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Molecular Structure and Chemical Reactivity. X-ray Analyses and $^{13}C-^{19}F$ Coupling Constants of 1-Phenyl-2,2,2-trifluoroethyl Tosylates

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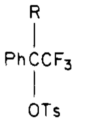
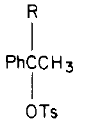
The X-ray structures and $^{13}C-^{19}F$ NMR coupling constants of the 1-phenyl-2,2,2-trifluoroethyl tosylates 1–4 are reported and the reactivities of these compounds are analyzed in terms of their molecular structures. Significant distortions from ideal tetrahedral geometries are observed, and some support is found for the proposal of Jones and Kirby of a direct relationship between reactivities and bond lengths to the substrate leaving groups. However limitations are also noted in the correlation of reactivities with bond angle and bond length distortions.

The solvolytic reactivities of the 1-phenyl-2,2,2-trifluoroethyl tosylates **1–4** have been under study in this laboratory,[1,2] and the relative rate data in Table I show several surprising trends in comparison to the model compounds **5–8**.[3-6]



$$\mathrm{PhC(R)(OTs)CF_3}$$

1, R = H
2, R = CH_3
3, R = CN
4, R = CF_3

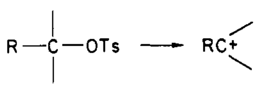


$$\mathrm{PhC(R)(OTs)CH_3}$$

5, R = CH_3
6, R = H
7, R = CN

$PhCH_2OTs$
8

There is an enormous spread of reactivities of 10^{18} between compound **5** with two CH_3 substituents and compound **4** with two CF_3 groups. The rate ratio $k(H)/k(CF_3)$ is 2×10^5 for **6**/**2** and 2×10^5 for **8**/**1**, and the $k(H)/k(CN)$ ratio is 90 for **6**/**7**. These ratios show very strong decellerating effects due to the CF_3 and CN groups in solvolysis reactions leading to carbocation intermediates (eq 1). This is expected from the strongly electron-withdrawing character of these groups, as measured for example by their σ_p^+ values of 0.61 and 0.66, respectively.[7] In other systems[1-3] these ratios can be as large as 10^7. The ratio $k(CN)/k(CF_3)$ is 2×10^3 for **7**/**2**; the greater reactivity of the cyano compound evidently arises from a resonance donation by this substituent (eq 2). This phenomenon has been postulated[2,3] to occur in situations of high electron demand and to reduce the electron-withdrawing tendency of this group.



(1)

(2)

Table I. Relative Solvolytic Reactivities of Benzylic Tosylates PhCRR′(OTs)[a]

R, R′	k_{rel}	R, R′	k_{rel}
CF_3, H (**1**)	4.4×10^{-6} [b]	CH_3, CH_3 (**5**)	2.4×10^{10} [e]
CF_3, CH_3 (**2**)	0.32[c]	CH_3, H (**6**)	6.1×10^{4} [f]
CF_3, CN (**3**)	6.1×10^{-7} [d]	CH_3, CN (**7**)	6.9×10^{2} [g]
CF_3, CF_3 (**4**)	1.2×10^{-8} [d]	H, H (**8**)	1.0[a]

[a] Rates are calculated relative to $PhCH_2OMs$ in HFIP at 25 °C (ref 5). Rates for OMs and OTs leaving groups were assumed to be equal, and rates in 97% HFIP or TFE were assumed to be equal to the rates in the pure solvents. HFIP is $(CF_3)_2CHOH$, TFE is CF_3CH_2OH, TFA is CF_3CO_2H, Ms is CH_3SO_2, Ts is *p*-$TolSO_2$. [b] Reference 1b. [c] Reference 1a. [d] Reference 1c, by comparison to the rate of **2** in TFA. [e] By comparison to the rate of **2** in HOAc with the rate for **5** in HOAc derived from the rate of the *p*-nitrobenzoate in 80% acetone (ref 6) and the relation $k_{HOAc}^{Ts} = (3.06 \times 10^{10})k_{80\%\ acetone}^{PNB}$ (Peters, E. N. *J. Am. Chem. Soc.* **1976**, *98*, 5627–5632). [f] By comparison to the rate of **2** in 100% EtOH with *k* (**6**, 100% EtOH) of 8.23×10^{-3} from Hoffmann, H. M. R. *J. Chem. Soc.* **1965**, 6753–6761. [g] Reference 3; by comparison to the rate of **2** in TFE.

When two destabilizing groups are present these rate ratios are surprisingly reduced, as manifested in the $k(H)/k(CF_3)$ ratio of 54 for **1**/**4** and $k(H)/k(CN)$ of 1.1 for **1**/**3** (in TFA),[1c] and we have found even smaller values for these ratios in other solvents and with different leaving groups.[1c] We have suggested[1c] three possible causes for these greatly diminished rate ratios, namely "strong electron donation by the group R, ground-state strain, and charge delocalization onto the aryl group". The possibility of ground-state strain can be elucidated by determination of the structural properties of **1–4** and two experimental methods that are particularly appropriate for this task are X-ray crystallography and NMR. We have previously[8] used the former method in the study of tri-*tert*-butylcarbinyl *p*-nitrobenzoate (**9**), a substrate which is known to have exceptionally high reactivity due to ground-state strain.[8] This topic of the correlation of ground-state structure and reactivity has become of considerable current interest[9] so an analysis of **1–4** seems especially timely. The use of NMR has proven to be of considerable utility in the

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(4) Available rate data from published sources have been adjusted to a common leaving group in a common solvent as noted in Table I. The use of other proportionality factors gives somewhat different quantitative results but the qualitative trends are the same.

