perimentally observed,[28] for bridging angles close to 90°.

Examining Table V, one can notice that the F situation related to the real orthogonality of the magnetic orbitals is exceptional. It only occurs in the $x^2 - y^2 \leftrightarrow xy$ interaction, as found in Cu^{II}–VO^{II} and also in low-spin Co^{II}–Cu^{II}. In this latter case, unfortunately, we have not been able to grow single crystals, so that the structure of the complex is not known with accuracy.[29] There is one new pair of A–B ions with a pure ferromagnetic coupling, and apparently only one, namely the d^9–d^3 pair in which the magnetic orbitals are xy and $x^2 - y^2$, xz and yz, respectively. In the quite near future, we expect to be able to describe a Cu^{II}–Cr^{III} complex corresponding to this situation.[30]

Registry No. 1, 80765-14-6; $CuH_2(fsa)_2en$, 59229-83-3; $VO(CH_3CO-O)_2$, 3473-84-5; $VO(OH)_2$, 30486-37-4.

Supplementary Material Available: A listing of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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Kinetic Acidity of Diastereotopic Protons in Sulfonium Ions. 2. Thiolanium Cations. X-ray Molecular Structure of 8-Methyl-8-thioniabicyclo[4.3.0]nonane Tetrafluoroborate and Quantitative Perturbational Molecular Orbital Analysis of Diastereomeric Model Sulfonium Ylides

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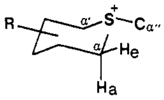
Abstract: The X-ray molecular structure has been determined for the title compound **2**, a rigid sulfonium salt which is known[3b,9e] to exchange its α protons with high stereoselectivity. The geometry thus obtained has been utilized to compute by ab initio SCF MO methods the relative stabilities of the $^-CH_2$-SH_2^+ model ylide in the various geometrical arrangements corresponding to the diastereomeric ylides arising from **2** by removal of the α protons one at a time. The computed trend of ylide stability appears to largely match the trend of kinetic acidity, indicating the model is a suitable one. A quantitative PMO analysis[10] has been carried out, allowing for the estimation of the relative energy effects associated with the various orbital interactions. Contrary to recent suggestions,[8,24a] the lone-pair destabilizing interaction never becomes dominant, while the hyperconjugative effect associated to the n_c–σ^*_{SH} interaction appears to play a major conformational role, in agreement with a previous proposal.[6]

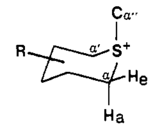
Tricoordinated organic sulfur functions Z–S(X)–CH_2R (Z = R, Ar, OR, ...; X = O, OR, R′, NR, Ar′, ...) are pyramidal and configurationally stable. Therefore, whenever X ≠ Z, the methylene protons are diastereotopic and have different reactivity.[2] As these functions are strongly acid enhancing, a conspicous chemical manifestation of this phenomenon is provided by the differential kinetic acidity (base-catalyzed H–D exchange) of the α-CH_2 protons which in a number of cases has been found to reach very high values, ranging into the thousands.[3]

Although the phenomenon is important theoretically, in relation to the general problem of reaction stereospecificity, and practically, in view of a rational approach to the transfer of chirality from sulfur to carbon,[4] the fundamental geometrical factors presiding over it are not clear. To the extent that the transition states for base-catalyzed H–D exchange resembles the carbanionic intermediate, the question of the differential kinetic acidity may be approached in terms of the relative stability of the diastereomeric carbanions (or ylides, as the case may be) arising from the removal of the corresponding diastereotopic protons one at a time.[5] We adopted[6] this approach in an attempt to rationalize the following observations in the *rigid* S-methylthianium cations **1e** and **1a**—in the former, the equatorial α proton is considerably more reactive than its geminal axial companion, while, in the latter, the two protons are about equally reactive.[6]



1e

$k_e > k_a$



1a

$k_e > k_a$

If the ylide is a suitable model for the transition state of the base-catalyzed H–D exchange, these results appeared to be consistent with the idea, which emerged in the mid 70's,[7] that the

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(5) This approach is obviously limited since it does not account for solvent and salt effects. These are known to be quite large in the case of sulfoxides;[3a] no evidence is available for similar effects in sulfonium salts.[3b] However, medium effects are likely to be small here (compared to sulfoxides), and, especially in aqueous media, the carbanion intermediates closely approximate free ylides.

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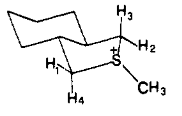
conformational properties of α-thia carbanions are largely determined by stereoelectronic factors and in particularly by the hyperconjugative stabilization associated with the interaction of the carbon lone-pair orbital with the antibonding σ orbital of an adjacent S–C bond.[7] Such interaction has been found to be at a maximum when the orbitals involved are either syn- or antiperiplanar.[7d] From the geometry of the six-membered ring (chair) it is apparent that, in the ylide formed from **1e** by removal of H_e, the lone-pair orbital is antiperiplanar to the $S–C_{\alpha'}$ bond, while, in the ylide formed by removal of H_a, the lone pair is gauche to both the $S–C_{\alpha'}$ and $S–C_{\alpha''}$ bonds. Therefore the former ylide enjoys maximum hyperconjugative stabilization, while the latter does not. On the other hand either ylide arising from the axial epimer **1a** by removal of H_e or H_a would have their carbon lone pair antiperiplanar to one of the adjacent S–C bonds ($S–C_{\alpha'}$ and $S–C_{\alpha''}$ for removal of H_e and H_a, respectively) and henceforth would be subject to hyperconjugative stabilization to substantially the same extent.

This interpretation has been recently challenged by Graham and Heathcock,[8] who suggested the prime determinant of the observed conformational behavior to be a destabilizing interaction, the lone pair–lone pair repulsion, rather than the stabilizing one suggested by us.[6] Unfortunately, unless one is able to dissect and separately evaluate the energy contribution associated to the various interactions, there is no clear-cut way of establishing which particular interaction may be predominant. We were fully aware of this difficulty and, in proposing our model, warned[6] that "...[the hyperconjugative factor]... may not be the only important one, just as the postulated interaction may not be the sole important factor determining it".[6] Additional experimental and theoretical work was deemed necessary in order to gauge the relative importance of the hyperconjugative effect relative to other steric and stereoelectronic effects.

Work in this direction has now been carried out and is reported herein. We have chosen to investigate the five-membered cyclic sulfonium cations system which, in view of the exceptionally large diastereotopic kinetic acidity differentials it often displays,[3b,9] appeared to be the most suitable testing ground. Thus we have considered the rigid thiolanium cation **2**, whose α protons had been



2

previously found to undergo highly stereoselective base-catalyzed H–D exchange,[3b,9e] and determined its X-ray molecular structure. In this system H_2, the quasi-equatorial proton cis to SCH_3, exchanges much more rapidly (~1300 times) than H_1, the quasi-equatorial proton trans to SCH_3, while the two quasi-axial protons H_3 and H_4 exchange at intermediate, and approximately equal, rates.[3b,9e] The structure of cation **2** has now been obtained by X-ray analysis of its tetrafluoroborate salt, and the geometrical parameters thus obtained have been utilized to compute by an initio SCF MO methods the relative stabilities of the $^-CH_2–SH_2^+$ model ylide in various geometrical arrangements patterned after the four diastereomeric ylides originating from **2** by removal of the α protons one at the time. Within the framework of the SCF MO computations,[10] a quantitative orbital analysis has also been carried out, allowing us to estimate the energy effects associated with the various orbital interactions. From this analysis it appears that, contrary to Graham and Heathcock's suggestion,[8] and to "chemical intuition", the lone pair–lone pair destabilizing interaction never becomes dominant, while the hyperconjugative effect related to the $n_c–\sigma^*_{SH}$ interaction does play a major conformational role.

