Stereochemistry in Trivalent Nitrogen Compounds. 30. Torsional and Inversional Barriers in Sulfenylaziridines[1]

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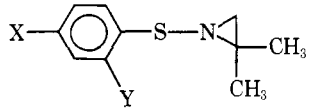
Abstract: The barriers to nitrogen inversion in a series of *N*-benzenesulfenyl-2,2-dimethylaziridines substituted in the sulfenyl phenyl ring have been measured using nuclear magnetic resonance spectroscopy. Substituents, coalescence temperatures (°C), and free energies of activation (kcal/mol) were: *p*-OCH_3, −20, 12.6; *p*-CH_3, −21, 12.5; H, −23, 12.4; *p*-Cl −21, 12.5; *p*-Br, −24, 12.4; *p*-NO_2, −17, 12.8, *o,p*-$(NO_2)_2$, −10, 13.3. Hammett analysis afforded a reaction constant (at 300 °C) of −0.3 ± 0.1. The small magnitude and negative sign argue against the possibility that d-orbital conjugation has a significant effect on nitrogen inversion barriers in sulfenylaziridines. On the other hand, low coalescence temperatures and free energies of activation were obtained for *N*-trifluoromethanesulfenyl-2,2-dimethylaziridine (−61 °C, 10.4 kcal/mol) and *N*-trichloromethanesulfenyl-2,2-dimethylaziridine (−86 °C, 9.2 kcal/mol). An analysis of steric effects indicated that the barriers in these compounds were 2–3 kcal/mol lower than could be accounted for on the basis of steric factors. This additional lowering was ascribed to an electronegativity effect involving overlap between the nitrogen lone pair orbital with the antibonding orbital associated with the S–C σ-bond, i.e., σ–π conjugation or negative hyperconjugation. The experimental data obtained also serve to provide upper limits to the barriers to torsion about N–S bonds in sulfenylaziridines. These limits indicate that torsional barriers are considerably lower in some sulfenylaziridines than in their acyclic analogues. Possible reasons for this lowering are discussed.

The chemical and stereochemical properties of bonds between atoms bearing nonbonded valence electrons has been the subject of intense experimental and theoretical inquiry.[3] The diverse experimental manifestations of this structural feature have been variously referred to as the anomeric effect, the Edward–Lemieux effect, the gauche effect, the α effect, and conjugative destabilization. Among the experimental consequences of the presence of lone pairs of electrons on an atom bonded to trivalent nitrogen are the significantly enhanced barriers to inversion of the nitrogen pyramid and to torsion about the nitrogen–heteroatom bond.[4]

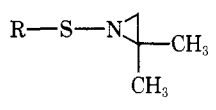
The nitrogen–sulfur bond in sulfenamides has represented a useful substrate for the investigations of a variety of effects on torsional barriers in such systems.[5] Examination of torsional barriers in acyclic sulfenamides using linear free energy relationships has provided a useful means for gaining insight into the factors which are responsible for the exceptionally high torsional barriers in some members of this series.[5b] This paper discusses electronic effects on the barriers to nitrogen inversion in sulfenylaziridines.

Results and Discussion

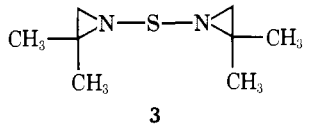
A series of substituted benzenesulfenamides, **1,** was prepared by reaction of the appropriate sulfenyl chlorides with 2,2-dimethylaziridine. Two additional trihalomethanesulfenylaziridines, **2,** and the thiobisamine, **3,** were also examined. The



1a, X = OCH_3, Y = H
1b, X = CH_3, Y = H
1c, X = Y = H
1d, X = Cl, Y = H
1e, X = Br, Y = H
1f, X = NO_2, Y = H
1g, X = Y = NO_2



2a, R = CCl_3
2b, R = CF_3



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NMR spectra of these compounds, with the exception of **3,** exhibited chemical shift nonequivalence of the diastereotopic ring methylene protons at low temperature (Figures 1 and 2). The diastereotopic methylene protons appear as pairs of broadened singlets rather than as AB quartets because of the small geminal coupling constants commonly observed for aziridines due to the combined effects of the electronegative nitrogen atom and the large HCH angle.[6] Very considerable differences in chemical shifts were observed for the ring methylene protons (ca. 30 Hz except for **1g**). By contrast, smaller chemical shift differences were observed for the diastereotopic geminal methyl groups. The separation was moderately small for several compounds, while in some cases the nonequivalence was so small as to be unresolvable (Figure 2).

