical ab initio results, lending support to the reliability of these calculations also in cases where experimental data are not available, in particular for the sulfonate esters.

$$HSO_2O\text{-}R + H_2 \rightarrow HSO_2H + H\text{-}R \qquad (5)$$

$$HCOO\text{-}R + H_2 \rightarrow HCOOH + H\text{-}R \qquad (6)$$

$$HO\text{-}R + H_2 \rightarrow HOH + H\text{-}R \qquad (7)$$

The hydrogenation energies of the sulfonate and the carboxylate esters (eqs 5 and 6) are all exothermic, and they change similarly and quite significantly as a function of R, following the order alkynyl (most exothermic, ca. 30 kcal mol^{-1} for **7** and **10**) > CH_3 > vinyl (least exothermic). Thus, the stability of the C—O bond toward hydrogenation decreases along the series $H_2C{=}CH\text{—}O$ (most stable) > $CH_3\text{—}O$ > $HC{\equiv}C\text{—}O$, the alkynyl esters being the least stable. The alcohols behave differently; their hydrogenation energies (eq 7) follow the order methyl (most exothermic) > alkynyl ≫ vinyl (least exothermic).[37,38] It is particularly curious (but supported experimentally, Table XII) that the hydrogenation of CH_3OH to CH_4 is more exothermic by 12.1 kcal mol^{-1} than hydrogenation of $H_2C{=}CHOH$ to $CH_2{=}CH_2$, pointing to strong stabilizing interactions between the hydroxy substituent and the organic skeleton in $CH_2{=}CHOH$ (e.g., n–π^* interactions) relative to the interactions in CH_3OH. In $HC{\equiv}C\text{—}OH$, these stabilizing interactions are apparently much less effective and eq 7 is significantly more exothermic than for $CH_2{=}CHOH$.

The fact that the hydrogenation energies of the alkynyl sulfonate and carboxylate esters are by 8.9 and 7.9 kcal mol^{-1} more exothermic than those of the corresponding methyl esters while the hydrogenation energies of CH_3OH and $HC{\equiv}COH$ are similar points to a considerable weakening of the alkynyl-oxygen bond when the hydrogen in ROH is substituted with the electron-withdrawing ester groups—placing two strongly electron withdrawing groups on the same oxygen.

The semiempirical methods, both AM1 and PM3, give reaction energies that are in general in poor agreement, quantitatively as well as qualitatively,[24] with the ab initio calculations (Table XII). For example, according to AM1 and PM3, the hydrolysis energies of the esters are most exothermic for R = vinyl, while according to the MP3/6-31G* calculations it is most exothermic for R = alkynyl. Furthermore, according to the semiempirical method, the hydrogenation energies (eqs 5–7) are generally by 10–17 kcal mol^{-1} less exothermic than those of the MP3/6-31G* calculations. Which calculations are more reliable? The available (limited) experimental data are in poor agreement with the semiempirical results but in very good agreement with the MP3/6-31G* values (Table XII). For example, the experimental hydrogenation energies (kcal mol^{-1}) of vinyl and methyl formate are −15.6 and −23.3 respectively, while PM3 gives −3.0 and −7.0, respectively, AM1 produces −13.4 and −9.9, respectively, and MP3/6-31G* yields

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[34] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

[35] We realize, of course, that the rate of hydrolysis is not necessarily determined or affected by the thermochemistry of the process.

[36] In fact, the energy differences between eqs 2 and 4 or between eqs 1 and 3 (given by the equations $H_2O + H_2C{=}O \rightarrow H_2 + HCOOH$ (ΔH(exptl) = −6.8 kcal mol^{-1})[34] and $H_2O + HSO_2H \rightarrow H_2 + HSO_2OH$, respectively) are a constant.

[37] The fact that the energies of equs 1–4 on one hand and of eqs 5–7 on the other hand show a different qualitative dependence on the nature of R reflects mainly the fact that, in the first group of equations, the R–O bond appears on both sides of the equations while in eq 5–7 a C–O bond is compared with an R–H bond.

[38] There is no correlation between either of these energy trends and the R–O bond length (Chart I).