Table I. Summary of Crystal Data and Experimental Conditions

compd	$C_9H_{17}S^+BF_4^-$
mol wt	244.1
unit-cell dimens	
a, Å	19.489 (4)
b, Å	12.103 (2)
c, Å	11.888 (2)
β, deg	120.36 (3)
cell vol, $Å^3$	2419.6 (8)
Z	8
d(obsd), g cm^{-3}	1.35 (1)
d(calcd), g cm^{-3}	1.34
abs coeff, cm^{-1}	$\mu = 23.0$ (Cu Kα)
cryst vol, mm^3	0.0205
space group	$C2/c$ (C_{2h}^6–No. 15)
radiation, Å	λ(Cu Kα_1) = 1.54056
temp, °C	20
receiving aperture	diameter 4.0 mm
takeoff angle, deg	2.5
scan	θ-2θ, five-point technique
scan range	1.0° + doublet separation
two limits	$2° \leqslant 2\theta \leqslant 140°$
data collected	$\pm h,k,l$

Experimental Section

X-ray Structure. Well-developed colorless prismatic crystals of $C_9H_{17}S^+BF_4^-$ elongated along [001] were recrystallized from water. A preliminary photographic examination employing Weissenberg techniques indicated that the crystals were monoclinic. The density was measured by flotation in nitrobenzene/bromobenzene. Systematic absences *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, give space groups *Cc* or *C*2/*c*, and the latter was confirmed by a successful analysis. The distribution of $|F_o|$ and the $N(Z)$ test suggest the centrosymmetric space group. Crystal data are summarized in Table I.

A crystal of approximate dimensions 0.17 × 0.28 × 0.43 mm was chosen from which intensity data were recorded. It was mounted with the long dimension [001] slightly offset to the ϕ axis of the diffractometer. Six faces were identified by optical goniometry as {100}, {010}, and {100}. Intensity data were recorded on a Siemens AED automatic diffractometer. Cell constants and an orientation matrix were refined[11] by using 21 carefully centered reflections with $40° \leq 2\theta \leq 110°$ and in the two ϕ quadrants of the reciprocal space from which data were to be collected. Details of experimental conditions are given in Table I. During the data collection a standard reflection was examined regularly every 20 observations and showed only random fluctuations. Coincident losses in counting for strong reflections were minimized by the use of nickel foil attenuators.

A total of 2298 reflections were measured. The recorded intensities were corrected for Lorentz and polarization effects. A standard deviation $\sigma(I)$ was assigned to each intensity *I*, where $(\sigma(I))^2$ = total counts + $(cI)^2$. *c* was chosen as 0.005.[12] Of the 2298 reflections processed (excluding the standard reflections), 2188 unique reflections were obtained and 1584 with $I > 2\sigma(I)$ were used in the solution and refinement of the structure.

The structure was solved by direct methods[11] and refined by full-matrix least-squares techniques of *F*. Scattering factors for neutral nonhydrogen atoms were taken from Cromer and Waber,[13] while those for H were taken from Stewart, Davidson, and Simpson.[14] The real and imaginary anomalous dispersion corrections of Cromer and Liberman[15] were included for the S, F, and C atoms.

Two cycles of refinement varying positional and isotropic thermal parameters for nonhydrogen atoms gave agreement factors $R_1 = \sum|F_o| - |F_c|/\sum|F_o| = 0.14$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.18$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight *w* was calculated as $1/\sigma^2(F_o)$. In further refinement three more cycles with anisotropic

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Table II. Intramolecular Bond Distances (Å), Bond Angles (Deg), and Torsional Angles (Deg)

		Distances			
S–C(2)	1.813 (6)	C(1)–C(5)	1.482 (8)	C(8)–C(9)	1.340 (8)
S–C(4)	1.815 (6)	C(4)–C(5)	1.540 (9)	B–F(1)	1.340 (8)
S–C(10)	1.672 (7)	C(5)–C(6)	1.481 (8)	B–F(2)	1.363 (8)
C(1)–C(2)	1.520 (9)	C(6)–C(7)	1.534 (10)	B–F(3)	1.321 (8)
C(1)–C(9)	1.498 (8)	C(7)–C(8)	1.467 (10)	B–F(4)	1.320 (8)
		Angles			
C(2)–S–C(4)	94.5 (3)	S–C(4)–C(5)	105.2 (4)	C(8)–C(9)–C(1)	109.8 (6)
C(2)–S–C(10)	100.3 (4)	C(1)–C(5)–C(4)	106.0 (5)	F(1)–B–F(2)	109.5 (6)
C(4)–S–C(10)	100.4 (3)	C(1)–C(5)–C(6)	112.6 (6)	F(1)–B–F(3)	110.3 (7)
C(2)–C(1)–C(5)	107.2 (5)	C(4)–C(5)–C(6)	114.1 (5)	F(1)–B–F(4)	111.9 (7)
C(2)–C(1)–C(9)	115.2 (6)	C(5)–C(6)–C(7)	109.5 (6)	F(2)–B–F(3)	106.6 (7)
C(5)–C(1)–C(9)	113.0 (5)	C(6)–C(7)–C(8)	113.4 (8)	F(2)–B–F(4)	109.3 (6)
C(1)–C(2)–S	105.5 (4)	C(7)–C(8)–C(9)	112.8 (7)	F(3)–B–F(4)	109.2 (7)
		Torsional Angles			
C(5)–C(1)–C(2)–S	38.3 (7)	C(2)–C(1)–C(5)–C(6)	−175.7 (6)	C(1)–C(5)–C(6)–C(7)	−53.2 (9)
C(1)–C(2)–S–C(4)	−13.2 (6)	C(2)–C(1)–C(9)–C(8)	−177.5 (7)	C(5)–C(6)–C(7)–C(8)	52.5 (1.0)
C(2)–S–C(4)–C(5)	−13.9 (6)	C(4)–C(5)–C(1)–C(9)	−178.1 (6)	C(6)–C(7)–C(8)–C(9)	−53.3 (1.1)
S–C(4)–C(5)–C(1)	38.3 (7)	C(4)–C(5)–C(6)–C(7)	−174.3 (7)	C(7)–C(8)–C(9)–C(1)	52.6 (9)
C(4)–C(5)–C(1)–C(2)	−50.1 (7)	S–C(4)–C(5)–C(6)	162.9 (6)	C(8)–C(9)–C(1)–C(5)	−53.9 (9)
C(1)–C(2)–S–C(10)	−114.6 (6)	S–C(2)–C(1)–C(9)	165.0 (5)	C(9)–C(1)–C(5)–C(6)	56.4 (8)
C(5)–C(4)–S–C(10)	87.5 (6)				

thermal parameters were carried out (1584 observations and 136 variables), and a difference Fourier synthesis, calculated with reflections having $\sin^2 \theta \leq 0.3$, was examined. From the synthesis 14 of the 17 hydrogen atoms were apparent as smeared peaks. They appeared in the top of the list together with two spurious peaks near the sulfur position and with a height of 0.4 e Å^{-3} over a mean background of 0.2 e Å^{-3}. At this stage idealized coordinates were also calculated for the 14 hydrogen atoms (C–H = 1.08 Å) and they were near the positions of higher electron density. Two cycles were carried out refining the isotropic thermal parameters of the nonhydrogens and the positional and thermal parameters of the heaviest atoms. The hydrogens of the methyl were refined as a rigid group. The difference Fourier map showed at this stage no particular features and peaks with residual electron density of ±0.2 e Å^{-3}. Two final cycles (154 variables) converged at agreement values $R_1 = 0.072$ and $R_2 = 0.092$. In the final cycle the greatest shift was 0.4 esd. A statistical analysis of R_2 over various ranges of F_o and $\lambda^{-1} \sin \theta$ showed no abnormal trends.