Large chemical shift differences between geminal ring protons in *N*-alkylaziridines have been noted previously and explained on the basis of the magnetic anisotropy of the nitrogen atom and its ligands.[7] The ring protons syn to the substituent at nitrogen (i.e., anti to the lone pair of electrons) appear upfield by about 0.5 ppm in *N*-alkylaziridines.[7] The ring methylene protons in **1a–f** exhibited comparably large chemical shift differences. This similarity allows us to conclude that the upfield methylene signals in **1** and **2** probably derive from the protons syn to the sulfenyl sulfur. The small chemical shift differences observed for the diastereotopic ring methyl groups, except for that in **1g,** provide further support for supposing that the anisotropic effect of the aromatic ring contributes little to the chemical shift differences of the methylene protons.

Broadening of the methylene signals was observed at higher temperatures. Coalescence occurred in the range of −10 to −25 °C for the benzenesulfenyl compounds and −60 °C for the trihalomethanesulfenylaziridines. The chemical shift differences, coalescence temperatures, and associated free energies of activation calculated using the Eyring equation are given in Table I. One compound, **1g,** was selected for more detailed examination. The spectrum was measured at 11 temperatures in the range of −34.5 to 6 °C and the first-order rate constants were determined using complete line shape analysis. Linear least-squares fit furnished activation parameters: $\Delta H^{\ddagger}$ = 10.9 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = −8.6 ± 1.2 eu.

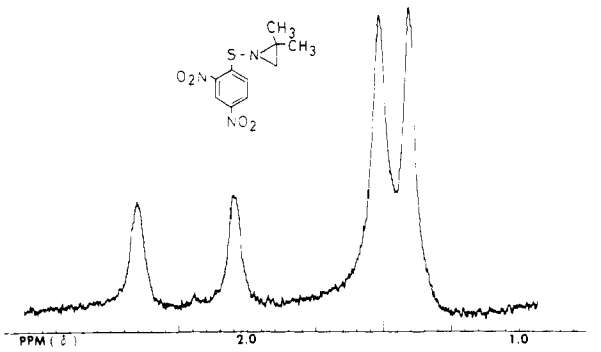
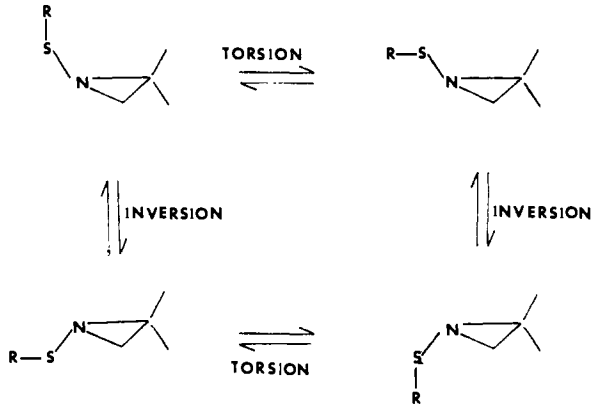


Figure 1. Low temperature (−30 °C) proton NMR spectrum of **1g** in methyiene chloride.

The observation of chemical shift nonequivalence for compounds **1** and **2** requires that the ground state for these molecules be chiral. The coalescence phenomenon, then, is associated with a loss of chirality, i.e., a degenerate racemization. As in the case of acyclic sulfenamides, two conformational changes, torsion about the S–N bond and inversion of the nitrogen pyramid, are necessary for racemization and both must occur rapidly in order that coalescence be observed. It seems most likely that torsion and inversion occur sequentially rather than synchronously, since both torsion and inversion are known to involve unfavorable distortions in geometries of analogous structures (for example, the hydroxylamines[3g]). The free energy of activation for topomerization, then, corresponds to the more difficult (i.e., the slower) of the two processes. Alternatively, it is conceivable that one of the two structural changes is not activated, i.e., that the pathway from one enantiomer to the other involves first one process then the other with but a single transition state. In this case, we regard the barrier as a torsional barrier if the reaction coordinate in the neighborhood of the transition state primarily involves a change in the S–N dihedral angle or an inversion barrier if the primary change is in the bond angles at nitrogen. In acyclic dialkylsulfenamides and *N*-alkyl-*N*-arenesulfonylsulfenamides, investigations of steric and electronic effects[5] have provided evidence that the torsional barrier is greater than the inversion barrier. An x-ray



crystallographic structure determination[8] has shown that the nitrogen in an acyclic sulfenamide is nearly planar, indicating that nitrogen inversion cannot be associated with a substantial activation energy. However, constraint of the nitrogen by incorporation into a three-membered ring is known to destabilize the transition state and increases the barrier for inversion and makes this process, rather than torsion, rate limiting.[9] Further evidence on this point may be adduced by comparing the effect of para substituents on the free energy of activation for degenerate racemization in sulfenylaziridines (**1**) with that for torsion about the N–S bond in acyclic *N*-arenesulfonylsulfenamides.