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Table II. Crystal Data, Details of Intensity Measurements, and Structure Refinements for $PhCRCF_3OTs$ (1–4)

	1 (R = H)	2 (R = CH_3)	3 (R = CN)	4 (R = CF_3)
		Crystal Data		
system	monoclinic	monoclinic	triclinic	monoclinic
a, Å	16.807 (5)	12.298 (3)	7.467 (2)	15.126 (5)
b, Å	5.712 (4)	6.029 (2)	8.084 (2)	8.402 (1)
c, Å	17.329 (5)	21.452 (5)	15.007 (5)	13.172 (5)
α, deg	90	90	78.64 (3)	90
β, deg	112.15 (3)	100.92 (2)	83.78 (3)	101.84 (3)
γ, deg	90	90	66.79 (3)	90
U, Å^3	1540.7	1561.8	815.7	1638.5
fw	330.3	344.4	355.3	398.3
Z	4	4	2	4
D_c, g cm^{-3}	1.424	1.464	1.447	1.615
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
μ(Mo K$\bar{\alpha}$), cm^{-1}	2.4	2.4	2.3	2.6
reflectn used in cell determin, no./deg	25 $4.7 < \theta < 14.3$	25 $4.1 < \theta < 12.7$	25 $3.2 < \theta < 13.3$	25 $4.8 < \theta < 15.6$
	Intensity Measurements (θ:2θ mode, Mo Kα (λ 0.71069 Å, graphite monochromater)			
scan width, deg	1.00 + 0.35 tan θ	1.00 + 0.35 tan θ	0.95 + 0.35 tan θ	1.10 + 0.35 tan θ
max scan time, s	90	100	90	180
std reflectn, no./interval in s	3/8000	3/12000	3/12000	3/10000
max 2θ, deg	50	55	50	50
quadrants	$h,k,\pm l$	$h,k,\pm l$	$h,\pm k,\pm l$	$h,k,\pm l$
prescan rate, deg min^{-1}	20/2	20/1	20/2	20/3
$\sigma(I)/I$ ratio	0.03	0.04	0.04	0.04
total reflectn collect	3211	5016	3189	3419
unique data	2297	3574	2870	2869
		Details of Refinements		
no. of data in final refinemnt	1393 $F > 5\sigma(F)$	1667 $F > 4\sigma(F)$	1775 $F > 4\sigma(F)$	1511 $F > 3\sigma(F)$
R factors				
R_1	0.0518	0.0633	0.0459	0.0835
R_2	0.0597	0.0543	0.0458	0.0809
max shift/error	0.19	0.30	0.28	0.26
weighting scheme 1[a] value of p	0.055	0.03	0.03	0.07
esd obsd unit wt	1.393	1.391	1.415	1.367

[a] $w = 4F^2[\sigma(I)^2 + (pF^2)^2]^{-1}$.

Table V. Bond Angles (deg) and Distances at the Carbinyl Carbon for 1–4 and t-Bu_3COPNB (9)

	1	2	3	4	9
Ph–C–OTs	111.3 (3)	110.0 (3)	113.7 (2)	115.1 (5)	102.6[a]
CF_3–C–OTs	104.2 (4)	100.4 (3)	102.2 (2)	101.7 (5)	98.7[a]
R–C–OTs	107 (2)	112.7 (4)	110.2 (2)	107.6 (5)	112.5[a]
Ph–C–CF_3	113.8 (4)	110.0 (3)	111.2 (2)	109.1 (5)	113.8[b]
Ph–C–R	113 (2)	113.9 (4)	112.2 (2)	114.8 (6)	115.4[b]
CF_3–C–R	107 (2)	109.0 (4)	106.9 (2)	107.5 (6)	112.1[b]
max diff[c]	9.6	13.5	11.5	13.4	16.7
next diff[d]	6.0	3.7	5.3	7.3	11.2
		Distance, Å			
C–Ph	1.496 (5)	1.518 (5)	1.505 (3)	1.510 (8)	
C–OTs	1.453 (5)	1.457 (4)	1.432 (3)	1.436 (7)	
C–CF_3	1.491 (6)	1.511 (6)	1.533 (4)	1.536 (9)	
C–R		1.525 (6)	1.479 (4)	1.559 (9)	

[a] t-Bu–C–OPNB. [b] t-Bu–C–t-Bu. [c] Difference between the largest and smallest angles. [d] Difference between the second largest and second smallest angles.

study of strained structures,[8c] and measurement of the ^{13}C–^{19}F coupling constants[10] is particularly appropriate for the study of 1–4. Finally the study of these compounds is relevent to the general interest in the structure of organofluorine compounds.[11]

Results and Discussion

A summary of the crystallographic details for 1–4, the measured bond lengths, and the bond angles are given in Tables II, III, and IV, respectively (for Tables III and IV see supplementary material). The ORTEP structural representations are shown in Figure 1, and views along the S(1)–C(8) vector are given in Figure 2. In Table V there is presented a summary of the bond angles at the carbinyl cation in 1–4 along with those of 9.