Final positional and thermal parameters and hydrogen atom parameters are reported in the supplementary material. Structure amplitudes, listed in $10|F_o|$ and $10F_c$ in electrons, have been deposited.

Description of the Structure of 8-Methyl-8-thioniabicyclo[4.3.0]nonane Tetrafluoroborate. The structure consists of discrete anion and cation molecules with relatively few van der Waals contacts between the organic components. The shortest contacts between the cationic and anionic parts are S···F(2) $(-x, y, {}^1/_2 - z)$ = 3.576 Å, S···F(3) $(-x, y, {}^1/_2 - z)$ = 3.243 Å, and S···F(2) $(x, 1 - y, {}^1/_2 + z)$ = 3.181 Å.

A perspective drawing of the molecule showing the atom numbering scheme is presented in Figure 1. Bond distances, bond angles, and torsional angles are given in Table II. The full covariance matrix was used in estimating the standard deviations of the bond distances and angles. Torsional angles are determined according to the right-hand rule[16] and their esd's are determined according Stanford and Wasser.[17]

In the anion the B–F bond distances show a significant shortening with respect to the 1.42–1.43-Å value usually reported for that group. The thermal motion of the group was analyzed in terms of rigid-body motion.[18] The root-mean-square deviation between observed and calculated U_{ij} values is 0.006 Å^2, comparable with the estimated standard deviations of the observed thermal parameters. Bond lengths corrected for thermal motion are B–F(i = 1, 4) = 1.415, 1.437, 1.388, and 1.426 Å.

Similar shortening is observed in some C–C bond lengths (C–C(av) = 1.503 Å to be compared with the 1.526-Å value found in cyclohexane by X-ray crystallography and corrected for thermal motion and with the 1.528-Å value determined by electron diffraction in the gas phase), but the cation molecule does not behave as a rigid group as indicated by the root-mean-square deviation of 0.08 Å^2. The bond S–C(10) = 1.672 (7) Å is quite short. In similar structures the S–C(methyl) distance ranges from 1.76 to 1.82 Å. The distance increases to 1.76 Å when the riding[19] of the methyl group on the sulfur has been taken into account. The S–C(10) direction forms an angle of 74.1° with the mean least-squares plane through the thiacyclopentane ring.

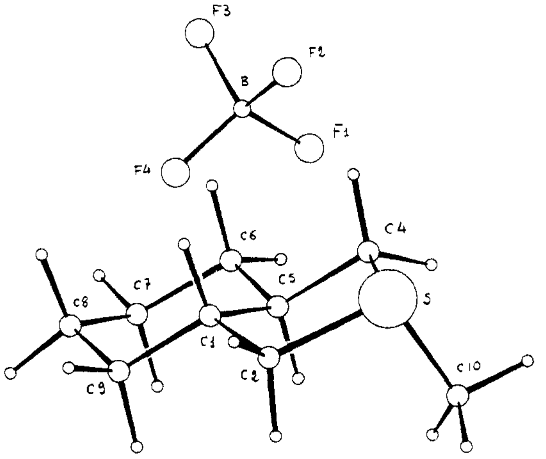

Figure 1. Perspective view of 8-methyl-8-thioniabicyclo[4.3.0]nonane tetrafluoroborate.

The conformation of the heterocyclic ring is twist with the ring puckering amplitude-phase pair of $Q = 0.437$ Å and $\phi = 90.8°$ and that of the cyclohexane ring is chair with the puckering spherical polar set $Q = 0.534$ Å, $\theta = 178.5°$, and $\phi = 209.1$.[20] The torsional angles within the cyclohexane ring are smaller than those observed in the cyclohexane itself (56°) but are comparable with those found in polynuclear compounds as decaline derivatives.[21] This flattening of the ring is probably triggered by repulsive 1,3-diaxial interactions involving the dicyclic system.

The geometry of the heterocyclic ring in the cation can be compared with that for tetrahydrothiophene[22] in the gas phase. No examples are available, to our knowledge, of geometries of such a ring, with no C_{sp^2} atoms, determined by X-ray methods. In both cases the ring has C_2 symmetry and the torsional angles C–S–C–C = 14.8 (5)°, S–C–C–C = 40.4 (1.2)°, and C–C–C–C 52.5 (1.6)°, to be compared with the 13.6 (6)°, 38.3 (7)°, and 50.1 values for the structure reported here, are very similar. Also the endocyclic C–S–C bond angle, 93.4 (5)°, is not significantly different from the 94.5 (3)° value. It seems that the presence of a formally positive sulfur atom has a small influence, in cyclic sulfonium ions, on the geometry of the heterocyclic ring,[23] but further structural work is certainly needed to detect smaller effects.

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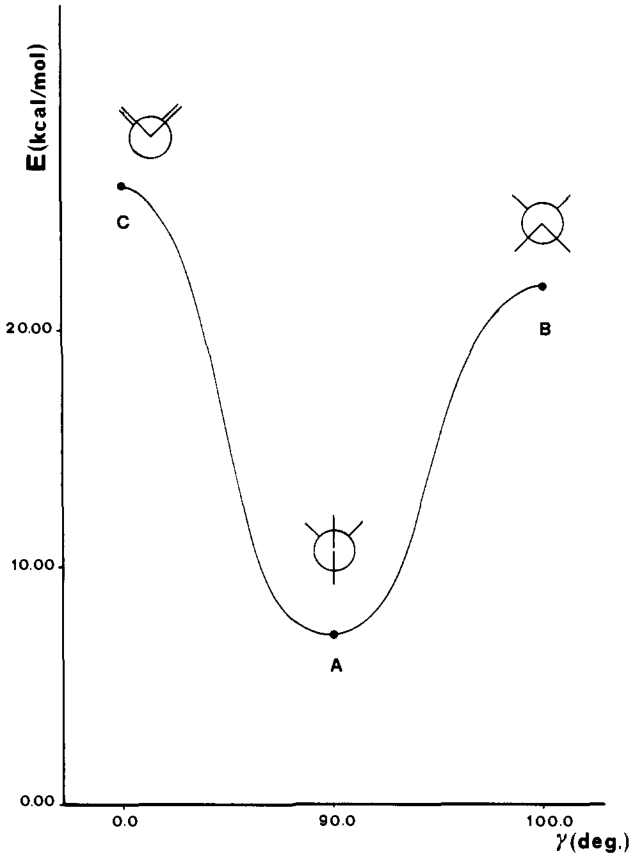
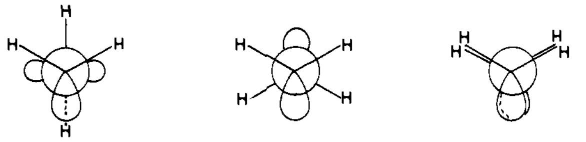


Figure 2. Total energy change, *E*, for rotation about the C–S bond in $^-CH_2-SH_2^+$, computed at the STO-3G* level. (The total energy of the more stable conformation, A, is -432.79874 au.)

