The Electrosteric Effect on Sulfenamide Torsional Barriers. Barriers in Trinitrobenzenesulfenamides and Perhalobenzenesulfenamides[1a-c]

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Abstract: A series of arenesulfenamides has been prepared from 2,4-dinitrobenzenesulfenyl chloride, 2,4,6-trinitrobenzenesulfenyl chloride, pentafluorobenzenesulfenyl chloride, and pentachlorobenzenesulfenyl chloride and a variety of dialkyl- and arylalkylamines and *N*-alkylsulfonamides. The barriers to torsion about the N-S bond have been measured by dynamic proton magnetic resonance spectroscopy. While sulfenamide barriers are increased by the presence of electronegative substituents in the sulfenyl aryl ring, this effect is absent when there are two ortho substituents in the aryl ring. The barrier-enhancing effect of electronegative substituents is interpreted in terms of an electrosteric effect since the electronegative substituents act as if they increase the steric bulk of the aryl ring. The removal of the electrosteric effect when two ortho substituents are present is ascribed to steric inhibition of resonance. The various effects on sulfenamide torsional barriers are discussed in detail.

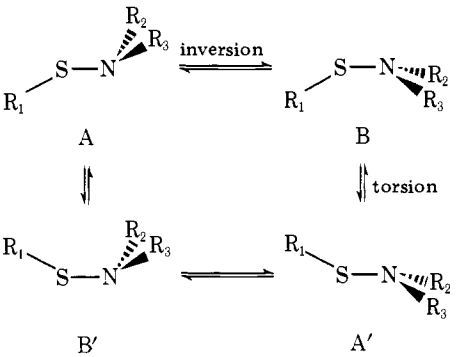
Introduction

Sulfenamides[2] ($R_1SNR_2R_3$) are members of a general class of compounds with bonds between two heteroatoms which bear nonbonding pairs of electrons. Members of this class of compounds exhibit chemical and stereochemical phenomena which have been associated with the presence of lone pairs of electrons on both adjacent atoms or interactions of a lone pair with an antibonding orbital on the adjacent atom. These phenomena include torsional preferences (the gauche effect), enhanced torsional barriers and nitrogen inversion barriers (conjugative destabilization), and increased nucleophilicity (the α effect).[3]

The barrier to torsion about the N-S bond in sulfenamides, which is among the largest exhibited within this class of compounds, renders the sulfenamide functional group an element of axial chirality.[4] This chirality is manifest in the low-temperature NMR spectra of suitably substituted sulfenamides, which exhibit chemical shift nonequivalence of diastereotopic atoms attached to prochiral carbon atoms in isopropyl, ethyl, or benzyl probe groups. The reversible equilibrium interconversion (degenerate racemization) of enantiomeric sulfenamides (A $\rightleftharpoons$ A′ or B $\rightleftharpoons$ B′) gives rise to a topomerization which renders such diastereotopic groups enantiotopic on time average, and coalescence of NMR resonances is observed when degenerate racemization becomes rapid on the NMR time scale (Scheme I).

Since degenerate racemization requires both torsion about the N-S bond and inversion of the nitrogen pyramid, either of these processes could be the slow (rate determining) step in the degenerate racemization, and thus provide the basis for the chirality of sulfenamides which can be observed experimentally. Molecules of both mechanistic types have been described and the nature of the rate-determining step (i.e., either nitrogen inversion or N-S torsion) has been characterized. In the acyclic sulfenamides the slow step is torsion about the N-S bond.[4] However, incorporation of the two ligands at nitrogen into a three-membered ring (in *N*-sulfenylaziridines) both increases the nitrogen inversion barrier and decreases the N-S torsional barrier. In these compounds it can be demonstrated that the slow step involves inversion of the nitrogen pyramid.[5] While chirality is a structural concept, we find it convenient to ascribe the chirality of the acyclic sulfenamides to the chiral axis of the N-S bond (since torsion about the N-S bond is the slow step in stereomutation of these compounds) while in the sulfenylaziridines we focus attention on the chiral center of the nitrogen pyramid as the chiral unit (since here the rate of stereomutation is that of nitrogen inversion).

Scheme I



Three influences on these stereomutation barriers have been characterized: steric factors,[4] the four-electron interaction (lone pair-lone pair repulsion),[4] and the two-electron interaction (negative hyperconjugation or n→σ* conjugation).[5,6] Referring first to the N-S torsional barriers we note that the two-electron interaction is an attractive interaction which leads to increased barriers by ground-state stabilization while steric interactions and the four-electron interaction are repulsive interactions which raise torsional barriers by destabilizing the transition state. The effects of these three factors on inversion barriers are different. Thus, while the two-electron interaction can stabilize the ground state, its effect is even greater in the inversion transition state, leading to decreased nitrogen inversion barriers when the two-electron interaction is maximized. Steric repulsion is diminished in the inversion transition state relative to the ground state so that we observe steric acceleration of inversion when bulky groups are present, rather than the steric deceleration which is observed when N-S torsion is the slow step in stereomutation.