Perhaps the most striking feature of these bond angles at the carbinyl carbon (C(8)) for structures 1–4 is their similarity, in that each has large deviations from the tetrahedral, with a notably compressed CF_3–C–O angle in each case. Even in the case of 1 where R is H this angle is reduced to 104.2°, and the angles between the hydrogen and the other three groups are all larger than 109°. Furthermore in all four compounds there is a significant difference between the largest and smallest angles observed

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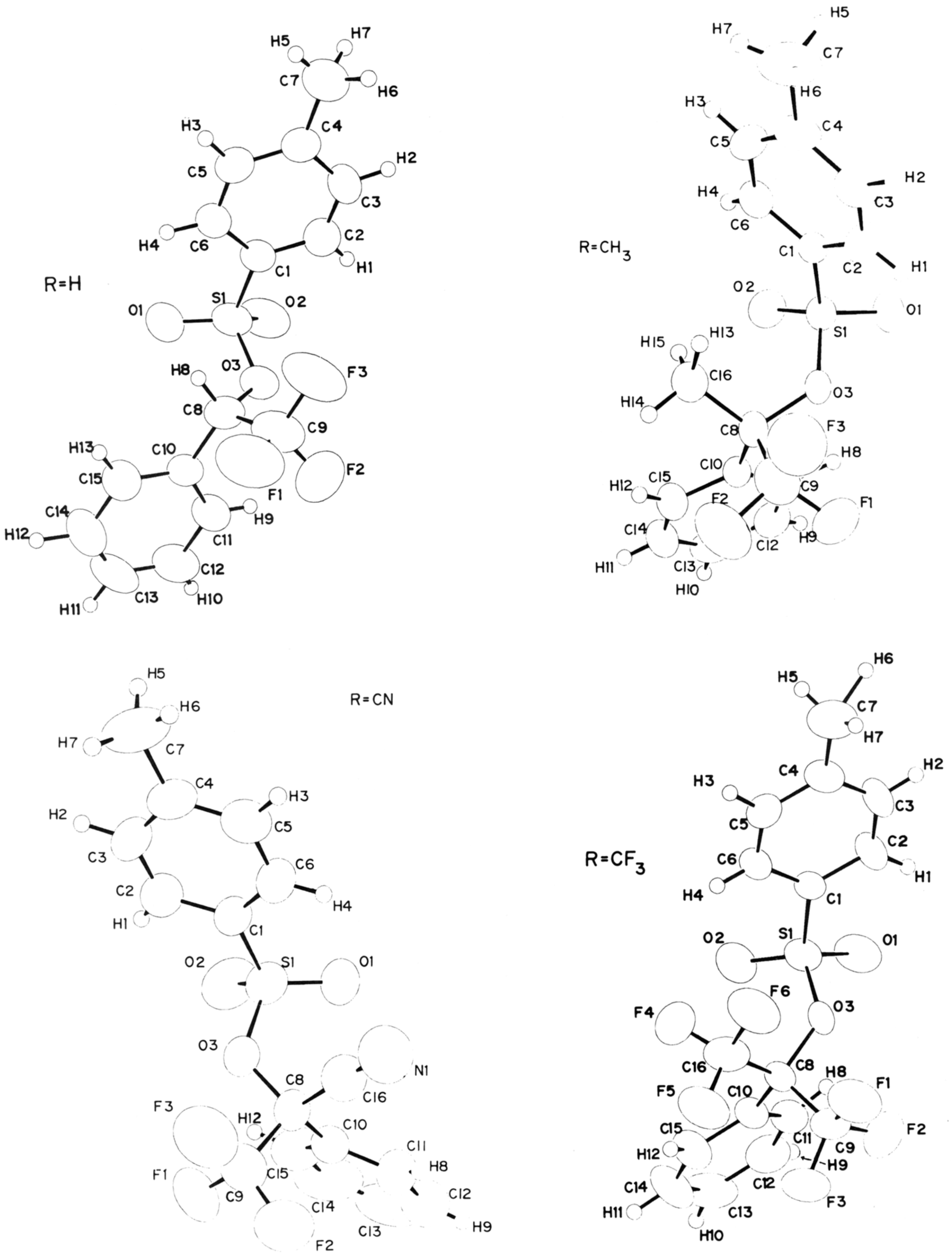
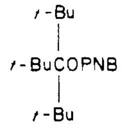


Figure 1. Parts a–d: ORTEP structural representations of **1**–**4**.

of 9.6° (**1**), 13.5° (**2**), 11.5° (**3**), and 13.4° (**4**) with an angle to the phenyl being the largest in each case. Overall there is no simple correspondence between these angles and the reactivity given in Table I, and further there is no great difference between the structure of **1**, the least crowded compound, and the structures of **3** and **4**.

The pattern of bond angles in **1**–**4** are in interesting contrast to those in **9**. This latter molecule has two compressed R–C–O angles of 98.7° and 102.6°, in contrast to the single compressed angle in **1**–**4**. It may be significant that this single small CF_3–C–O angle in 1–4 is opposite from the sulfonyl oxygens, suggesting that the repulsion between the three carbinyl substituents in 1–4 is best relieved by compressing this angle, which does not cause any added repulsion by the sulfonyl oxygens.