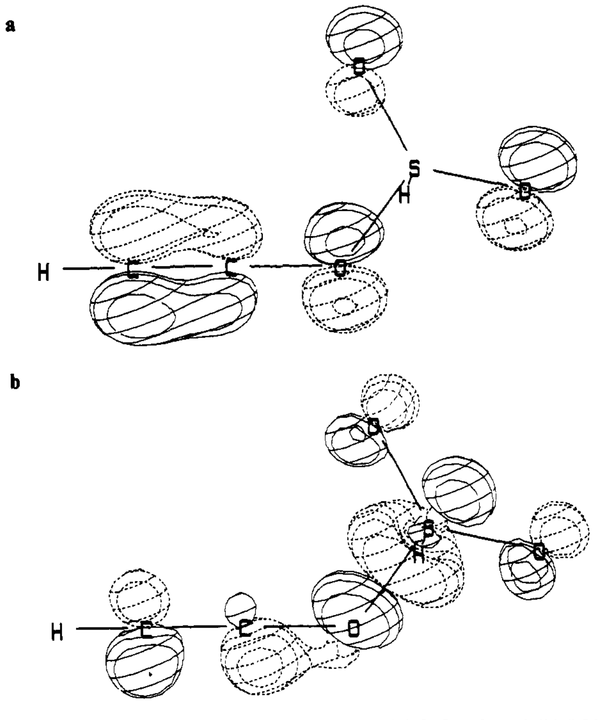

Figure 7. STO-3G contour diagrams of the (a) HOMO and (b) LUMO of ethynyl sulfonate (7).

−16.1 and −22.4, respectively (Table XII). The failure of the semiempirical methods is not surprising in view of their poor reproduction of heats of formation of simple molecules such as hydrogen and methanol that participate in these equations.[17a,b] The data in Table XII demonstrate the great caution that should be exercised[24] in the application of semiempirical methods, and it stresses the higher reliability of systematic ab initio studies.

The shape and energies of the frontier molecular orbitals of the alkynyl sulfonate **7**, which are shown in Figure 7, are also of interest in this context (the frontier orbitals of **10** are given in ref 11). The HOMO (Figure 7a) is composed of the antibonding combination between the acetylenic π-bond and the 2p lone-pair orbital on the oxygens, and it is polarized toward the β-carbon, thus favoring electrophilic attack at this site.[5,39] The calculated (6-31G*) ionization potential (IP) of **7** (using Koopmans' theory[40]) is 11.3 eV, 0.3 eV (6.9 kcal mol^{-1}) higher than the calculated IP of acetylene. In contrast, the IP of **10** is by 7.1 kcal mol^{-1} lower than the IP of acetylene. This can be understood in terms of the σ_I and σ_R values of the OSO_2R and OC(=O)R groups[30] (see above). The energy difference between the IPs of the alkynyl and alkenyl systems, which is 18.9 kcal mol^{-1} for acetylene and ethylene (acetylene being lower) is slightly smaller in the sulfonate esters, i.e., 16.7 kcal mol^{-1}, but larger (24.6 kcal mol^{-1}) for the carboxylate esters.

The LUMO (Figure 7b) is a combination of the σ^*(S—O) antibonding orbital with the in-plane π^*(C≡C) orbital, having bonding character between the α-carbon and oxygen. The larger coefficient at sulfur than at the C≡C bond suggests that nucleophilic attack on alkynyl sulfonates should occur mainly at sulfur. This is consistent with the fact that the reaction of alkynyl tosylates with methyllithium leads to cleavage of the S—O bond, while products resulting from attack of MeLi at the acetylenic bond (e.g., the corresponding methyl-substituted acetylenes) are not observed.[4] The LUMO of **7** is by 3.5 kcal mol^{-1} (6-31G*) higher in energy than the LUMO of **13**, suggesting that alkenyl sulfonate should undergo nucleophilic attack somewhat faster than the corresponding alkynyl sulfonates.

B. Alkynyl Carboxylic Esters. In our previous paper, we have pointed out the discrepancies between the calculated structures of the model alkynyl carboxylic esters **10–12** and the X-ray structure of **6**.[11] The major difference was found in the C(sp)—O distance—the most interesting bond in this novel molecule. The calculated C(sp)—O bond in **10** (1.312 Å at 6-31G*) was much shorter (by 0.054 Å) than the measured distance in **6** (1.366 ± 0.009 Å).[11] Corrections that may result from the inclusion of electron correlation, temperature effects, or the presence of the *p*-nitrophenyl substituent were estimated to be too small (i.e., 0.01–0.02 Å) to explain the experimental–computation gap.[11] A smaller difference of 0.024 Å between the calculations and experiment existed also for the C≡C bond (e.g., 1.175 Å in **10**, compared to 1.155 ± 0.009 Å in **6**[11]). These discrepancies between theory and experiment remained unclear.[11,12]

The new structural data for the alkynyl benzoate ester **5** as well as for the sulfonate ester **4** allows now resolution of this discrepancy in favor of theory. The X-ray data for **5** and **4** are in excellent agreement with the calculations, in particular for the C(sp)–O bond. Thus, the measured C(sp)–O bond length in **5** is 1.329 ± 0.004 Å (1.331 ± 0.004 Å in **4**), compared with the MP2/6-31G* value of 1.331 Å calculated for **10**.[41] The relatively long C(sp)–O bond length that was determined for **6**[11] probably resulted, as we have speculated, from inaccuracies in the experimental determination.[11,12]