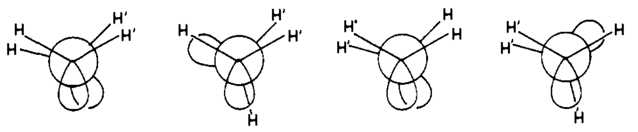
Ab Initio Computations and PMO Analysis

To keep the computing time within reasonable limits, we have considered the simplest possible sulfonium ylide, $^-CH_2-SH_2^+$. This species has been investigated previously. Early computations[7c] at the 4-31G level with incomplete geometry optimization and without d orbitals suggested the carbon atom to be pyramidal for all rotamers. However, more recent ab initio computations (double-ζ quality basis sets with heavy-atom polarization functions and diffuse s and p functions added to carbon[24a] or STO-3G and 4-31 G basis sets with sulfur d orbitals[24b]) with complete geometry optimization indicated the most stable conformation to be A, with a planar carbanionic center. On the other hand (see Figure 2) the anti and syn conformations B and C are at the maxima in the rotational curve about the ylide bond.[24b] The notion that, in the absence of firm geometrical constraints, the carbanionic carbon tends to be planar is consistent with most recent experimental evidence based on $^{13}C-H$ coupling constants.[25]



A B C

The question is how the energy of the $^-CH_2-SH_2^+$ model ylide would be affected by torsional and angular constraints, as it would be whenever the ylide bond was to be a part of a more or less rigid system restricting the conformational motion. We have carried out ab initio SCF MO computations of $^-CH_2-SH_2^+$ in four geometrical arrangements patterned after the geometry of the rigid cation **2**. We assume these four species Y_1–Y_4 to be the simplest approximations to the four diastereomeric ylides arising from **2** by removal of H_1–H_4, respectively. Though admittedly crude, this approach, by providing information on the energetic consequences resulting from conformational restrictions, may well give an insight into the factors contributing to the kinetic acidity differentials in a rigid real system such as **2**.



Y_1 Y_2 Y_3 Y_4

In the Newman projections above, the carbanionic carbon faces the observer. The primed H's correspond to ring carbons of cation **2**, namely, C_1,C_4 for the Y_1,Y_4 pair and C_5,C_2 for the Y_2,Y_3 pair. The dihedral angles at the ylide bond (ωH'CSH') have been assumed to be equal to the corresponding endocyclic dihedral angles at the C_2–S and C_4–S bonds (−13.2 and −13.9°, respectively, (Table II)). The computations have been carried out by using a STO-3G basis set supplemented by a set of five 3d-type functions for sulfur, consisting of one second-order Gaussian each (STO-3G*).[26,27] In the case of the $^-CH_2-SH_2^+$ model ylide, this basis set appears to provide results comparable to more extended basis sets.[24b] In order to examine the effect of the torsional constraint at the ylide bond on the geometry of the carbon center, we have computed the energy as a function of the pyramidal angle at carbon. We have found it useful to express this as a dihedral angle $\alpha = H_i(CS)H$, where H_i represents the proton remaining attached to the carbanionic center (i.e. H_4, H_3, H_2, and H_1 in Y_1, Y_2, Y_3, and Y_4, respectively) and H is the "exocyclic" proton. For each pair of ylides centered at the same carbon (C_2 or C_4), the energy was computed as a function of α, thus yielding energy curves for the interconversions $Y_2 \rightleftarrows Y_3$ and $Y_1 \rightleftarrows Y_4$ along this pathway. This choice of coordinate appears to be justified insofar as the parent cation structure is such that $\angle H_2C_2S \simeq \angle H_3C_2S \simeq \angle H_1C_4S \simeq \angle H_4C_4S$. For each pair of ylides an energy curve has been computed by using directly the geometrical parameters derived from the X-ray molecular structure of **2** (Table II), except that standard bond lengths were used, as required by the substitution of three hydrogens for three carbons (r(S–H) = 1.33 Å, r(C–H) = 1.08 Å). In view of the theoretical study by Wolfe and Schlegel[24b] showing that the parameter which critically affects the pyramidality at carbon is the C–S bond length, a second energy curve was calculated where the C–S bond distance was optimized at each point. In order to obtain a better description of the carbon lone pair, we computed a third curve where, besides the r(C–S) distance, the H_iCS angle was also optimized. These curves, labeled 1, 2 and 3, are reported in Figures 3 and 4 for the Y_2,Y_3 and Y_1,Y_4 pairs, respectively.[28,29] Finally, energy curves for the $Y_1 \rightleftarrows Y_4$ and $Y_2 \rightleftarrows Y_3$ interconversions have been computed also at the 4-31G level without sulfur d orbitals and without geometry optimization.[30] These curves are reported in Figure 5. Inspection of Figures 3–5 suggests the following remarks. (1) The presence of a torsional constraint renders the carbanionic carbon pyramidal

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[24] (a) Eates, R. A.; Gassman, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 1066. (b) Mitchell, D. J.; Wolfe, S.; Schlegel, H. B. *Can. J. Chem.* **1981**, *59*, 3280. We thank Professor S. Wolfe for letting us know of their results prior to publication.

[25] Barbarella, G.; Dembech, P.; Garbesi, A. *Tetrahedron Lett.* **1980**, 2109.

[26] Binckley, J. S.; Whitehead, R. A.; Hariharan, P. C.; Sieger, R.; Pople, J. A. *QCPE* **1978**, *11*, 368.

[27] Collins, J. B.; Schleyer, P. R.; Binckley, J. B.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

[28] Total energy values (au), dihedral angles, and r(C-S) bond distances, at the minima of curve 3 in Figures 3 and 4 are as follows: Y_4, -432.769 57, 130°, 1.737 Å; Y_1, -432.754 22, 0°, 1.777 Å; Y_2, -432.771 27, 153.5°, 1.715 Å; Y_3, -432.761 86, 33.5°, 1.748 Å.

[29] When the results of this optimization are transferred to the real ylides from **2**, it should be realized that in the latter the C-S bond shortening will be to some extent resisted by the rigidity of the molecular framework. Since the inversion barrier appears to increase with increasing C-S bond length, the behavior of the real system would be better represented by a curve laying somewhere between curves 2 and 3 (Figures 3 and 4).

[30] The total energy values (au) at the minima in Figure 5 are Y_4 (α = 124.1°) - 436.998 49; Y_1 (α = 0°) - 436.983 01, Y_2 (α = 145°) - 436.998 07, and Y_3 (α = 42°) - 436.990 13.

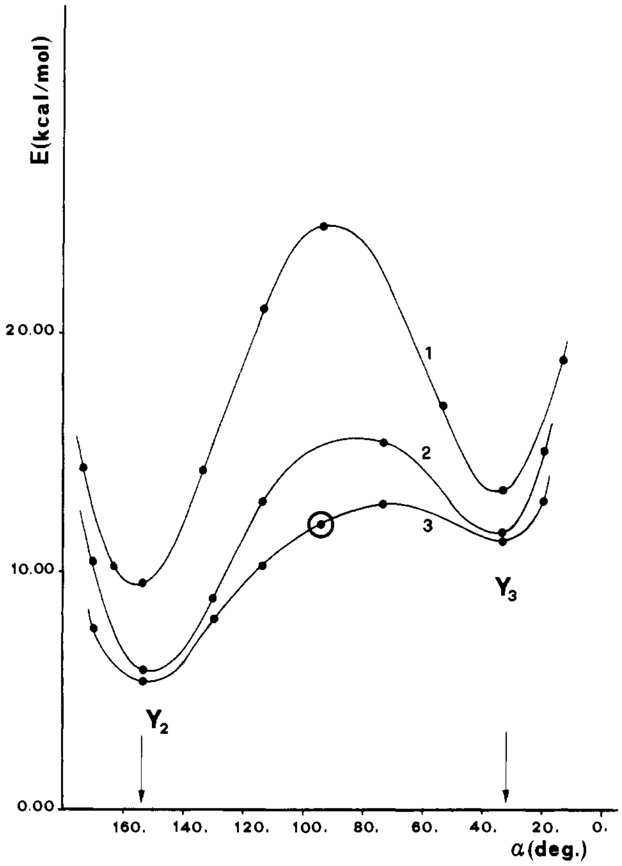

Figure 3. Total energy change, E, for variation of the dihedral angle α = H_i(CS)H in the pair of constrained model ylides centered at $C_2(Y_2,Y_3)$. H_i is the proton remaining attached to the carbanionic carbon. The circle indicates the conformation E with a planar carbon. The vertical arrow indicates the experimental angle in the parent cation. The various curves refer to STO-3G* computations at different levels of geometry optimization (see text).