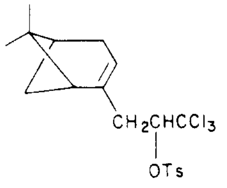


$(t\text{-Bu})_3\text{COPNB}$

9

The difference in the largest and smallest bond angles at the carbinyl carbon in **9** is 16.7°, and the difference between the next largest and smallest angles is 11.2°. These values are both much larger than the corresponding differences in 1–4, and it is surprising that **9**, which might have been expected to be more rigid and inflexible than 1–4, shows greater deviations from the tetrahedral.

For comparison the previously reported[12] molecular structures for secondary aliphatic arylsulfonate esters are summarized in Table VI (supplementary material). The sulfonate group is bonded to a cyclic structure in these cases with the notable exception of **10**.[12d] The difference between the largest and smallest angles at the carbinyl carbon for this compound was 5.3°, much less than the corresponding values for any of 1–4. The bond angles of the cyclic derivatives in Table VI are not directly comparable to the acyclic systems.



10

The conformations of **1** to **4** involve approximately staggered arrangements of the ligands bonded to S(1) and C(8) when viewed down the S(1)–C(8) vector, with the phenyl and tolyl groups approximately anti to one another with dihedral angles of 163.1° (**1**), 159.9° (**2**), −170.3° (**3**), and 159.2° (**4**) (Figure 2, Table VII (supplementary material)). Where 1–4 differ significantly is in the relative arrangement of the bridging atom O(3), and hence, its lone pairs, with respect to the ligands on S(1) and C(8). In **1** the lone pairs on O(3) are staggered with respect to two of the bonds S–C(1), S–O(1), and S–O(2), with the smallest dihedral angle of 40°, but are close to being eclipsed with the bonds C(8)–C(9 and C(8)–C(10) (smallest dihedral angle = 14°). Compound **2**, however, has the lone pairs on O(3) staggered with respect to the bonds to both S(1) and C(8) since the smallest dihedral angles involving bonds to S(1) and C(8) are 32° and 37°, respectively. In **3** and **4** the arrangement of the lone pairs is again different since they are virtually eclipsed with respect to the S–C and S–O bonds (largest dihedral angle = 6°) but are staggered with respect to the bonds to C(8) (smallest dihedral angle = 43°). This eclipsing is correlated with lengthening of the S(1)–O(3) bond lengths in **3** and **4** (1.619 (2) and 1.618 (4) Å, respectively) compared to those in **1** and **2** (1.577 (3) and 1.583 (3) Å, respectively), and an apparent shortening of O(3)–C(8) in **3** and **4** (1.432 (3) and 1.436 (7) Å) with respect to O(3)–C(8) in **1** and **2** (1.453 (5) and 1.457 (4) Å).

It is interesting to note that **1** and **2**, which are the most reactive compounds in this series (in HFIP, Table I) also have the longest C–OTs bonds, in agreement with the reported[9b] tendency for acetals that the more reactive compounds have longer bonds to the leaving group. However as **1** and **3** are close in reactivity, and as their relative reactivities are solvent dependent,[1c] this comparison must be applied with caution. For further comparison it may be noted from Table VI that cyclohexyl tosylate and the 3- and 4-*tert*-butylcyclohexyl tosylates[12a–d] have C–OTs bond distances of 1.474–1.503 Å that are significantly longer than those of 1–4. The solvolytic reactivity of cyclohexyl tosylate in TFA relative to 1–4 is 3×10^3, 5×10^{-3}, 3×10^3, and 1.4×10^4, respectively.[13] The greater reactivity of **2** relative to cyclohexyl tosylate, despite the longer C–OTs bond in the latter, is a definite exception to the correlation of leaving group bond length and reactivity[9b,i] and suggests this generalization does not apply in cases of significant structural variation.

The angular distortions around the sulfur atom involving O(3) are consistent with the longer S–O(3) bonds. Thus, in **3** and **4** the angles O–S–O(3) differ by up to 2.8° over corresponding angles in **1** and **2** with one angle increasing and the other decreasing in value. Similarly the C(1)–S–O(3) angles in **3** and **4** (101.4 (1)° and 101.2 (3)°) are smaller than those in **1** and **2** (104.0 (2)° and 103.1 (2)°) and O(1)–S(1)–O(2) angles in **3** and **4** are larger (121.7 (1)° and 121.0 (3)°) than those in **1** and **2** (120.2 (2)° and 119.9 (2)°).

The C–O–S angles for 1–4 of 118.3 (2)°, 125.5 (2)°, 122.0 (2)°, and 127.1 (4)° may be compared to the values of 118–124° in Table VI.[12] The largest of such angles which have been observed are for **2** and **4** and suggest that the widening of this angle helps to relieve some of the nonbonded interactions in these molecules, as is undoubtably also true for **9**,[8] which has a C–O–C angle of 132.8 (3)°.