The experimental–theoretical difference regarding the C≡C bond distance remains; the experimental C≡C distance in **5** of 1.150 ± 0.004 Å (1.159 Å in **4**) is significantly shorter than the calculated values in **10** (1.213 Å at MP2/6-31G*, 1.179 Å at 6-31G*). The experimental C≡C distance in the alkynyl esters **4–6** is also significantly shorter than the average C≡C bond length of 1.181–1.183 Å found in 350 acetylenes.[27a]

The C4–O1 acyl–oxygen bond length in **5** is 1.414 ± 0.003 Å, significantly longer than the average value of 1.349 ± 0.009 Å found previously in **6**.[11] The MP2/6-31G* calculated value of 1.390 Å is in better agreement with the longer C4–O1 bond length measured for **5**.[42] The agreement is further improved if the bond elongation effect of 0.021 Å by methyl substitution at the carbonyl (based on comparison of the C4–O1 distance in **10** and **11**) is included.[43] The acyl–oxygen bond in **5** is one of the longest bonds of this type known (the average acyl–oxygen bond length measured in 26 vinylic esters is 1.362 Å; only in 7 structures is this bond length longer than 1.374 Å).[27] This fact is also in full agreement with the calculations (Chart I).

Conclusions. Single-crystal molecular structure determinations are reported for propynyl tosylate, **4**, and enthynyl benzoate, **5**, and compared to theoretical calculations. Both esters are linear acetylenes with remarkably similar C_{sp}–O bond lengths of 1.331 and 1.329 Å, respectively, in excellent agreement with ab initio theoretical calculations. Ab initio molecular orbital calculations (6-31G*) reproduce structural trends as a function of R (R = alkyl, vinyl, alkynyl) for both sulfonate and carboxylate esters remarkably well (as do the PM3 and AM1 semiempirical methods). The calculated 6-31G* HOMO and LUMO orbital coefficients nicely account for the known reactivity of these two classes of alkynyl esters. Ab initio, 6-31G* calculations, in contrast to the PM3 and AM1 semiempirical methods, accurately account for the hydrolysis and hydrogenation behavior of sulfonate and carboxylate esters, pointing to the fact that alkynyl esters are

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(39) The fact that electrophilic addition to C_β leads to a more stable vinyl cation than addition to C_α probably plays the major role in dictating this regiochemistry. See: Stang, P. J.; Roberts, K. A. *J. Org. Chem.* **1987**, *52*, 5213.

(40) Koopmans, T. *Physica* **1933**, *1*, 104.

(41) (a) MP2/6-31G* geometry optimizations were beyond our capabilities when ref 11 was written. (b) The effect of electron correlation on the C(sp)—O and C≡C bond lengths in **10** is similar to that found previously in HC≡COH, on which we based our previous predictions.[11]

(42) The effect of electron correlation on this bond length is particularly large,[23] i.e., lengthening by 0.036 Å. It can be expected that electron correlation will have a similar effect on the acyl–oxygen bond length also in other esters, e.g., vinyl and alkyl esters (see Chart I); e.g., in H_2C=CHOC(=O)H, the acyl–oxygen bond length is 1.327 Å at 6-31G*, 0.023 Å shorter than the experimental value of 1.350 Å.[11] Interestingly, the AM1 and PM3 calculated esteric C—O bond lengths in **5** of 1.403 and 1.393 Å, respectively, are in better agreement with the experimental values than the HF/6-31G* values.

(43) Substitution of methyl with a phenyl group has no effect on the C–O bond distance (compare the PM3 or AM1 calculations for **5** and **11**; Table XI).

thermodynamically less stable than the corresponding alkenyl and alkyl esters.

Experimental Section

A. Preparation of 1-Propynyl Tosylate.[1] Phenyl(propynyl)iodonium tosylate[1] (5.0 g, 12 mmol) was decomposed in a solution of silver tosylate (0.1 g) in CH_2Cl_2 (50 mL). Decomposition was complete in 3 h. The solvent was removed in vacuo, and the residue was taken up in CH_2Cl_2/hexanes, filtered, concentrated, and chromatographed on silica gel (15 g). The column was eluted first with hexanes and followed with 10%, 20%, and 50% CH_2Cl_2 in hexanes. The fractions containing the product were combined and concentrated to give an oil (0.81 g, 32% yield), which solidified upon cooling (10 °C). The product was then recrystallized several times from hot pentane (mp 21 °C). X-ray quality crystals were obtained by slowly cooling a concentrated solution of propynyl tosylate in pentane to −20 °C.