in every case and at every computational level. (2) The inversion barrier decreases significantly with optimization of the H_iCS bond angle and r(C–S) bond distance, as well as with the inclusion of sulfur d orbitals in the basis set. However, the energy trend is the same with or without d orbitals, indicating the major factor which determines the total behavior is the torsional constraint at the ylide bond. (3) At all computational levels investigated, the dihedral angles at the minima (which can be estimated from the curves in Figures 3–5) do not substantially differ from the corresponding (experimental) angles in the parent cation (marked by a vertical arrow in Figures 3–5). In other words the abstraction of the proton does not cause any major flattening of the carbon involved. (4) For each pair of ylides centered at the same carbon atom, the "cis" ylide (i.e., that arising from the removal of the proton cis to CH_3) is more stable than the "trans" ylide, that is $Y_2 > Y_3$ and $Y_4 > Y_1$. Furthermore the "trans axial" ylide, Y_3, is found to be more stable than the "trans equatorial" one, Y_1, while the "cis equatorial", Y_2, and the "cis axial" ylide, Y_4, have comparable stabilities. The computed orders of model ylide stability ($Y_2 > Y_3$, $Y_4 > Y_1$; $Y_2 \simeq Y_4 > Y_3 > Y_1$) compare well with the experimental order of kinetic acidity of the corresponding α protons of **2** ($H_2 > H_3$, $H_4 > H_1$; $H_2 > H_3 \simeq H_4 > H_1$).[9e]

The satisfactory match between the calculated total energy trend for the model ylide and the kinetic acidity trend for the real system encourages a detailed analysis of the effects associated to the various factors concurring to the computed order of ylide stability. To this end a quantitative orbital analysis has been performed, within the framework of the corresponding ab initio SCF MO computations, with the procedure previously described.[10] In order to assess the role of the sulfur d orbitals, we have performed this analysis at the STO-3G* level. However, because of its limitations in the s and p parts, this basis set undoubtedly overestimates the contribution of the d orbitals.

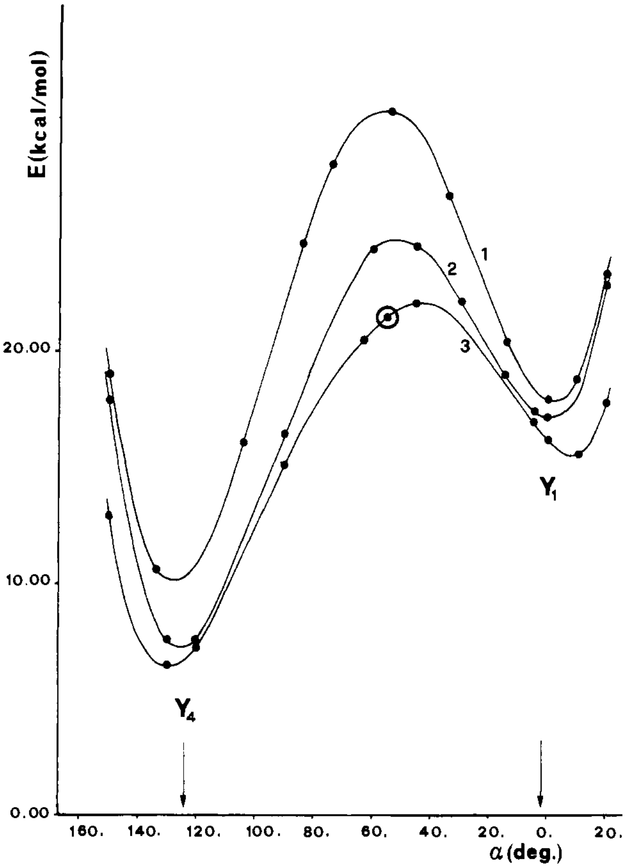

Figure 4. Total energy change, E, for variation of the dihedral angle α = H_i(CS)H in the pair of constrained model ylides centered at $C_4(Y_1,Y_4)$. The circles indicates the conformation D with a planar carbon. For symbols and computational levels see caption to Figure 3.

In every case the model ylide has been dissected into the H_2C^-– and –$^+SH_2$ fragments; the orbitals explicitly included in the analysis were the valence localized MO's of CH_2^-– and for –$^+SH_2$ the set of valence localized MO's and the set of the noninteracting empty sulfur 3d orbitals. We have then computed the energy effects associated with all possible nonbonded interactions between these MO's of the two fragments. The various valence localized MO's of the two interacting fragments together with the possible nonbonded interactions are shown in Figure 6.

The energy effects associated with the various orbital interactions are estimated on the basis of eq 1 and 2.

$$\Delta E_{ij}^2 = 2(H_{ij} - \epsilon_i\epsilon_{ij})^2/(\epsilon_i - \epsilon_j) \quad (1)$$

$$\Delta E_{ij}^4 = 4S_{ij}(S_{ij}\epsilon_0 - H_{ij})/(1 - S_{ij}^2) \quad (2)$$

Here ΔE_{ij}^4 represents the destabilization energy associated with the interaction between two doubly occupied MO's ϕ_i and ϕ_j and ΔE_{ij}^2 the stabilization energy associated with the interaction between a doubly occupied MO, ϕ_i, and a vacant MO, ϕ_j. In these expressions ϵ_i and ϵ_j denote the energies of the two unperturbed MO's ϕ_i and ϕ_j, S_{ij} denotes their overlap integral, H_{ij} denotes their matrix element, and ϵ_0 denotes the mean of the energies ϵ_i and ϵ_j. Equation 2 is obtained by application of the variational method to the case of a two-orbital interaction problem,[31] while eq 1 is a well-known result of perturbation theory.[32]

The various terms appearing in these expressions are computed by using the results of the ab initio SCF MO computations. In

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(31) Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 4427. Müller, K. *Helv. Chim. Acta* **1970**, *53*, 1112.

(32) See: Heilbronner, E.; Bock, H. "Das HMO-Modell und Seine Annendung"; Verlag Chemie: Weinheim/Bergstr., 1968. Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

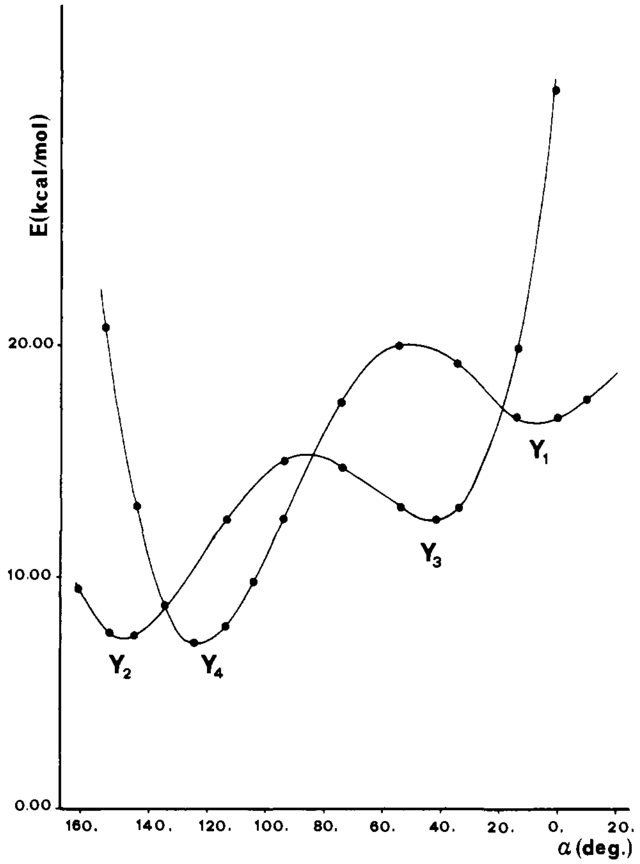

Figure 5. Total energy change, E, for variation of the dihedral angle α = H_i(C–S)H, in the two pairs of ylides centered at $C_2(Y_2,Y_3)$ and $C_4(Y_1,Y_4)$. Computations were performed at the 4-31G level, without geometry optimization.