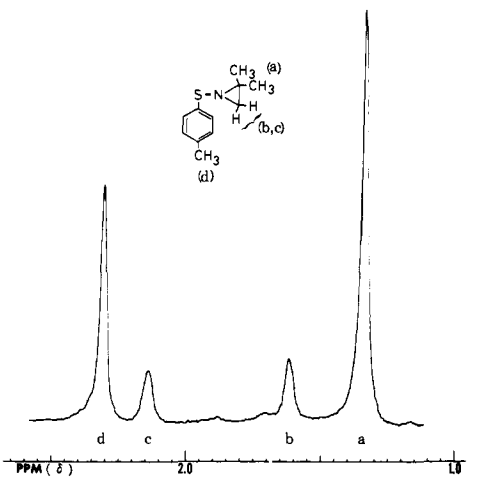


Figure 2. Low temperature (−60 °C) proton NMR spectrum of **1b** in methylene chloride.

Table I[a]

Compd	$\Delta\nu_{CH_2}$,[b] Hz	$\Delta\nu_{CH_3}$,[c] Hz	T_C,[b] °C	$\Delta G^{\ddagger}$,[b] kcal/mol
1a	30	6	−20	12.6
1b	31		−21	12.5
1c	32		−23	12.4
1d	31	2	−21	12.5
1e	31	2	−23.5	12.4
1f	30	2	−17	12.8
1g	23	6	−10	13.3
2a	31		−86	9.2
2b	34	4	−61	10.4

[a] NMR spectra were measured in methylene chloride solvent with the exception of compound **2a**, for which the solvent was a mixture of methylene chloride and dichlorofluoromethane. [b] Chemical shift differences, coalescence points, and free energies of activation obtained for the diastereotopic ring methylene protons. [c] Chemical shift differences for diastereotopic methyl groups.

The effect of para substituents is most easily analyzed in quantitative fashion by using the temperature-independent form of the Hammett equation.[5b]

$$\Delta G^{\ddagger} = R\sigma\rho' + \Delta G_0^{\ddagger} \qquad (1)$$

As we have pointed out previously this form of the Hammett equation is the most convenient for evaluation of polar effects on conformational processes which are determined using NMR spectroscopy.[5b] Since, in general, the free energy of activation at the coalescence point is the most reliable and reproducible rate datum which can be obtained using dynamic nuclear magnetic resonance spectroscopy, the data obtained refer to different temperatures. Further, entropies of activation for simple conformational processes are small and comparable within a series and permit comparison of data obtained at different temperatures. Equation 1 yields a temperature-independent reaction constant ρ', which is proportional to the conventional Hammett reaction constant ρ, the proportionality constant being the absolute temperature. In order to compare reaction constants obtained in this manner with those obtained previously, recourse may be taken to the adjusted constant, ρ_{300}, obtained by division of ρ' by 300. These values are comparable to conventional ρ values obtained at 300 K.

The free energies of activation for degenerate racemization of sulfenamides **1** were correlated with Hammett[10] σ-values[11] (Figure 3) using linear least-squares best fit. Reaction constants and correlation coefficients were obtained for the entire

series: $\rho' = -97 \pm 22$, $\rho_{300} = -0.3 \pm 0.1$, $r = 0.891$ as well as the series of para-substituted compounds, i.e., excluding **1g**, $\rho' = -49 \pm 37$, $\rho_{300} = -0.16 \pm 0.11$, $r = 0.554$. Ortho substituted compounds commonly deviated from Hammett plots, for steric reasons, and it is therefore felt that the line excluding the point for **1g** better represents polar substituent effects in this series. We feel that these data should be evaluated in terms of a negligible effect of substituents on the barrier to degenerate racemization.

By comparison with these data obtained for compounds **1**, *torsional* barriers in acyclic sulfenylsulfonamides exhibit a very marked dependence on polar substituents on the sulfenyl phenyl ring. The barriers for para substituted *N*-benzenesulfenyl-*N*-isopropylbenzenesulfonamides afforded reaction constants which were well outside of experimental error: $\rho' = -282 \pm 20$, $\rho_{300} = -0.9 \pm 0.1$, $r = 0.963$. Comparison of the ρ values for the two systems provides confirming evidence that the rate-determining steps for degenerate racemization are different in the two systems, inversion of the nitrogen pyramid in sulfenylaziridines and torsion about the N–S bond in acyclic sulfenylsulfonamides.