There are several nonbonded contacts for each of 1–4 that are less than the sum of the van der Waals radii as included in Table VIII (supplementary material). The maximum difference from the van der Waals limiting distance is 0.48 Å. For comparison **9** possesses three H···H contacts of 2.0 Å and an O···H contact of 2.13 Å, all closer than any of the contacts in 1–4.

The C–CF_3 bond distances in 1–3 of 1.491 (6), 1.516 (6), and 1.533 (4) Å and those for **4** of 1.536 (9) and 1.559 (9) Å show significant differences particularly in the longer bonds for **3** and **4** which have two electronegative substituents. None of these bond lengths however approach the C-*t*-Bu bond lengths in **9** (average 1.618 (6) Å) or those in some crowded ethanes which have central C–C bonds as long as 1.64 Å.[9f] For comparison a reported[3b] structure of a system with the CF_3CH_2O grouping has a C–CF_3 bond length of 1.491 Å. The distinctly longer bonds in **3** and **4** could result from mutual $CF_3 \cdots CF_3$ or $CF_3 \cdots CN$ repul-

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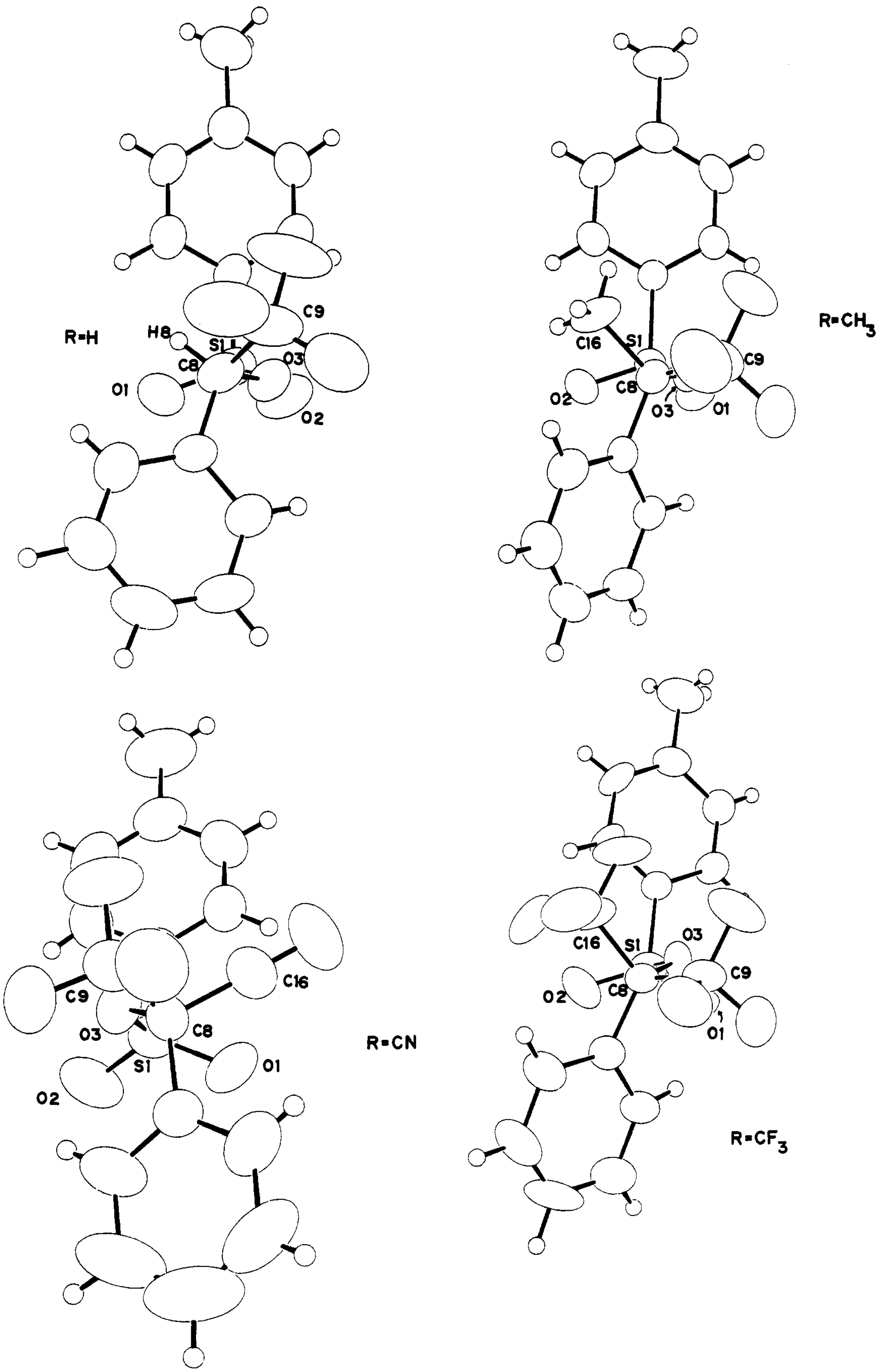
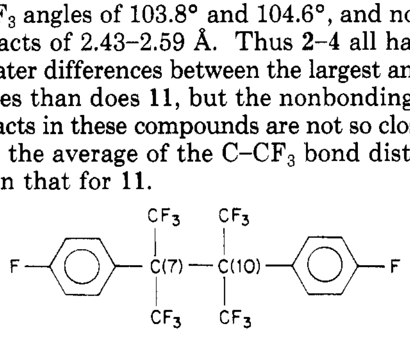


Figure 2. Parts a–d: ORTEP conformational representations of 1–4 viewed approximately along the S(1)–C(8) vector.

sions or from substituent induced changes in hybridization at the substituted carbon.