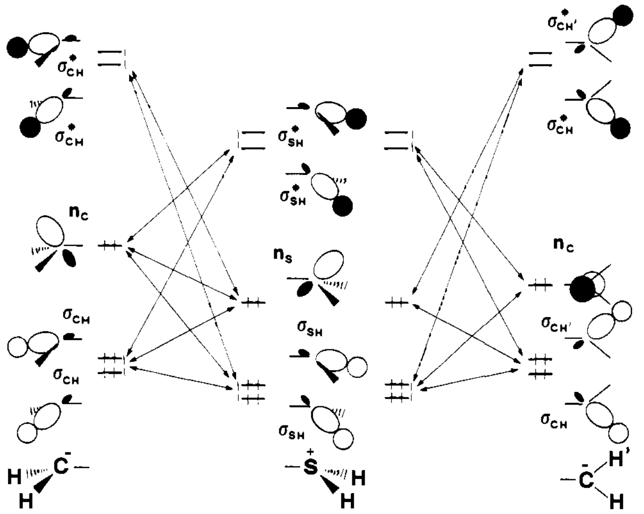

Figure 6. Orbital interaction diagram for CH_2^- and SH_2^+ fragments in the planar and pyramidal carbon ylides.

particular (i) the matrix elements H_{ij} and overlap integrals S_{ij} between the interacting fragment localized MO's are computed according to the relations

$$\mathbf{H} = (\mathbf{C_L}^0)^+\mathbf{F}\mathbf{C_L}^0$$

$$\mathbf{S} = (\mathbf{C_L}^0)^+\tilde{\mathbf{S}}\mathbf{C_L}^0$$

where $\mathbf{C_L}^0$ denotes the coefficient matrix of the fragment localized MO's and $\mathbf{F}$ and $\tilde{\mathbf{S}}$ the Fock and the overlap matrices for the composite system over the atomic orbital basis and (ii) the values of the energies of the fragment localized MO's ϵ_i are the diagonal elements of the $\mathbf{H}$ matrix.

Table III. Energy Effects[a] Associated with Nonbonded Interactions Occurring in Various Conformations (A–E, See Text) of the $^-H_2C-^+SH_2$ Ylide Computed at the STO-3G Level

	A	B	C	D	E
$\Delta E^4(\sigma_{CH'},\sigma_{SH'})$	1.12	2.19	6.70	14.83	15.53
$\Delta E^4(\sigma_{CH'},\sigma_{SH})$	1.12	1.88	0.01	0.15	0.51
$\Delta E^4(\sigma_{CH},\sigma_{SH'})$	1.22	1.88	0.01	2.11	2.11
$\Delta E^4(\sigma_{CH},\sigma_{SH})$	1.22	2.19	6.70	0.78	0.00
$\Delta E^4(\sigma_{CH'},n_S)$	6.75	0.69	1.37	1.82	5.39
$\Delta E^4(\sigma_{CH},n_S)$	5.60	0.69	1.37	0.00	0.23
$\Delta E^4(n_C,\sigma_{SH'})$	15.69	1.74	2.05	0.68	2.42
$\Delta E^4(n_C,\sigma_{SH})$	15.69	1.74	2.05	14.93	21.89
$\Delta E^4(n_C,n_S)$	0.00	6.40	4.58	12.72	6.16
$\Delta E^2(\sigma_{CH'},\sigma^*_{SH'})$	−0.61	−0.15	−0.16	−0.66	−0.64
$\Delta E^2(\sigma_{CH'},\sigma^*_{SH})$	−0.61	−1.10	−0.75	−0.18	−0.01
$\Delta E^2(\sigma_{CH},\sigma^*_{SH'})$	−0.07	−1.10	−0.75	−0.19	−0.17
$\Delta E^2(\sigma_{CH},\sigma^*_{SH})$	−0.07	−0.15	−0.16	−0.08	0.00
$\Delta E^2(n_C,\sigma^*_{SH'})$	−30.50	−1.95	−3.08	−0.37	−3.19
$\Delta E^2(n_C,\sigma^*_{SH})$	−30.50	−1.95	−3.08	−21.84	−29.81
$\Sigma\Delta E^4$	48.41	19.40	24.84	47.95	54.24
$\Sigma\Delta E^2$	−63.74	−6.54	−8.16	−23.73	−34.41
$\Sigma\Delta E$[b]	−15.33	12.86	16.68	24.22	19.83
$\Sigma\Delta E^2$(3d)	−93.25	−48.99	−46.93	−71.76	−78.00
$\Sigma\Delta E_T$[c]	−108.58	−36.13	−30.25	−47.54	−58.17

[a] kcal/mol. [b] $\Sigma\Delta E = \Sigma\Delta E^4 + \Sigma\Delta E^2$. [c] $\Sigma\Delta E_T = \Sigma\Delta E + \Sigma\Delta E^2(3d)$.

For a better understanding of the various geometrical effects, the procedure has been also applied to the three conformers of the unconstrained ylide A, located at the minimum, B, and C, located at the maxima of the rotational curve reported in Figure 2. Let us consider these three conformers first. The energy contributions are listed in Table III and illustrated by the interaction diagram in Figure 6. The overall energy effect associated with the various nonbonded interactions, ΔE_T, is stabilizing, and its trend parallels that of the total energies (Figure 2). In fact, the overall effect is more stabilizing in the minimum, A, than in either of the two maxima, and, between these two, it is more stabilizing in the anti, B, than in the syn conformation, C. To understand the origin of this trend, we dissected the overall effect into the gross component terms, i.e. (i) the overall destabilizing effect, $\sum\Delta E^4$, (ii) the stabilizing effect, $\sum\Delta E^2$, associated with the interactions of the bonding and lone-pair orbitals with the vacant antibonding orbitals, and (iii) the stabilizing effect associated with the interactions of the valence localized MO's of the H_2C^-– fragment with the sulfur 3d orbitals, $\sum\Delta E^2$(3d).

The destabilizing effect, $\sum\Delta E^4$, is considerably *smaller* in the *two maximum energy conformations*, B and C, than it is in the most stable conformation, A. The data (Table III) show that this is obtained because the lone pair–bond pair repulsions (n_c–σ_{SH}) are much larger in A than in either B or C. It is remarkable that this interaction is more important than the lone pair–lone pair repulsion, n_c–n_s, which had been claimed to be the major determinant of the conformational behavior of sulfonium ylides.[8] The conformational preference appears to be determined instead by the stabilizing effects, of which the major contributors appear to be the n_c–σ^*_{SH} interactions and the interactions involving the 3d orbitals. The stabilizing effect associated with the n_c–σ^*_{SH} interactions becomes in fact very large in A, whose geometry is the most favorable for the effective interaction of the carbon lone pair with both σ^*_{SH} MO's simultaneously. Likewise the interaction involving 3d orbitals is maximum in A because of the very efficient overlap of the carbon lone-pair p orbital with the sulfur 3d orbital of the appropriate symmetry. These particular contributions are the major factors associated with the nonbonded interactions discriminating between the three conformations (A–C).[33]

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(33) A quantitative PMO analysis on this ylide has also been performed by Wolfe et al.,[24b] who, however, have limited their attention to conformation A and to the conformation which is obtained from A by a rigid 90° rotation about the S–C bond. Moreover their computational procedure[24b] is significantly different in the definition of the various fragment MO's and type of interactions explicitly examined, and in fact these authors have considered only effects arising from interactions of the carbon lone-pair orbital.[24b] Therefore the two analyses are quite different, though their conclusions are similar.