Linear free-energy relationships have provided a useful means for probing the extent of conjugation of the nitrogen lone pair and its effect on nitrogen inversion barriers. Andose et al.[12] have examined the nitrogen inversion barriers in series of para-substituted *N*-phenylaziridines. The barriers were found to be strongly dependent on the Hammett substituent constants of the para substituents, reflecting the importance of (p–p) π conjugation; the barrier decreased markedly when the para substituent was electron withdrawing and could exhalt the (p–p) π bonding in the transition state.

The same kind of behavior would be expected were (p–d) π conjugation an important determinant of nitrogen inversion barriers. Early results did support the view that (p–d) π bonding was responsible for lowered inversion barriers in some nitrogen compounds. Planar (or nearly planar) geometries have been found for nitrogen in amines bearing sulfur[8,13] and phosphorus[14] attached to trivalent nitrogen. While p–d π bonding provided one possible explanation for the planarity or low inversion barriers in silylamines and aminophosphoranes, more recent work has cast doubt on this attribution.[4b,15] The data obtained in this study also support the view that (p–d) π bonding does not substantially alter nitrogen inversion barriers in sulfenylaziridines even when a very electronegative group, e.g., 2,4-dinitrophenyl, is present as a ligand at the sulfenyl sulfur atom.

The failure to detect differences in effects of (p–d) π bonding on aziridine barriers rules out an explanation involving d-orbital resonance for the lowered barriers in sulfenylaziridines as compared with alkylaziridines. Available data do indicate that the sulfur atom does indeed increase the rate of nitrogen inversion. Thus barriers to inversion in *N*-arenesulfenylaziridines are close to 13 kcal/mol, considerably lower than those in *N*-alkylaziridines. We are unable, on the basis of available evidence, to offer convincing explanation for this phenomenon. It may be that a difference in the sensitivity of the strength of the S–N bond (as compared with the C–N bond) to hybridization at nitrogen or with the greater polarizability of the sulfur orbitals is responsible. In this regard, it may be noted that the inversion barriers in silyl and germyl amines also are lowered, and it has been concluded that electronegativity alone can account for the lowering.[4b]

Comparison of the barrier in **1g** with the barrier to rotation about the N–S bond in *N*-benzyl-*N*-isopropyl-2,4-dinitrobenzenesulfenamide[5a] reveals that the constraint of the nitrogen atom into a three-membered ring not only raises the nitrogen inversion barrier, but also lowers the torsional barrier. Since both processes, torsion and inversion, are required for degenerate racemization, the experimentally obtained free energy of activation sets an upper limit for both processes. Although the free energy of activation in **1g** corresponds to the inversion barrier, we may also conclude that the torsional barrier must be lower than 13.8 kcal/mol. Thus, the torsional barrier for **1g** is at least 2.7 kcal/mol lower than in the acyclic analogue *N*-benzyl-*N*-isopropyl-2,4-dinitrobenzenesulfenamide.[5a] Possible reasons for this lowering of S–N torsional barriers in aziridines are discussed below.

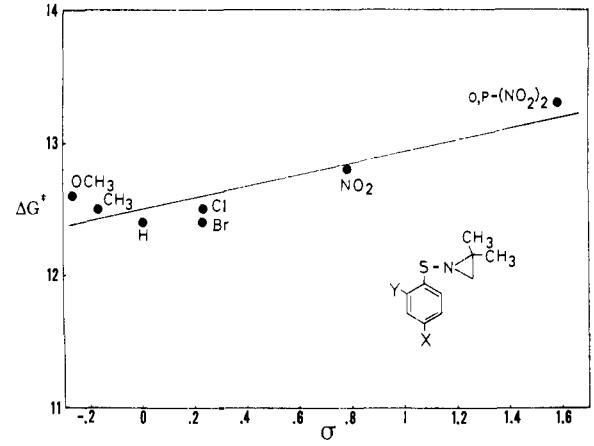


Figure 3. Hammett plot of free energies of activation for degenerate racemization in series 1.

In light of the failure to detect an important effect from (p–d) π bonding to nitrogen inversion barriers in arenesulfenylaziridines, the low barriers reported for the trichloromethanesulfenylaziridine[9a] **2a**, the trifluoromethyl analogue **2b** (Table I), and the planarity at nitrogen in a trichloromethanesulfenamide[8] suggest the operation of another factor. Unless we are to suppose that the trihalomethyl groups are electron releasing in comparison with alkyl and aryl groups, we may exclude from consideration a simple inductive effect, since theoretical and experimental investigations have concluded that the effect of electron-withdrawing substituents must be to augment nitrogen inversion barriers.[4] Two alternative explanations suggest themselves, steric acceleration and σ–π conjugation.