The four-electron interaction arises from overlap between filled nonbonding orbitals on nitrogen and sulfur (Figure 1). This interaction is greatest in the transition state for N-S torsion (Figure 1b) in which the sulfur lone pair with pure p character is in the correct geometry for π overlap with the nitrogen lone pair which has substantial p character. Since both localized orbitals are filled, the π and π* orbitals resulting from overlap[7] are filled and no net bonding occurs. Rather, overlap results in a net destabilizing action (conjugative destabilization). This destabilization will be greater in the transition state, when the overlapping sulfur lone pair has 100% p character, than in the ground state (Figure 1a), where the sulfur lone pair which is in the correct geometry for π overlap has very little p character.

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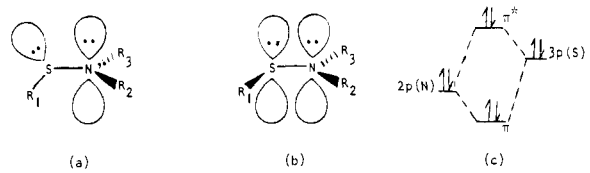


Figure 1. The four-electron interaction in sulfenamides: (a) torsion ground state; (b) torsion transition state; (c) schematic PMO energy level diagram.

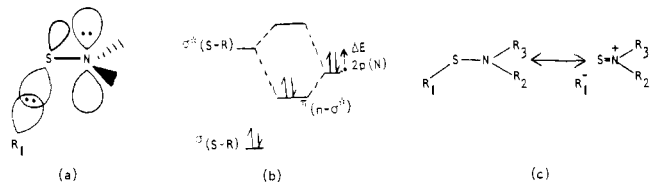


Figure 2. The two-electron interaction in sulfenamides: (a) torsional ground state; (b) schematic PMO energy level diagram; (c) canonical structures corresponding to the two-electron interaction.

The magnitude of the transition-state destabilization will be related to the overlap between the two orbitals as well as their energy levels. While it may be difficult to evaluate these two factors, it seems clear that the interaction should be diminished when the nitrogen lone pair has decreased p character, as is the case in the ground state of the sulfenylaziridines. It may be for this reason that the N–S torsional barriers in *N*-trihalomethanesulfenylaziridines are considerably lower[5] than in the acyclic analogues. Since the nitrogen lone pair has much less p character in the sulfenylaziridines than in the acyclic sulfenamides we expect the torsional barrier enchancement due to the four-electron interaction to be less. Of course, decreased steric interactions in the sulfenylaziridines may account for a major portion of the barrier lowering.

The very small amount of p character in the sulfur lone pair in the torsional ground state (Figure 1a) should limit the magnitude of the four-electron interaction even when the nitrogen becomes sp^2 hybridized (with a pure p lone pair) as occurs at the nitrogen inversion transition state. Thus, the four-electron interaction is not expected to have much of an effect on nitrogen inversion barriers as long as the molecule is free to achieve the geometry corresponding to minimum lone pair–lone pair overlap (i.e., that in Figure 1a). This seems in accord with the finding that aziridines do not suffer increased inversion barriers when an *N*-alkyl group is replaced by an *N*-arenesulfenyl or *N*-alkanesulfenyl group.

The two-electron interaction is illustrated in Figure 2. This interaction arises from π overlap of the nitrogen lone-pair orbital with the antibonding orbital corresponding to the S–R bond. This is an attractive interaction which is possible only in the torsional ground state and hence should lead to *increased torsional barriers* because of ground-state stabilization. Because the overlap will be increased as the p character of the nitrogen lone-pair orbital is increased, the two-electron interaction should lead to *decreased nitrogen inversion barriers*. The magnitude of the two-electron interaction is inversely proportional to the energy gap between the nitrogen lone-pair orbital and the S–R σ^* orbital. The energy of the antibonding orbital can be lowered and the coefficient on the sulfur atom increased by attachment of inductively withdrawing groups R_1 at sulfur. This is illustrated in the canonical structures in Figure 2c, which also suggest that the magnitude of the two-electron interaction will be increased as R is better able to bear a negative charge.