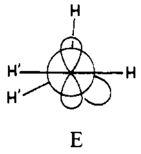
Table IV. Energy Effects[a] Associated with Nonbonded Interactions in Ylides Y_1–Y_4, Computed at the STO-3G* Level

	Y_4	Y_1	Y_2	Y_3
$\Delta E^4(\sigma_{CH},\sigma_{SH'})$	0.23	0.00	0.00	0.76
$\Delta E^4(\sigma_{CH},\sigma_{SH})$	0.59	8.84	2.22	6.12
$\Delta E^4(\sigma_{CH},n_S)$	2.48	3.08	2.00	0.62
$\Delta E^4(n_C,\sigma_{SH'})$	0.21	2.16	2.60	0.00
$\Delta E^4(n_C,\sigma_{SH})$	12.22	1.03	11.33	4.94
$\Delta E^4(n_C,n_S)$	4.54	3.11	1.43	3.33
$\Delta E^2(\sigma_{CH},\sigma^*_{SH'})$	−0.08	−0.72	−0.01	−0.21
$\Delta E^2(\sigma_{CH},\sigma^*_{SH})$	−0.46	0.00	−1.01	−0.66
$\Delta E^2(n_C,\sigma^*_{SH'})$	−0.60	−1.62	−3.43	−0.01
$\Delta E^2(n_C,\sigma^*_{SH})$	−10.42	−1.71	−9.43	−7.55
$\Sigma\Delta E^4$	20.27	18.22	19.88	15.77
$\Sigma\Delta E^2$	−11.56	−4.05	−13.88	−8.43
$\Sigma\Delta E$[b]	8.71	14.17	6.00	7.34
$\Sigma\Delta E^2$(3d)	−63.36	−49.41	−64.28	−55.14
$\Sigma\Delta E_T$[c]	−54.65	−35.24	−58.28	−47.80

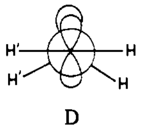
[a] kcal/mol. [b] $\Sigma\Delta E = \Sigma\Delta E^4 + \Sigma\Delta E^2$. [c] $\Sigma\Delta E_T = \Sigma\Delta E + \Sigma\Delta E^2$(3d).

It should be realized, however, that any comparison between the planar conformation, A, and the pyramidal ones, B and C, based only on nonbonded interactions, is improper. In fact the $-CH^-$ fragment has an intrinsic preference for pyramidality.[34] (For example, at the STO-3G level, CH_3^- is pyramidal with an inversion barrier of 23.5 kcal/mol,[34] and, at the same level, $^-CH_2$–SH_2^+ also turns out to be pyramidal.[24b]) Therefore a proper comparison between conformations A–C would require consideration of this pyramidalization effect.[35] This is, of course, included in the total energies, and their trend appears to parallel that of the nonbonded interaction, though less markedly. Thus the pyramidalization energy factor reduces the preference for the planar carbon conformer A.

It is now instructive to compare conformation A (minimum energy, unconstrained ylide, planar carbon) with conformations D and E, also characterized by planar carbon but possessing a torsional constraint, namely, that imposed by the geometry of cation **2**. To be specific, D and E are the planar carbon conformations located near the maximum along the interconversion curves $Y_2 \rightleftarrows Y_3$ and $Y_1 \rightleftarrows Y_4$, respectively (Figures 3 and 4, curve 3).



E



D

It is immediately apparent that, with the torsional constraints imposed by the cyclic rigid structure, a planar carbon center cannot fulfill the conditions for effective stabilization by the n_c–σ^*_{SH} interactions. The quantitative analysis (Table III) shows that the energy effect due to the n_c–σ^*_{SH} interactions amounts to only −22.2 and −33.0 kcal/mol in D and E, respectively (vs. −61 kcal/mol in A), not enough to counterbalance the overall destabilizing effect, $\sum\Delta E^4$, and the intrinsic preference for pyramidal conformation, which then become the leading factors. Indeed, for torsion angles at the ylide bond corresponding to those prevailing in cation **2**, the destabilizing effect is minimal for geometries close to those of the parent cation **2** which, in addition, have the advantage of a pyramidal carbon center.

Let us now turn our attention to the interactions occurring in the four model ylides, Y_1–Y_4, whose pertinent energy effects, associated with the nonbonding interactions, are listed in Table IV. The data show that $\sum\Delta E$, which is the sum of all the second-order energy contributions, except those associated with sulfur 3d orbitals, has the same trend as the total energy (i.e., Y_4 favored over Y_1 and Y_2 over Y_3). The major contributors among the repulsive terms are the bond pair–lone pair and bond pair–bond pair interactions and among the stabilizing ones are the hyperconjugative n_c–σ^*_{SH} interactions. The overall repulsive energy, $\sum\Delta E^4$ however, changes less, from one ylide to the next, than the contribution associated with stabilizing interactions, $\sum\Delta E^2$, the end result being that the stability order is determined by the latter. The trend is further strengthened by the energy effect associated with the 3d orbitals.

The factors affecting the relative stabilities of diastereomeric ylides centered at the same carbon may be better appreciated by focusing our attention on those energy effects that change from one ylide to the other, i.e., those associated with the σ_{CH} and the n_c MOS's. Consider, for example, the Y_1,Y_4 pair. The nonbonded energy effect associated with the removal of H_4 from the parent cation (to give Y_4) is given by the interactions of the lone pair in Y_4 [$\Delta E^4(n_c\sigma_{SH}) + \Delta E^4n(n_c\sigma_{SH'}) + \Delta E^4(n_cn_s) + \Delta E^2(n_c\sigma^*_{SH'}) + \Delta E^2(n_c\sigma^*_{SH})$ = 5.95 kcal/mol] minus the interactions of σ_{CH} before being removed. Since the geometry of the carbon center is not appreciably affected by the removal of one or the other proton (see Figures 3 and 4), the latter energy effects may be simply approximated by the interactions of σ_{C-H} in Y_1 [$\Delta E^4(\sigma_{CH}\sigma_{SH'}) + \Delta E^4(\sigma_{CH}\sigma_{SH}) + \Delta E^4(\sigma_{CH}n_S) + \Delta E^2(\sigma_{CH}\sigma^*_{SH'}) + \Delta E^2(\sigma_{CH}\sigma^*_{SH})$ = 11.20 kcal/mol]. Thus, the substitution of the C–H_4 bond by a lone pair is accompanied by a decrease in the nonbonded interaction energy by 5.2 kcal/mol.[36] Application of the same criterion to the removal of the H_1 (to give Y_1) yields instead a slight energy increase (from 2.8 to 3 kcal/mol). Therefore Y_4 is more stable than Y_1 by 5.2 + 0.2 = 5.4 kcal/mol. Similar arguments lead to the result that Y_2 is more stable than Y_3 by some 1.3 kcal/mol.