Steric bulk has a significant effect on nitrogen inversion in aziridines as well as upon pyramidal inversion in general. Since the bond angles are increased upon going to a planar transition state, bulky ligands at nitrogen create more steric hindrance in the ground state than in the transition state. Thus more bulky ligands result in lower inversion barriers. The effect is most marked for α-branched ligands. Thus, the barrier in *N*-*tert*-butylaziridine is 17.6 kcal/mol, while that in *N*-methylaziridine is 22.3 kcal/mol. The effect of β-branching is somewhat less, but has also been observed in the sulfenylaziridine system; the barrier in *N*-*tert*-butanesulfenylaziridine is 12.2 kcal/mol, while that in *N*-methanesulfenylaziridine is 13.3 kcal/mol. Since the trihalomethyl groups have considerable steric bulk, steric acceleration may be considered as a possible explanation for the lowered barriers in compounds **2** in comparison to those in alkanesulfenyl and arenesulfenyl analogues.

The steric bulk of the trichloromethyl group cannot be specified unequivocally. The *A* value for this ligand has not been measured,[16] although one steric parameter, Taft's E_s, is available.[17] On the other hand, both parameters for the trifluoromethyl group are available. The *A* value for CF_3 is somewhat smaller than for phenyl and we may judge that the E_s value cannot be much larger than the value estimated for phenyl. Certainly, we may be confident in supposing that the trifluoromethyl group is less bulky than *tert*-butyl. Yet, the barrier for inversion in **2b** is about 2 kcal/mol lower than that

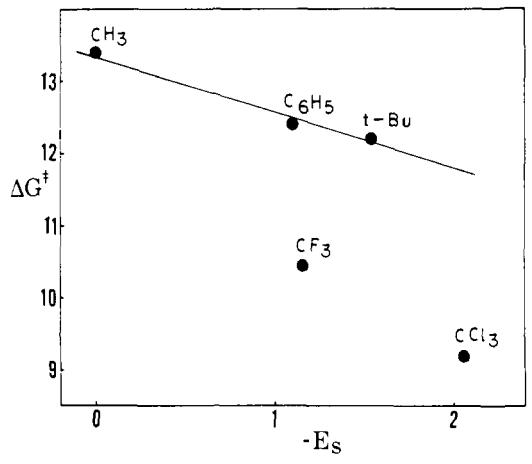


Figure 4. Plot of free energies of activation in sulfenylaziridines as a function of Taft's steric parameter, E_s.

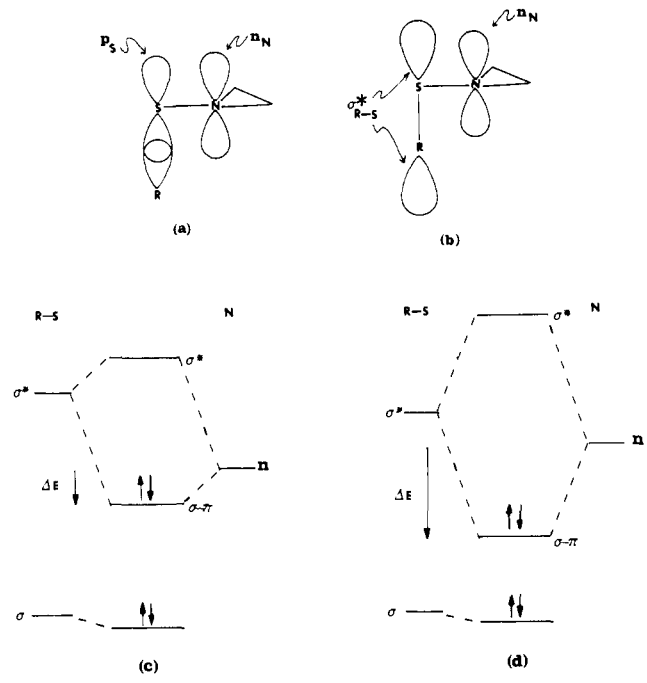


Figure 5. Schematic illustration of the interaction of the nitrogen lone-pair orbital with the antibonding orbitals associated with the S–R bond (c) when R is not electronegative and (d) when R is electronegative.

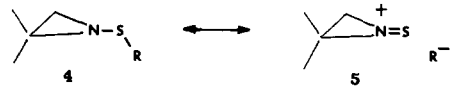
in either the comparable benzenesulfenyl- or *tert*-butanesulfenylaziridines; pointing to the importance of an electronic effect on barriers in sulfenylaziridines. A plot of $\Delta G^{\ddagger}$ as a function of E_s of R for compounds **2** as well as their analogues, in which R is methyl, phenyl, and *tert*-butyl, illustrates this point (Figure 4). The alkane and arenesulfenyl compounds have barriers which are in accord with predictions on the basis of steric bulk,[9] while deviations are observed for **2a** and **2b**. Both compounds exhibit free energies of activation which are 2–2.5 kcal/mol lower than would be expected on steric grounds alone. The use of A values affords a comparable estimate. On the basis of the A values given for methyl, phenyl, and trifluoromethyl,[18] the free energy of activation for **2b** deviates by 2.5 kcal/mol from the line formed by the other two points. While these calculations are admittedly crude, we feel confident in concluding that steric acceleration cannot account for the low inversion barriers in **2a** and **2b** and that an electronic explanation must be sought. Since experimental evidence discussed above rules out p–d π bonding as a possibility, we believe that σ–π conjugation, (negative hyperconjugation), as discussed below, represents an attractive rationale.