The results for 1–4 may be compared to those of a systematic effort to study the molecular geometries and reactivity in C–C bond homolysis of a large series of ethane hydrocarbons.[9f] It was generally noted in this latter study that significant bond angle deformations are more common than bond stretching, and the same trend applies to 1–4 as well.

The fluorinated ethane **11** is particularly interesting, and has the longest acyclic C–C bond length yet reported of 1.671 Å for the central bond.[14] This compound had C–CF_3 distances of 1.559–1.582 Å, CF_3–C(7)–C(10) angles of 110.5–114.5°, aryl-C(7)–C(10) angles of 110.8° and 112.0°, CF_3–C–CF_3 angles of 103.8° and 104.6°, and nonbonding F···F contacts of 2.43–2.59 Å. Thus **2**–**4** all have significantly greater differences between the largest and smallest bond angles than does **11**, but the nonbonding F···F and F···O contacts in these compounds are not so close as those in **11**, and the average of the C–CF_3 bond distances in **4** is less than that for **11**.



11

The $J_{^{13}C-^{19}F}$ coupling constants were obtained from the ^{13}C NMR spectra and were 281.1, 284.4, 286.9, and 290.2 Hz for **1**–**4**, respectively, and presumably have negative sign.[10] Both **3** and **4**, which are substituted with electronegative groups, display larger $^{13}C-^{19}F$ coupling constants and C–CF_3 bond distances than the other substrates. In the case of **4** the two CF_3 groups are nonequivalent in the crystal but in solution rapid conformation equilibration renders these groups equivalent on the time scale of the NMR measurements.

The $^{13}C-^{19}F$ coupling constants for the alcohols corresponding to **3** and **4** were also recorded and equalled 286.2 and 287.0 Hz, respectively. The values were less than those for the tosylates and in the case of **4** the difference of 3.2 Hz is appreciable. Values of 279 and 280 Hz have been reported for two compounds containing the CF_3CH_2O group,[3b] so it appears that there is a distinct increase in this parameter associated with the presence of other electronegative groups and/or steric interactions. The parallel between the bond lengths and coupling constants extends to the CF_3CH_2O derivatives and suggest that there is a structural connection between these two parameters.

There was an initial report[10a] that $^{13}C-^{19}F$ coupling constants were sensitive to steric effects, with a maximum change of 10.8 Hz being observed in some aryl fluorides. Thus the changes for **1**–**4** are of comparable magnitude, confirm the occurrence of this phenomenon, and indicate there will be further useful applications of this principle.

The current work is the first effort to correlate the observed reactivities of sulfonate esters with experimental molecular structures, although it has been recognized that ground-state repulsions between the alkyl groups and sulfonyl or carbonyl oxygens could be a major driving force in the solvolysis of sulfonate and benzoate esters.[8,15,16] In order to estimate the steric effects due to this interaction molecular mechanics calculations have been utilized, but these efforts have suffered from the lack of reliable parameterization for oxygen functions and have relied on hydrocarbon parameters.[15] Experimental efforts to demonstrate F-strain effects due to *p*-nitrobenzoate leaving groups have also been reported,[16] but there is still no reliable and general method to quantify these effects. It is to be hoped that continued studies of experimentally determined molecular structures, calculated geometries and energies, and measured reactivities will permit the accurate assessment of the factors contributing to reactivity properties.

Experimental Section[17]

Solvents were distilled just prior to use: diethyl ether from shining sodium ribbon, pyridine from barium oxide (vacuum dried at 110°), and pentanes and hexanes from lithium aluminium hydride. *p*-Toluenesulfonyl chloride (*p*-TsCl) was recrystallized from ether. Mineral oil suspensions of potassium hydride (35%) (Alfa) were weighed out in a N_2 atmosphere in a glove bag and washed several times with pentane.[18] Glassware was flame dried and reactions were carried out in an atmosphere of dry N_2. Reagents and solutions were transferred via syringes with positive pressures of N_2. Workups included drying of the ether solution of the product mixtures over anhydrous magnesium sulfate and removal of ether on a rotary evaporator under water aspirator vacuum. Tosylates were recrystallized at −10 to −70 °C. Compounds **1** and **2** were described previously.[1] ^1H and ^{13}C chemical shifts are reported in ppm from internal Me_4Si and ^{19}F chemical shifts are reported in ppm from external CF_3CO_2H.