The predicted effects on both inversion and torsional barriers in sulfenamides have been observed. Trihalomethanesulfenylaziridines show the predicted decreased barriers to nitrogen inversion,[5] while acyclic trihalomethanesulfenamides exhibit large torsional barriers.[4] The X-ray crystallographic structure of a trichloromethanesulfenamide exhibited a nearly planar nitrogen atom.[8] While it was suggested that this might be due to p–d π bonding, it now seems more likely that this flattening of the nitrogen pyramid should be ascribed to the two-electron interaction. Further, the barriers in a series of sulfenamides with different heteroatoms attached to sulfur $XSNR_2$ showed large torsional barriers when the heteroatom, X, was O or Cl but smaller torsional barriers when the atom was less electronegative (i.e., N or S).[6]

This paper deals with a fourth effect on torsional barriers in substituted benzenesulfenamides which we have termed an *electrosteric effect* to indicate that it results from an interplay between electronic and steric interactions.

Results and Discussion

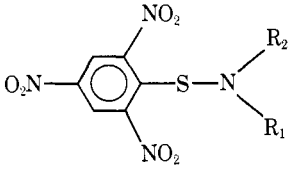
The presence of electronegative substituents on the phenyl ring of benzenesulfenamides dramatically increases the torsional barrier about the N–S bond. This effect could be quantified using the free-energy form of the Hammett equation.[9] A plot of free energies of activation for a series of sulfenylsulfonamides as a function of the Hammett substituent constants, σ, yielded a reasonably linear plot from which a temperature-independent reaction constant, ρ', could be derived. The ρ' obtained, -582 ± 55, corresponded to a conventional Hammett reaction constant of -2 indicating a substantial polar substituent effect for a process, torsion about the N–S bond, in which formal charges are not developed.

Extrapolation of this trend indicated that benzenesulfenamides with very electronegative substituents in the phenyl ring should have torsional barriers large enough that sulfenamides containing no other chiral unit should be resolvable and optically stable at room temperature.

Stimulated by this expectation we developed a synthesis of 2,4,6-trinitrobenzenesulfenyl chloride[10] and prepared a series of derivative sulfenamides, **1**. The barriers to topomerization for this series of compounds are given in Table I. The barriers for a series of corresponding 2,4-dinitrobenzenesulfenamides are also given in this table. Since sulfenamide barriers are very sensitive to the steric bulk of substituents at nitrogen, an amine and a sulfonamide with very bulky substituents at nitrogen, viz., *N*-mesitylbenzylamine and *N*-(1,1-dimethyl-2-methoxyethyl)-*p*-toluenesulfonamide, were among those used. One of the sulfenamides prepared from the latter, viz., **2g**, has the highest barrier yet reported for a sulfenamide. The NMR spectral behavior of the sulfenamides, **1c** and **2c**, deserves special comment.

At low temperature, in $CDCl_3$, both **1c** and **2c** exhibited nonequivalence of the mesityl *o*-methyl groups, although the benzyl methylene group remained a singlet. Although the benzyl methylene protons do not exhibit observable chemical shift nonequivalence, we can be sure that they are diastereotopic since there is no (reasonable) conformation in which the mesityl *o*-methyl groups are diastereotopic while the benzyl methylene protons are enantiotopic. However, topomerization of the mesityl methyl groups can be accomplished by *either* torsion about the bond between nitrogen and the mesityl group *or* torsion about the sulfenamide bond, and the observed barrier must correspond to the more facile of these two processes. The behavior of **2c** in toluene-d_8 indicates that the topomerization is effected by torsion about the N–S bond. In this solvent the methylene protons split into an AB quartet below -6 °C. This must be associated with rotation about the N–S bond which is slow on the NMR time scale. The mesityl *o*-methyl also splits into a doublet, although overlap with solvent and the *p*-methyl singlet prevented accurate measurement of the barrier by following the coalescence of these signals in this

Table I. Torsional Barriers in 2,4,6-Trinitrobenzenesulfenamides and 2,4-Dinitrobenzenesulfenamides



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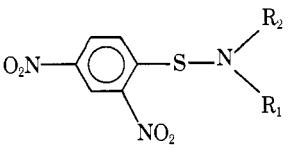