Bystrov et al.[19] have suggested that negative hyperconjugation[20] can lead to lowered inversion barriers in *N*-hydroxymethyl- and *N*-alkoxymethylaziridines as compared to the barriers in *N*-alkylaziridines. Perturbational analysis indicates that the attachment of an electronegative group R to sulfenyl sulfur should lessen the energy difference between σ and σ^* S–R orbitals and the interaction between the nonbonding orbital at nitrogen and the S–R antibonding orbital becomes greater when the ligand is more inductively withdrawing, as qualitatively illustrated in Figure 5. The geometrical requirements for this kind of n–σ^* overlap can be visualized by considering the molecular orbitals (or hybrid orbitals) on nitrogen and sulfur disposed to overlap in π fashion and a third atomic orbital from the R group, which can overlap in σ fashion with the sulfur orbital. The atomic orbital system leads to three molecular orbitals, involving both π and σ overlap. This overlap is maximized when the projection of the S–R bond bisects the CNC angle and the nitrogen lone pair is in a p orbital (Figure 5a).

The effect of the electronegativity of the R ligand can be estimated by considering the perturbation of the empty S–R σ^* orbital upon the filled nitrogen lone-pair orbital (Figure 5b). The geometrical requirements for overlap with this σ^* orbital are the same as for overlap with the sulfur atomic orbital used in making the S–R bond. Indeed, the more electron withdrawing (in an inductive sense) the R group, the more the σ^* orbital will resemble the sulfur atomic orbital. In the extreme where R was completely ionized, we would speak of a formal N–S double bond as a result of such overlap.[21]

The mixing of the filled lone-pair orbital and the empty σ^* orbital will result in a stabilization of the filled-lone-pair orbital and a destabilization of the σ^* orbital. Since the lone pair orbital has gained in stability by π overlap with the S–R σ bond, we have designated the perturbed orbital as the σ–π orbital. The magnitude of the perturbation (ΔE) will depend on the electronegativity of R.[3f] As the electronegativity of R increases the energy of the σ^* orbital will be decreased and as the energies of the σ^* orbital and the lone-pair orbital become more similar the magnitude of the perturbational stabilization will increase. This interaction can lessen the buildup of positive charge on sulfur and can partially compensate for inductive withdrawal by R.

Alternatively, the same phenomenon can be expressed with a resonance framework by reference to canonical structures **4** and **5**. When R is highly electron withdrawing and able to



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(a) R = CCl_3
(b) R = CF_3
(c) R = N
(d) R = NO_2, NO_2

bear a negative charge (e.g., CCl_3 or CF_3), considerable stabilization can be provided by contribution from canonical structure **5**. This contribution will be greater in the planar transition state for nitrogen inversion than in the pyramidal ground state, decreasing the free energy of activation for nitrogen inversion.

Nitrogen inversion in *N*-methoxymethylisoxazolidine is considerably more rapid than can be accounted for by steric

considerations,[22] possibly reflecting stabilization of the inversion transition state by $\sigma-\pi$ conjugation. The low barriers observed in some fluorine-substituted aziridines may also be evidence of this phenomenon.[4]

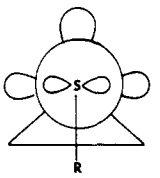
An x-ray crystallographic investigation has confirmed the near planarity at nitrogen in a *N*-trichloromethanesulfenylsulfonamide.[9] When this work was published, (p–d) π bonding seemed a possible explanation for the flattening of the nitrogen pyramid. However, in light of the apparent insensitivity of nitrogen inversion barriers to para substituents in arenesulfenylaziridines and the demonstrated lowering of the inversion barrier in trihalomethanesulfenylaziridines, $\sigma-\pi$ conjugation offers a more consistent explanation.