B. Preparation of Ethynyl Benzoate. (Phenylethynyl)iodonium triflate[44] (3.78 g, 10 mmol) was dissolved in 50 mL of methylene chloride and cooled to 0 °C in an ice–water bath. A solution of sodium benzoate (5.76 g, 40 mmol) in 40 mL of water was added, and the mixture was stirred vigorously for 2 min. The organic phase was separated, and the aqueous phase was extracted with additional methylene chloride. The combined organic phase was dried over $MgSO_4$ and concentrated. The resulting oil was chromatographed on silica. The column was eluted at first with hexanes followed with 20% CH_2Cl_2 in hexanes. The fractions containing ethyl benzoate were combined and concentrated. The resulting solid was then recrystallized from pentane to give 0.59 g (40% yield) of product. A concentrated solution of ethynyl benzoate in pentane at room temperature was cooled to −20 °C to yield X-ray quality crystals.

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Registry No. 4, 94957-44-5; **5**, 130468-62-1; **6**, 113779-41-2; **7**, 135074-94-1; **8**, 135074-95-2; **9**, 135074-96-3; **10**, 123812-75-9; **11**, 83313-98-8; **12**, 123812-74-8; **13**, 135074-97-4; **14**, 135074-98-5; phenyl(propynyl)iodonium tosylate, 94957-41-2; phenyl(ethynyl)iodonium triflate, 125803-61-4.

Supplementary Material Available: Details of the X-ray crystal and structural data for compounds **4** and **5** (25 pages); listing of calculated and observed structure factors for **4** and **5** (8 pages). Ordering information is given on any current masthead page.

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[44] Stang, P. J.; Arif, A. M.; Crittell, C. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 287.

Free Energy and Solvent Dependence of Intramolecular Electron Transfer in Donor-Substituted Re(I) Complexes

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Abstract: A comprehensive investigation of photoinduced intramolecular electron transfer (ET) in a series of six complexes of the type *fac*-(b)$Re^I(CO)_3$–D (where b is a diimine ligand and D is a dimethylaniline electron donor) is reported. Photoexcitation of the dπ (Re) → π^* (diimine) metal-to-ligand charge-transfer excited state initiates a sequence of forward and back ET reactions:

$$(b)Re^I(CO)_3\text{–}D \xrightarrow{h\nu} (b^-)Re^{II}(CO)_3\text{–}D \xrightarrow[\Delta G_{FET}]{k_{FET}} (b^-)Re^I(CO)_3\text{–}D^+ \xrightarrow[\Delta G_{BET}]{k_{BET}} (b)Re^I(CO)_3\text{–}D$$

The driving force for forward and back ET (ΔG_{FET} and ΔG_{BET}, respectively) is varied by changing the electron demand of the diimine ligand. Cyclic voltammetry and steady-state emission studies were carried out for each complex in three solvents (CH_2Cl_2, DMF, and CH_3CN) to allow estimation of ΔG_{FET} and ΔG_{BET}. The forward ET reactions are weakly exothermic (-0.5 eV < ΔG_{FET} < -0.1 eV) and the back ET reactions are highly exothermic (-2.6 eV < ΔG_{BET} < -1.5 eV). Rates for forward ET (k_{FET}) for each of the complexes in the three solvents were determined by using time-resolved emission spectroscopy. The forward ET rate ranges from $10^7\ s^{-1}$ to $>10^9\ s^{-1}$ and is strongly dependent on ΔG_{FET} and solvent polarity. The dependence of k_{FET} on ΔG_{FET} is consistent with nonadiabatic semiclassical Marcus theory. The solvent dependence of k_{FET} suggests that the reorganization energy increases with solvent polarity in a manner that is consistent with the Marcus–Hush dielectric continuum model. Rates for back ET (k_{BET}) were determined by using laser flash photolysis in two solvents. The back ET rate ranges from $10^7\ s^{-1}$ to $5 \times 10^8\ s^{-1}$ and is not solvent dependent. Interestingly, k_{BET} displays a weak, inverted dependence on ΔG_{BET}. Analysis of the rate data using a multimode quantum mechanical expression suggests that a possible explanation for the weak free-energy dependence may be that metal complex-based high-frequency acceptor modes are coupled to the back ET process.

Introduction

The importance of electron transfer (ET) in a variety of chemical, biological, and physical processes has stimulated much interest in the factors that control ET between molecular sites.[1-4] Studies have examined the effects of free energy (ΔG_{ET}),[1-3,5-9] donor–acceptor electronic coupling,[1,2,10-37] and medi-

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