2

compd	R_1	R_2	solvent	obsd protons	$\Delta\nu$,[a] Hz	T_c, °C	ΔG^*_c,[a] kcal/mol	ref
1a	$CH_2C_6H_5$	$CH(CH_3)_2$	$CDCl_3$	$CH(CH_3)_2$	3.5	8	15.5	*b*
				$CH_2C_6H_5$	22.8 (J_{AB} = 12.4)	40	15.6	*b*
1b	$CH(CH_3)_2$	$CH(CH_3)_2$	$C_6D_5CD_3$	$CH(CH_3)_2$	12.7	62	17.6	*b*
1c	$CH_2C_6H_5$	2,4,6-$(CH_3)_3C_6H_2$	$CDCl_3$	*o*-CH_3[c]	24	−34	12.0	*b*
1d	$CH_2C_6H_5$	*p*-$CH_3C_6H_4SO_2$	$CDCl_3$	$CH_2C_6H_5$	25.8 (J_{AB} = 15.3)	21	14.6	*b*
1e	$CH(CH_3)_2$	*p*-$CH_3C_6H_4SO_2$	$CDCl_3$	$CH(CH_3)_2$	4.2	−11	14.2	*b*
1f	$CH(CH_3)C_6H_5$	*p*-$CH_3C_6H_4SO_2$	$CDCl_3$	CH_3[d]	18.3	−4	13.8	*b*
				$(NO_2)_3C_6H_2$[d]	15.1	−6	13.8	*b*
1g	$C(CH_3)_2CH_2OCH_3$	*p*-$CH_3C_6H_4SO_2$	$CDCl_3$	CH_2OCH_3	33.0 (J_{AB} = 10)	41	15.6	*b*
1h	$CH(CH_3)C_6H_5$	$C(CH_3)_3$	$CDCl_3$	$C(CH_3)_3$	16.0	65	18.2	*b*
2a	$CH_2C_6H_5$	$CH(CH_3)_2$	$C_6D_5CD_3$	$CH_2C_6H_5$	5.9 (J_{AB} = 13.9)	57	16.5	4
2b	$CH(CH_3)_2$	$CH(CH_3)_2$	$C_6D_5CD_3$	$CH(CH_3)_2$	5.0	105	20.6	*b, e*
2c	$CH_2C_6H_5$	2,4,6-$(CH_3)_3C_6H_2$	$CDCl_3$	*o*-CH_3[c]	17.0	−10	13.4	*b*
			$C_6D_5CD_3$	$CH_2C_6H_5$	12 (J_{AB} = 14)	−6	13.4	*b*
2d	$CH_2C_6H_5$	*p*-$CH_3C_6H_4SO_2$	$C_6D_5CD_3$–CD_3SOCD_3	$CH_2C_6H_5$	23.5 (J_{AB} = 14.5)	68	17.0	*b*
2e	$CH(CH_3)_2$	*p*-$CH_3C_6H_4SO_2$	$C_6D_5CD_3$	$CH(CH_3)_2$	18.4	115	20.1	9
2f	$CH(CH_3)C_6H_5$	*p*-$CH_3C_6H_4SO_2$	$C_6D_5CD_3$	$CH(CH_3)C_6H_5$[d]	19.0	103	19.7	11b
2g	$C(CH_3)_2CH_2OCH_3$	*p*-$CH_3C_6H_4SO_2$	$C_6D_5CD_3$	CH_2OCH_3	10.7 (J_{AB} = 9.8)	143	21.4	*b*

[a] Chemical shift differences are expressed in hertz at 60 MHz. Geminal coupling constants for diastereotopic methylene protons are given in parentheses. All free energies of activation in this work were determined using complete line-shape analysis at the coalescence point. [b] This work. [c] This data refers to topomerization of mesityl methyl groups which could be accomplished by torsion about the N–S bond *or* the bond between nitrogen and the mesityl ring. [d] This data refers to external topomerization (i.e., interconversion of two diastereomers epimeric at the S–N chiral axis). [e] A barrier (in nitrobenzene) of 86.2 kJ/mol (20.6 kcal/mol) has been reported for this compound.[26]

solvent. The barriers for topomerization using the two probe groups, one in toluene-d_8, the other in deuteriochloroform, are in good agreement (Table I), indicating that they represent the same dynamic process, viz., torsion about the sulfenamide bond. Accordingly, we may conclude that the barrier to torsion about the nitrogen–mesityl bond must be greater than the measured barriers.