The failure to observe chemical shift nonequivalence in the thiobisamine **3** is in accord with the postulation of $\sigma-\pi$ conjugation in the inversion transition state, since contribution of resonance structure **5c,** where the negative charge is borne on the electronegative nitrogen atom, should be quite substantial and a low barrier is predicted. The fairly high barrier in the 2,4-dinitrobenzenesulfenamide, **1g,** is also consistent with this view. Resonance withdrawal by the nitro groups cannot effect a rate acceleration comparable to that effected by the trihalomethyl groups, since the bond (as well as the approximate symmetry axis of the σ^* orbital) lies within the nodal plane of the aromatic π system. Similarly, within the resonance framework, we note that the nitro groups are unable to delocalize the negative charge in **5d** by resonance.

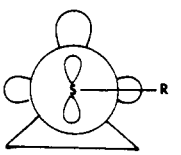
The effects of the two groups, trichloromethyl and 2,4-dinitrophenyl, on barriers in acyclic and aziridinylsulfenamides vividly illustrate the difference in the conformational properties of the two systems. Both groups are effective at increasing torsional barriers in acyclic compounds. This effect in arene sulfenylsulfonamides is apparently due to electron withdrawal from an orbital on sulfur, which can conjugate with the aromatic π system. While the involvement of sulfur d orbitals[5b,23b] seemed to provide a rationale for this barrier increase,[5b] the more recent examinations of *N*-arenesulfenyl-*N*-benzylurethanes[23a] and *N*-sulfenylimines[23b] casts some doubt on this assessment. On the other hand, this resonance effect has a negligible influence on nitrogen inversion barriers, while $\sigma-\pi$ conjugation has a demonstrable result and the effects of these two groups on sulfenylaziridine inversion barriers are sharply divergent.

Comparison of acyclic and aziridinylsulfenamides focuses attention on the surprising conclusion, alluded to above, that N–S torsional barriers in sulfenylaziridines are considerably reduced with respect to their acyclic analogues. It might be supposed that if the nitrogen inversion barrier were to be lowered enough, the rate-limiting step in the degenerate racemization would become torsion about the N–S single bond. The experimental evidence is inconsistent with torsion as the slow step in the trihalomethyl derivatives **2a** and **2b.** If torsion were the slow step for both **2a** and **2b,** the experimental barrier for the trichloromethyl compound **2a** would surely be higher, since torsional barriers in acyclic trichloromethanesulfenamides are higher than in their trifluoromethyl analogues.[5a] While we cannot be certain that the slow step for **2a** is nitrogen inversion, the nearly parallel trends illustrated in Figure 4 seem to argue against such a crossover. However, whether or not the slow step for **2a** is torsion about the N–S bond the experimental barrier furnishes an upper limit for torsion in this system. When this limit is compared with the torsional barrier in *N*-benzyl-*N*-isopropyltrichloromethanesulfenamide (16.0 kcal/mol)[5a] it can be seen that closure of the three-membered ring lowers the barrier by nearly 7 kcal/mol, i.e., by more than 40%! While the removal of steric interactions at the torsional transition state would be expected to lower the barrier, the experimental difference seems, to us, too large to be accounted for by steric effects alone.

The aziridine ring introduces two additional structural peculiarities which might be implicated. First, the ring strain of the three-membered ring constrains the nitrogen to employ a hybrid orbital which has considerable s character for its lone pair. It may well be that the lone pair–lone pair interactions which appear to play a role in sulfenamide torsional barriers are enhanced when the lone-pair orbital has greater p character. The second possible effect of ring contraction is best understood by considering the implications of electron interactions with the atomic orbitals used in the Walsh model. In the rotamer which corresponds to the torsional ground state in acyclic sulfenamide **6a,** the repulsive interaction between



6a



6b

the nitrogen lone pair and the sulfenamide **6a,** the repulsive interaction between the nitrogen lone pair and the sulfur p lone-pair orbital is minimized. However, the Walsh p orbital at nitrogen is in a good geometry for interaction. Conversely, the interaction with the Walsh orbital is minimized in rotamer **6b,** while at the same time, interaction with the lone-pair orbital is maximized. In a sense then, we might imagine that the nitrogen atom might appear to have less "cylindrical asymmetry" in aziridines than in acyclic amines, resulting in a reduced torsional barrier.

Experimental Section

NMR spectra were measured on a Varian A-60A spectrometer equipped with a Varian variable temperature probe using ca. 10–20% solutions. Duplicate measurements indicated that the line shapes were not dependent upon concentration within this range. Temperatures were determined using methanol spectra as described in the Varian manual. Theoretical spectra were generated by an IBM 360 computer and plotted on a Calcomp plotter using a program (CLAS) based on the solution to the exchange-modified Bloch equations. The determination of rates of exchange by complete line-shape analysis involved obtaining correspondence between experimental and theoretical spectra.