1-Cyano-1-phenyl-2,2,2-trifluoroethanol (12). A solution of sodium bisulfite (4.23 g, 41 mmol) in water (50 mL) and 1,1,1-trifluoroacetophenone (3.48 g, 20 mmol) was stirred at room temperature for 1 h and then on cooling in ice the crystalline bisulfite addition product formed. Addition of KCN (2.64 g, 41 mmol) in water (20 mL) over a period of 20 min resulted in the formation of a solid which was extracted with four 15-mL portions of ether. The combined ether solution was washed once with 20% NaCl (30 mL) and dried. After evaporation of the solvent and recrystallization from pentane colorless crystals of **12** were obtained: mp 73–75 °C (55%); ^1H NMR (CCl_4) δ 4.63 (s, 1, OH); 7.32–7.80 (m, 5, Ph); ^{19}F NMR (C_6D_6) δ −1.84 (s); ^{13}C NMR ($CDCl_3$) δ 74.13 (q, J_{CCF} = 33.8 Hz, COH), 115.56 (s, 1, CN), 121.64 (q, J_{CF} = 286.2 Hz, CF_3), 126.63 (J_{CCCCF} = 1.1 Hz, 2 *o*-C), 129.03 (2 *m*-C) 130.59 (*ipso*-C), 131.11 (*p*-C); IR (CCl_4) 3600 cm^{-1} (OH); mass spectrum, *m/e* (relative intensity) 201 (6, M^+), 174 (16, M − HCN), 132 (23, M^+ − CF_3); high-resolution mass spectrum 201.0420, calcd for $C_9H_6F_3NO$ 201.0402. Anal. Calcd: C, 53.74; H, 3.01; N, 7.95. Found: C, 54.18; H, 3.41; N, 7.13.

1-Cyano-1-phenyl-2,2,2-trifluoroethyl Tosylate (3). Pyridine (12.5 mL), *p*-TsCl (1.01 g, 5 mmol), and **12** (0.52 g, 2.5 mmol) were mixed and cooled at 0 °C for 22 days. The solution was then poured into ice–water (125 mL) and extracted with ether 4 times. The combined ether solution was washed successively with ice cold 3 N HCl, ice–water, and chilled brine and dried. On removal of the ether a viscous liquid was obtained which solidified after cooling at 0 °C for 2 days and gave colorless crystals from pentane: mp 69–70 °C (20% yield); ^1H NMR (CCl_4) δ 2.45 (s, 3, Me), 7.24–7.90 (m, 9, Ar); ^{13}C NMR ($CDCl_3$) δ 79.25 (q, J_{CCF} = 34.2 Hz, CO), 111.54 (CN), 120.38 (q, J_{CF} = 286.9 Hz, CF_3), 127.31 (J_{CCCCF} = 1.2 Hz, 2 *o*-C), 128.06 (*ipso*-C), 129.10 (2 *m*-C), 131.72 (*p*-C), and for the tolyl group 21.75 (Me), 128.31 (*m*-C), 130.13 (*o*-C), 132.87 (*p*-C), 146.53 (*ipso*-C); mass spectrum, *m/e* (relative intensity) 355 (23, M^+), 200 (34, M^+ − Ts), 184 (49, M^+ − TsO); high-resolution mass spectrum 355.0475, calcd for $C_{16}H_{12}F_3NO_3S$ 355.0490. Anal. Calcd: C, 54.08; H, 3.40; N, 3.94. Found: C, 54.17; H, 3.47; N, 3.84.

1-Phenyl-1-(trifluoromethyl)-2,2,2-trifluoroethyl tosylate (4) was prepared from the known alcohol[19] by reaction with KH followed by TsCl[1] and gave white crystals that slowly decomposed on heating: ^1H NMR (CCl_4) δ 2.48 (s, 3, Me), 7.22–7.94 (m, 9, Ar); ^{19}F NMR (C_6D_6) δ 2.21 (s); ^{13}C NMR ($CDCl_3$) δ 87.05 (septet, J_{CCF} = 30.9 Hz, CO), 121.25 (q, J_{CF} = 290.5 Hz, CF_3), 127.22

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(*ipso*-C), 127.73 (J_{CCCCF} = 1.7 Hz, 2 *o*-C), 128.53 (2 *m*-C), 130.95 (*p*-C), and for the tolyl group 21.71 (Me), 127.90 (*m*-C), 129.90 (*o*-C), 134.38 (*p*-C), 145.88 (*ipso*-C); mass spectrum, *m/e* (relative intensity) 398 (14, M$^+$), 243 (6, M$^+$ − Ts) 227 (7, M$^+$ − TsO); high-resolution mass spectrum 398.0429, calcd for $C_{16}H_{12}F_6O_3S$ 398.0411. Anal. Calcd: C, 48.25; H, 3.04. Found: C, 48.32; H, 3.20.

1-Phenyl-1-methyl-2,2,2-trifluoroethyl tosylate (2):[1a] ^{13}C NMR ($CDCl_3$) δ 18.77 (q, J_{CCCF} = 1.3 Hz, CH_3CCF_3), 87.45 (q, J_{CCF} = 30.5 Hz, CO), 123.36 (q, J_{CF} = 284.4 Hz, CF_3), 127.12 (J_{CCCCF} = 1.1 Hz, 2 *o*-C), 128.34 (2 *m*-C), 129.68 (*p*-C), 135.58 (*ipso*-C) and for the tolyl group 21.62 (Me), 127.46 (*m*-C), 129.82 (*o*-C), 134.69 (*p*-C), 145.01 (*ipso*-C).