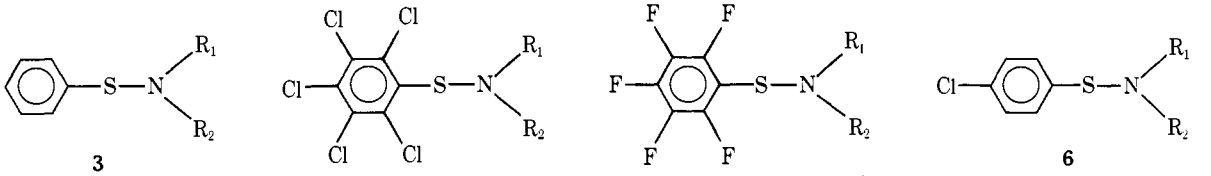
As a part of this study we have also prepared a series of pentahalobenzenesulfenamides, **4** and **5**, whose barriers are given in Table II, along with data for the corresponding benzenesulfenamide, **3**, which is given for comparison. As indicated in the table the barriers of the perhalophenyl compounds are abnormally low. Thus in the series **3a, 6a, 4a** the introduction of a *p*-chlorine produces a small increase in the torsional barrier, while perchlorination results in a substantial barrier decrease. While neither type of substituent at sulfenyl sulfur was effective in raising torsional barriers to the point where configurationally stable isomers could be obtained, these data provide a key to understanding the origin of the effect of polar substituent in the para position of benzenesulfenamides.

The data in Tables I and II indicate that the presence of two ortho substituents dramatically lowers torsional barriers in arenesulfenamides. The torsional barriers have been measured for a series of sulfenylsulfonamides, **7**, bearing zero, one, two, or three nitro groups in the sulfenyl phenyl ring (Table III).[11] A plot of the free energies for topomerization as a function of the number of nitro groups (Figure 3) illustrates both the increase in the barrier upon successive introduction of nitro groups and the interruption of this trend when two ortho nitro groups are present.

The data in Tables I–III indicate that both of these phenomena, the polar substituent effect and its interruption, are due to steric effects caused and controlled by electronic factors; hence our description of the barrier increase as an *electrosteric effect*. First, we note that the magnitudes of the barrier decrease upon introduction of the third nitro group, $\Delta G^*_{2-1} = \Delta G^*_2 - \Delta G^*_1$, fall into two categories. When there is a primary substituent at nitrogen, i.e., benzyl, the difference is less than 3 kcal/mol: **1a, 2a,** 1.0 kcal/mol; **1c, 2c,** 1.4 kcal/mol; **1d, 2d,** 2.4 kcal/mol. In these compounds, the torsion presumably involves a passing interaction of the sulfenyl aryl group with this primary substituent. When the nitrogen bears two larger substituents (either two secondary alkyl groups or an arenesulfonyl and a secondary or tertiary alkyl group) the difference is larger: **1b, 2b,** 3.0 kcal/mol; **1e, 2e,** 5.9 kcal/mol; **1f, 2f,** 5.9 kcal/mol; **1g, 2g,** 5.8 kcal/mol. The magnitude of the decrease in the barrier depends on the steric bulk of the substituents at nitrogen, pointing to an interpretation in terms of steric factors.

The correlation between equilibrium constants and torsional barriers for compounds **7** provides another piece of evidence for the electrosteric effect. Compounds **7** possess an additional unit of chirality, the chiral center of the phenethyl group, and

Table II. Torsional Barriers in Halobenzenesulfenamides

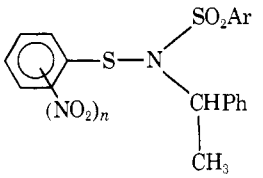


3 4 5 6

compd	R_1	R_2	solvent	$\Delta\nu$,[a] Hz	T_c, °C	ΔG^*_c,[a] kcal/mol	ref
3a	$CH(CH_3)_2$	$CH(CH_3)_2$	CH_2Cl_2	3.7	−12	14.3	*b*
4a	$CH(CH_3)_2$	$CH(CH_3)_2$	$CDCl_3$	22.5	−35	12.1	*b*
6a	$CH(CH_3)_2$	$CH(CH_3)_2$	CH_2Cl_2	3.5	− 6	14.6	*b*
3b	$CH(CH_3)_2$	p-$CH_3C_6H_4SO_2$	$C_6D_5CD_3$	16.7	−11	13.4	9
5b	$CH(CH_3)_2$	p-$CH_3C_6H_4SO_2$	CH_2Cl_2	21.4	−35	12.1	*b*
4c	$C(CH_3)_2CH_2OCH_3$	p-$CH_3C_6H_4SO_2$	$CDCl_3$	33.0 (J_{AB} = 10.0)	−25	12.2	*b*
5c	$C(CH_3)_2CH_2OCH_3$	p-$CH_3C_6H_4SO_2$	CH_2Cl_2-$CDCl_3$	15.1 (J_{AB} = 10.0)	−15	13.0	*b*
3d	$CH(CH_3)C_6H_5$	p-$CH_3C_6H_4SO_2$	$CDCl_3$	16.5	−17.5	13.0	11b
5d	$CH(CH_3)C_6H_5$	p-$CH_3C_6H_4SO_2$	CH_2Cl_2	24.5	−47	11.4	*b*

[a] Chemical shift differences are expressed in hertz at 60 MHz. Geminal coupling constants for diastereotopic methylene protons are given in parentheses. All free energies of activation in this work were determined using complete line-shape analysis at the coalescence point. [b] This work.