Conclusions

The $^-CH_2$–SH_2^+ model ylide has been investigated by ab initio SCF MO methods and quantitative PMO analyses. While in a fully relaxed geometry the carbanionic carbon is planar, it becomes pyramidal in the presence of a torsional constraint at the ylide bond. The PMO analysis provides a rationalization of this behavior in terms of the energy effects associated with the nonbonded interactions and of the pyramidalization energy factor. In the unconstrained ylide the hyperconjugative stabilizing interactions of the carbon lone pair with the antibonding orbitals σ^*_{SH} and with the sulfur 3d orbitals are largely dominant, favoring the planar carbon geometry. When a rigid torsional constraint is present, the hyperconjugative interactions, in particular those involving the σ^*_{SH} orbitals, can no longer exercise fully their stabilizing role and are overcome by steric and pyramidalization effects, favoring a pyramidal carbon. However, the hyperconjugative stabilizations still play a major role in determining the relative energy of a pair of diastereomeric pyramidal ylides.

The results of the theoretical analysis allow an insight into the behavior of real sulfonium ylides. In torsionally unconstrained (or slightly constrained) systems, the ylide would tend to become planar, and, to the extent that the free ylide is a good representation of the transition state for proton abstraction, the kinetic acidity differential of a pair of diastereotopic protons would tend to vanish. In these instances any stereoselectivity that may be observed in reactions with electrophiles must arise from differences in energy of the diastereomeric transition states for the reaction of the electrophile on one or the other diastereotopic face of the planar ylide. A case in point appears to be that of the ylide from 1-phenylthianium which reacts stereospecifically with methyl iodide to give *trans*-2-methyl-1-phenylthianium essentially exclusively,[37] although, according to recent ^{13}C NMR evidence, it is very nearly planar.[38]

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[34] Bernardi, F.; Bottoni, A., unpublished results.

[35] (a) Levine, C. C. *J. Am. Chem. Soc.* **1975**, *97*, 5649. (b) Cherry, W.; Epiotis, N. D. *Ibid.* **1976**, *98*, 1135.

[36] This decrease should not be taken to indicate the ylide to be more stable than the parent cation. Such a comparison would require consideration of the first-order effects also.

[37] Garbesi, A. *Tetrahedron Lett.* **1980**, 547.

[38] Barbarella, G.; Dembech, P.; Garbesi, A., submitted for publication in *Tetrahedron Lett.* We thank the authors for letting us know their results prior to publication.

In systems possessing a rigid torsional constraint, such as cation **2** and *trans*-1-thioniabicyclo[4.4.0]decane,[6] pyramidal ylides will be formed, giving rise to kinetic acidity differentials related to the energy differentials of the corresponding ylides. The PMO analysis above suggests that, although no single factor determines the relative energy of the ylides, the hyperconjugative $n_{C_\alpha}\sigma^*_{SC_{\alpha'}}$ interactions play a special role insofar as their trend is the same as that for the total energy. Since such interactions are at maxima when the n_{C_α} and the S–$C_{\alpha'}$ or S–$C_{\alpha''}$ bond orbitals are syn or anti aligned and the geometry of the ylide is very much the same as that of the cation precursor, it is often possible to guess, purely on geometrical grounds, which pair of ylides will enjoy greater hyperconjugative stabilization. That ylide is also likely to be the more stable one and the proton, whose removal gives rise to it, the more acidic. In the case of torsionally constrained ylides, the overall stereochemistry of products arising from their reaction with electrophiles will depend on (i) the ylide populations and (ii) the rates of ylide interconversions relative to their rate of reaction with electrophile. Lacking this kinetic information, the overall stereochemical course may not be simply related to the relative thermodynamic stability of the various ylides. A fortiori, a parallelism is not to be expected between kinetic acidity in one solvent (such as water) and stereochemistry of alkylation of ylides in another nonpolar solvent such as THF, where, in addition, the Li cation may complicate the issue by associating with the carbanionic carbon.[38,39] In view of the above, it is not surprising that a system such as **2**, while exhibiting highly stereoselective base-catalyzed H–D exchange in water,[9] undergoes nonstereoselective alkylation (LDA followed by CH_3I) in tetrahydrofuran.[37]

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Supplementary Material Available: Talbes of positional and thermal parameters for hydrogen and for nonhydrogen atoms (Tables S1 and S2), structure amplitudes (Table S3), and molecular packing (Figure S1) (12 pages). Ordering information is given on any current masthead page.

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Transition-State Structures of Base-Promoted, Imine-Forming Eliminations from *N*-Benzyl-*O*-(arylsulfonyl)hydroxylamines[1]

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Abstract: Eliminations in $XC_6H_4CH_2NHOSO_2C_6H_4Y$ promoted by amine bases were examined in 2.25 M H_2O in THF–EtOAc (3:1) and methanol. Transition-state parameters in methanol were found to be $\rho = 0.11$, $k_H/k_D = 1.2$, for the benzylic group and $\rho = 1.65$ for the leaving group. These data indicate that the polar solvent methanol causes an E1-like transition state in this elimination. Brønsted parameters were determined for both solvents and found to be $\alpha = 0.3$ and $\beta = 2.32$ for the former and $\alpha = 0.1$ and $\beta = 2.65$ for methanol. These parameters can be used to map the transition-state structure in a More-O'Ferrall–Jencks diagram. Values of β_{lg} for a variety of reactions are found to be a useful gauge of reaction type and leaving group loss in the transition state.

In an earlier paper it was established that *N*-benzyl-*O*-(arylsulfonyl)hydroxylamines, **3**, produced from the reaction of benzylamines, **1**, with arylsulfonyl peroxides, **2**, undergo base-promoted elimination of imines **4** (eq 1).[2] A variety of mechanistic

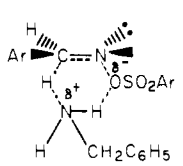
$$\underset{\mathbf{1a-f}}{XC_6H_4CH_2NH_2} + \underset{\mathbf{2a-e}}{(YC_6H_4SO_2O)_2} \longrightarrow \underset{\mathbf{3x,y}}{XC_6H_4CH_2NHOSO_2C_6H_4Y} \xrightarrow[k_2]{:B} \underset{\mathbf{4}}{XC_6H_4CH{=}NH} + BH^+ + ArSO_3^- \quad (1)$$

1: **a**, X = H; **b**, X = p-CH_3; **c**, X = m-CH_3; **d**, X = p-Cl; **e**, X = m-Cl; **f**, X = m-CF_3

2: **a**, Y = p-NO_2; **b**, Y = m-CF_3; **c**, Y = p-Br; **d**, Y = H; **e**, Y = 3,5-$(CF_3)_2$

probes indicated that the transition state is E1-like in that the loss of the arylsulfonate leaving group is well-advanced while benzylic proton removal lags behind.[1c]

Several interesting features were noted for this elimination. In the first place it exhibits a rather large, negative entropy of activation, which is significantly more negative than other common E2 types. Since benzylamine was used as the promoting base, hydrogen bonding between the promoting base and the anionic leaving group via a cyclic, syn-transition state, **5**, would result in



5

a highly ordered transition state and a large negative activation entropy.[3] Alternatively, the elimination is of an unusual charge type—neutral reactants giving charged products.[4] Since the transition state would be more charged than the reactants, electrostatic solvation of the transition state and consequent solvent

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[1] (a) Taken in part from the Ph.D. Thesis of ELB submitted to the Graduate School of New Mexico State University, May 1981. (b) Presented in part at the 179th Meeting of the American Chemical Society, Houston, Texas, March, 1980, (c) Part 6 in "The Oxidation of Amines with Sulfonyl Peroxides"; for part 5 see: Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 5687–5691.

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(3) Harris, J. M.; Wamser, C. C. "Fundamentals of Organic Reaction Mechanisms"; Wiley; New York, 1976; pp 108–110.

(4) Banthorpe, D. V. "Elimination Reactions"; Elsevier Publishing Co.: New York, 1963; pp 43–49.

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