2,2-Dimethylaziridine.[24] 2-Amino-2-methylpropanol (100 g) and 110 g of concentrated sulfuric acid were dissolved in 300 ml of water. The mixture was distilled at atmospheric pressure until the temperature of the solution reached 115 °C. Distillation was continued under aspirator vacuum until the pot temperature reached 185 °C. The mixture was cooled, 200 ml of 40% aqueous NaOH and 150 ml of water were added, and the product aziridine was steam distilled. The distillate was saturated with KOH and the upper layer separated, dried, and distilled at atmospheric pressure, bp 68–69 °C (lit.[24] 69–70 °C).

2,4-Dinitrobenzenesulfenyl-2,2-dimethylaziridine (1). 2,4-Dinitrobenzenesulfenyl chloride (9.4 g, 0.04 mol) was dissolved in 20 ml of benzene and added dropwise to a solution of 3.6 g of 2,2-dimethylaziridine (0.05 mol) and 7 g of triethylamine (0.07 mol) in 20 ml of benzene. The mixture was allowed to stir at room temperature for 30 min and filtered to remove triethylamine hydrochloride. The filtrate was evaporated under reduced pressure and the solid recrystallized from benzene:hexane (1:1) (crude yield, 8.42 g, 79%). Two subsequent recrystallizations from benzene:hexane afforded analytically pure material whose melting point was unchanged upon subsequent recrystallization, mp 103.5–105 °C. Anal. Calcd for $C_{10}H_{11}N_3O_4S$: C, 44.60; H, 4.12; N, 15.60. Found: C, 44.8; H, 4.4; N, 15.8. The other sulfenylaziridines **1** and **2** were prepared in a similar fashion.

Acknowledgment. We thank Mr. Willard A. Stacer for his assistance in the preparation of some of the compounds used in this study.

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Vapor-Phase Structure and Conformation of a Long-Chain *n*-Alkane. An Electron Diffraction Study

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Abstract: The structure of *n*-hexadecane has been determined at a nozzle temperature of 150 °C by gas-phase electron diffraction. Molecular parameters, averaged over the diverse conformers present, were found to be $(\pm 3\sigma)r_g$(C–C) = 1.542 ± 0.004 Å, r_g(C–H) = 1.130 ± 0.008 Å, ∠CCC = 114.6 ± 0.6°, ∠CCH = 110.4 ± 1.1°, gauche CCCC dihedral angle = 64.9 ± 10°, and ΔG° (the gauche-trans free energy difference per gauche link) = 275 ± 350 cal/mol. Amplitudes of vibration were also measured. The average C–C bond is 0.01 Å longer than C–C bonds reported in short-chain vapor-phase *n*-alkanes. This increase is interpreted as indicating a difference between interior methylene–methylene bonds and bonds at or near a chain end. Other evidence, including ab initio and potential energy minimization calculations, is cited in support of such an effect of environment on bond length. The diffraction data also suggest site-to-site variations in structure consistent with a picture in which gauche $CH_2\cdots CH_2$ steric interactions deform local CCC bond angles and trans CCCC dihedral angles. A value for the characteristic ratio of condensed polymethylene was calculated, based on the *n*-hexadecane vapor-phase parameters and a three-state model. The result, 7.9 ± 2 (3σ), agreed with the experimental value of 6.8 ± 0.3 to within experimental error.

Information about the structure and rotational isomerization of hydrocarbon chains is of concern to chemists in varied areas of research. Extensive studies have been made of the structures of both short and long chains as they exist in crystals, constrained to be in their all-trans form. Only a few investigations of the structures and conformational energy differences of free vapor-phase hydrocarbon chains have been published and, heretofore, these have been carried out on relatively short *n*-alkanes (*n*-heptane or shorter).[1-3] Because the short chains appear to possess very similar structures and conformational energy differences, it has been often assumed, in the absence of other information, that average bond lengths, angles, and gauche-trans energy differences are independent of the chain length. In view of the fact that long hydrocarbon chains commonly occur in compounds of concern to chemists and biologists, it was of interest to learn from electron diffraction studies that this assumption may not be quantitatively valid. Therefore, we report our findings for *n*-hexadecane, a considerably longer chain hydrocarbon than has previously been studied in the vapor phase.

Experimental Section

A sample of *n*-hexadecane with a stated purity of 99 mol % was obtained from the Aldrich Chemical Co. and was used without further purification. The sample was heated to 150 °C in a nozzle furnace of Hargittai's design[4] to provide a pressure[5] of 23 Torr [1 Torr = (101.325/760) kPa]. Scattering patterns provided by 40 kV incident electrons were obtained at the 21-, 11-, and 7-cm camera distances through a rotating r^3 sector and at the 21-cm distance through a rotating r^2 sector. Diffraction patterns were recorded on 4 × 5 in. Kodak Electron Image plates using the University of Michigan apparatus.[6] Experimental conditions are summarized in Table I.