Table III. Effect of Nitro-Group Substitution on Torsional Barriers and Thermodynamic Asymmetric Induction



7

	n =	Ar	K_{eq}	ρ[a]	$\Delta\nu$	T_c	ΔG^*c	ref
7a	0	phenyl	1.0	0	16.5	−17.5	13.0	11b
7b	1 (*o*)	*p*-tolyl	1.9	2.2	13.0	75.0	18.4	11b
7c	1 (*p*)	phenyl	1.8	2.0	14.8	12.0	14.7	11c
2f	2 (2,4)	*p*-tolyl	2.4	3.1	19.0	102.5	19.7	11b
1f	3 (2,4,6)	*p*-tolyl	1.1	0.3	18.3	−4	13.8	*b*

[a] Reaction constant from the Ruch-Ugi equation. [b] This work.

exist as mixtures of diastereomers which differ in configuration at the sulfenamide chiral axis.[11b] Since, at temperatures below the coalescence point, torsion about the S–N bond is fast on the isolation time scale but slow on the NMR time scale, integration of the phenethyl methyl resonances of the two diastereomers yields the equilibrium constants. These equilibrium constants reflect a thermodynamic asymmetric induction[12] of the labile chiral unit, the sulfenamide chiral axis, by the stable chiral unit, the phenethyl group. Use of the Ruch–Ugi expression[13] $\log K_{eq} = \rho\chi$, with a chirality product of 1.24 for the phenethyl group, furnishes reaction constants, ρ, which reflect the susceptibility to asymmetric induction of the labile chiral unit, and which are linearly related to free energy. As illustrated in Table III and Figure 4 the magnitude of the asymmetric induction increases with the magnitude of the torsional barrier. Since asymmetric induction is usually associated with steric interactions and the application of the Ugi–Ruch equation to this system supports a steric origin for the asymmetric induction, we conclude that the polar substituent effect and its interruption should be interpreted in steric terms. It is noteworthy that the point for the trinitrobenzenesulfenamide **1f** which appears anomalous in Figure 3 fits in well in Figure 4.

The Exner analysis[14] of the polar substituent effect provides

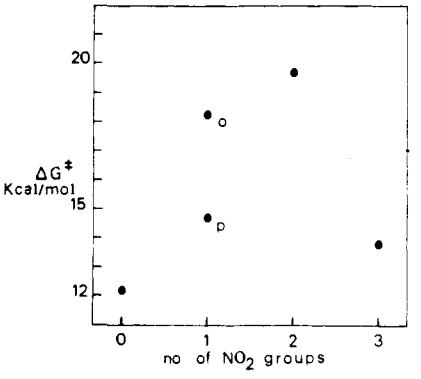


Figure 3. Torsional barriers in *N*-(1-phenylethyl)-*N*-arenesulfonylnitrobenzenesulfenamides as a function of the number of nitro groups in the sulfenyl phenyl ring. The two points for the mononitrobenzene sulfenamides refer to substitution at the ortho (*o*) and para (*p*) positions.

further evidence concerning the steric requirements for the polar substituent effect. Examination of the differential effect of meta and para substituents in a series of compounds $XC_6H_4SNR_1R_2$ demonstrated[9] that the electronegativity ef-

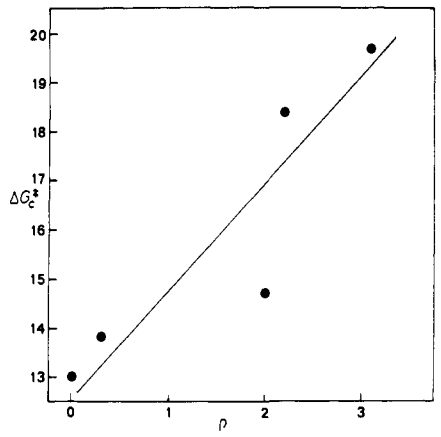
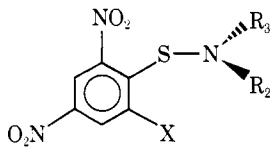