1-Phenyl-2,2,2-trifluoroethyl tosylate (1):[1b] ^{13}C NMR ($CDCl_3$) δ 78.13 (q, J_{CCF} = 34.3 Hz, CO), 122.30 (q, J_{CF} = 281.1 Hz, CF_3), 127.92 (2 *o*-C), 128.10 (2 *m*-C), 129.65 (*ipso*-C), 130.24 (*p*-C), and for the tolyl group 21.56 (Me), 128.63 (*m*-C), 129.79 (*o*-C), 132.98 (*p*-C), 145.44 (*ipso*-C).

1-Phenyl-1-(trifluoromethyl)-2,2,2-trifluoroethanol (13): ^{13}C NMR ($CDCl_3$) δ 77.08 (sep, J_{CCF} = 30.0 Hz, CO), 123.02 (q, J_{CF} = 287.0 Hz, CF_3), 126.72 (J_{CCCCF} = 1.5 Hz, 2 *o*-C), 128.80 (2 *m*-C), 129.63 (ipso-C), 130.42 (*p*-C). This spectrum has been reported [19b] and while the spectral data are in agreement our assignments of the ring carbons, which are based on the observed ^{13}C–^{1}H couplings, are different.

Crystals of the compounds **1**–**4**[1c] were sealed in 0.2–0.3 mm Lindemann capillaries. Precession photographs were used to obtain preliminary cell and symmetry information. Further work on each crystal on an Enraf-Nonuis CAD-4 diffractometer with graphite monochromatized Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å) gave the crystal data summarized in Table II. Cell constants were obtained by least-squares refinement of the setting angles of 25 reflections within the θ ranges specified. Conditions used for each data collection are also summarized in Table II. For each reflection backgrounds were measured by extending the scan by 25% on either side of the peak and were measured for half the time taken to collect the peak. During each data collection several standard reflections were periodically checked for crystal and instrument stability. No significant fluctuations were observed.

For each data set, Lorentz and polarization corrections were applied. Averaging symmetry equivalent data and excluding reflections which were either systematically absent or had F_{obsd} = 0.0 gave the final totals of independent reflections shown in Table II.

Each structure was routinely solved by the use of the program MULTAN 11 on a PDP 11/23 computer followed by cycles of least-squares and Fourier calculations to locate any missing atoms in the trial structures. Hydrogen atoms were located in difference Fourier maps or were placed in calculated positions. For each structure, full-matrix least-squares calculations minimizing $\sum w[|F_0| - |F_c|]^2$ have converged to the residuals in Table II. In these final cycles of refinement weights were given by expressions of the form $w = 4F^2[\sigma(I)^2 + (pF^2)^2]^{-1}$ with values for p indicated in Table II. Final difference Fourier maps for each structure were featureless. A PDP 11/23 computer and programs in the Enraf-Nonius SDP package were used throughout the refinements. Final positional parameters for all atoms (Table IX), tables of thermal parameters (Table X), and final structure factor amplitudes (Table XI) are deposited as supplementary material.

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Registry No. **1**, 13652-13-6; **2**, 73572-26-6; **3**, 86669-62-7; **4**, 86669-60-5; **12**, 93923-55-8; **13**, 718-64-9; $PhCOCF_3$, 434-45-7; $NaHSO_3$, 7631-90-5; KCN, 151-50-8.

Supplementary Material Available: Complete bond length and bond angle information for **1**–**4** (Tables III and IV), reported structures of secondary tosylates (Table VI), selected torsion angles and contact distances (Tables VII, VIII), atomic coordinates for **1**–**4** (Table IX), and thermal parameters (Table X) (20 pages). Structure factor tables available from authors. Ordering information is given on any current masthead.

Specification of Relative Stereochemistry in Bridged Bicyclic and Spirobicyclic Systems

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A system is proposed for the specification of relative stereochemical relationships within bridged, bicyclic systems with three equal length bridges, most notably bicyclo[2.2.2]octanes, in bicyclic arrays with two identical bridges when the third is larger, such as bicyclo[3.2.2]nonanes, and in spirobicyclic compounds. For any bridged, bicyclic array with two equal and one larger or three equal bridges, a numbering scheme is assigned on the basis of an appropriate and convenient nomenclature system. A sense of rotation is then defined for the axis passing through both bridgehead atoms on the basis of the relative numbering of the three bridging atoms attached to bridgehead atom number 1. Then, substituents that are oriented with this sense of rotation are tagged *M* (mit) and those with the opposite orientation are referred to as *G* (gegen). For any spirobicyclic system, the framework atoms are numbered according to classical nomenclature rules (e.g., the smallest bridge is numbered first). The stereochemical positioning of substituents on each ring is then specified to be *M* if they are on the same face of that ring as the lower numbered atom of the other ring while *G* is used for the opposite relationship.

The specification of relative stereochemical relationships within bicyclic systems of both the bridged and spiro kind has represented a significant nomenclature problem that has not as yet been adequately addressed. Difficulties are found with all spirobicyclic systems, while problems are most apparent in bridged bicyclic arrays that have two identical length bridges and where the third is at least the same size or larger (e.g., bicyclo[2.2.2]octanes and bicyclo[3.2.2]nonanes). In response to these needs we have developed a scheme that simplifies such nomenclature problems to the greatest extent possible. We propose its adoption by the organic chemical community at large.

Bridged Bicyclics

While several different systems have evolved independently for the specification of relative stereochemistry

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