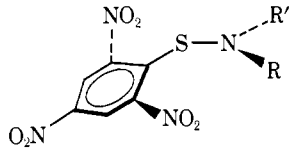
Figure 4. Free energies of activation for torsion about the N-S bond in *N*-(1-phenylethyl)-*N*-arenesulfonylnitrobenzenesulfenamides plotted as a function of the magnitude of the thermodynamic asymmetric induction (Ruch and Ugi's ρ function).

fect is associated with direct conjugation of the aromatic π system with an orbital on sulfur rather than simple inductive withdrawal. A plot (Exner plot) of the barriers in the para-substituted compounds (ΔG^*_{p-X}) as a function of those in the meta-substituted compounds (ΔG^*_{m-X}) afforded a slope of 4.5. This value for an Exner slope is characteristic of direct conjugation since inductive withdrawal results in a much lower value of Exner slope, about 1.1-1.2.[15]

The large value of the Exner slope indicates that the aromatic π system is in direct conjugation with an orbital on sulfur. The interruption of the polar substituent effect upon the introduction of two ortho substituents suggests an identification of this orbital. The effect of the second *o*-nitro group seems to be due to steric inhibition of resonance. The lowered barriers in the perhalobenzenesulfenamides indicate that this is not due to a specific *o*-nitro interaction but is associated with a substituent which is more bulky than hydrogen. This interpretation suggests that the conformation of the dinitrobenzenesulfenamides (and other benzenesulfenamides with at least one ortho hydrogen) is one in which the plane of the sulfenyl benzene ring is nearly coplanar to the CSN plane, **8**.



8, X = H
9, X = NO_2



10

This geometry is one in which the aromatic π system can conjugate with the nonbonding p orbital on sulfur but is perpendicular to the nitrogen lone-pair orbital. Thus the conjugative interaction between the aromatic π system and the nitrogen lone pair through a sulfur d orbital, which we had proposed earlier,[9] is not in accord with the barrier lowering attendant upon the presence of two ortho substituents.[16]

Replacement of the ortho hydrogen with a larger nitro group would result in a structure **9**, with substantial steric interaction between the nitro and NR_2R_3 moieties. The steric destabilization must be great enough that the conformation is changed to one in which the plane of the trinitrophenyl ring makes a substantial angle with the CNS plane **10**.

At the torsional transition state steric interactions between the sulfenyl aryl ring and the NR_1R_2 moiety are increased, and torsion about the aryl-fulfur bond occurs leading to deconjugation and increasing the torsional barrier. The magnitude of the twist at the torsional transition state should be related to the steric bulk of the smaller of the two substituents at nitrogen, which is closest to the aryl group. This is in accord with our finding that the barrier lowering $\Delta\Delta G^*_{2-1}$ is smaller when there is at least one primary group at nitrogen as described above.

Our interpretation is based on a ground-state effect: a stabilization associated with conjugation of the sulfur lone pair p orbital whose magnitude depends on the presence of electron-withdrawing groups on the aryl ring. The correlation between topomerization free energies and the degree of thermodynamic asymmetric induction provides further support for this notion. The asymmetric induction is a ground-state phenomenon and the good correlation (R = 0.90) argues that the polar substituent effect on topomerization barriers must also involve a ground-state effect. The interruption of the polar substituent effect on the thermodynamic asymmetric induction indicates that the introduction of the second *o*-nitro group changes the ground-state conformation to one with substantially less interaction of the aromatic substituent and the chiral substituent on nitrogen in accord with our postulation of conformations **8** and **10** for **2** and **3**.

The polar substituent effect on both torsional barriers and asymmetric induction derives from a true electronic interactions, the conjugation of the aromatic π system with the sulfur lone pair p orbital. However, this electronic interaction is made manifest through phenomena which are generally described as due to steric hindrance. Indeed, we might describe the present situation by noting that electron-withdrawing substituents confer greater effective steric bulk on the sulfenyl phenyl ring. Because of the intermingling of steric and electronic components in the mechanism by which electron-withdrawing substituents affect barriers and equilibrium constants in this system we term this an *electrosteric effect*.

Experimental Section

NMR spectra were obtained using a Varian A-60A spectrometer equipped with a variable-temperature accessory. The spectra were calibrated by the sideband technique, using a Hewlett-Packard 523B counter. Chemical shifts are reported in δ units relative to internal tetramethylsilane. Temperatures were calibrated using the spectrum of a standard methanol sample as described in the Varian manual. The first-order rate constants at the coalescence point (k_c) were obtained by complete line-shape analysis using CLAS, a classical mechanical two-site program for exchanging singlets, or CLASAB, a similar quantum-mechanical program for the coupled AB system, or calibration curves or equations derived from these programs.[17] We regard the uncertainty in free energies of activation obtained using this procedure to be ±0.2 kcal/mol.

Melting points were measured on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses on all new compounds were preformed by Midwest Microlab and were within 0.3% of the calculated values.

2,4,6-Trinitrobenzenesulfenyl chloride,[10] pentafluorobenzenesulfenyl chloride,[18] and pentachlorobenzenesulfenyl chloride[19] were prepared according to the previously described procedures. 2,4-Dinitrobenzenesulfenyl chloride was available commercially.

N,N-Dialkylarenesulfenamides. A solution of 10 mmol of arenesulfenyl chloride in 20 mL of benzene was addeddropwise to a solution of 20 mmol of the appropriate secondary amine in 50 mL of benzene or 10 mmol of the amine and 10 mmol of triethylamine. The mixture was stirred at room temperature for 5 h and the solid was removed by filtration. The solution was evaporated and the residue chromatographed on silica gel with hexane-benzene (9:1) as eluent. The products were obtained by recrystallization from tetrahydrofuran-ethanol: **2b**, mp 96-97 °C (lit.[20] 98-99 °C); **4a**, mp 65.5-66.5 °C (lit.[21] 62-63 °C). Properties of **1a** and **1b** have been described by us elsewhere.[10]

N-tert-Butyl-*N*-1-phenethyl-2,4,6-trinitrobenzenesulfenamide (**1h**) was prepared via the silver salt of the amine. *N-tert*-Butyl-*N*-(1-phenylethyl)amine[22] (5 mmol) in 60 mL of diethyl ether was treated with an equimolar amount of *n*-butyllithium at −20 °C, stirred

for 1 h at −20 °C, and chilled to −78 °C. A solution of silver perchlorate (5 mmol) in 8 mL of tetrahydrofuran was added dropwise and the mixture stirred at −78 °C for 30 min. A solution of 2,4,6-trinitrobenzenesulfenyl chloride (5 mmol) in 8 mL of tetrahydrofuran was added dropwise at −78 °C. The solution was allowed to warm slowly to room temperature and allowed to stir for 15 h. Column chromatography afforded 296 mg (14%) of red-orange crystals, mp 159–161 °C (from tetrahydrofuran–hexane). Anal. Calcd for $C_{18}H_{20}N_4SO_6$: C, 51.42; H, 4.79; N, 13.33; S, 7.63. Found: C, 51.54; H, 4.74; N, 13.21; S, 7.74. NMR ($CDCl_3$) at ambient temperature indicated the presence of two diastereomers in a ratio of ca. 3/1: Major isomer: δ 1.44 (s, $C(CH_3)_3$), 1.61 (d, J = 6.8 Hz, CH_3), 4.49 (q, J = 6.8 Hz, $CHCH_3$), 6.92 (s, C_6H_5), and 8.13 (s, $(O_2N)_3C_6H_2$). Minor isomer: δ 1.16 (s, $C(CH_3)_3$), 1.57 (d, CH_3), 7.20 (s, C_6H_5), and 8.55 (s, $(O_2N)_2C_6H_2$). The methine quartet from the minor isomer was not observed.

***N*-Benzyl-2,4,6-trimethylaniline.** Mesidine prepared by nitration of mesitylene[23a] followed by catalytic hydrogenation (Pd/C) was condensed with benzaldehyde using a Dean-Stark trap and *p*-toluenesulfonic acid catalysis. The crude benzalmesidine[23b] thus obtained was reduced by an equimolar amount of sodium borohydride to the amine which was isolated after distillation as a pale yellow oil, bp 116 °C (0.4 Torr). NMR (CCl_4): δ 2.16 (9 H, s), 2.63 (1 H, br s), 3.94 (2 H, s), 6.62 (2 H, s), and 7.15 (5 H, s). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.20; H, 84.0; N, 6.18.

***N*-Benzyl-*N*-mesitylnitrobenzenesulfenamides 1c and 2c.** An equimolar mixture of *N*-benzyl-2,4,6-trimethylaniline, triethylamine, and the arenesulfenyl chloride was stirred for 18 h in benzene at room temperature. After filtration, the solution was evaporated and chromatographed on silica gel (benzene–hexane (1:4) eluent) and recrystallized from tetrahydrofuran–hexane. **2c:** yield 26%, mp 158–160 °C. Anal. Calcd for $C_{22}H_{21}N_3O_4S$: C, 62.40; H, 5.00; N, 9.92; S, 7.57. Found: C, 62.29; H, 5.06; N, 9.87; S, 7.38. **1c:** yield 19%, mp 164–165 °C Anal. Calcd for $C_{22}H_{20}N_4O_6S$: C, 56.40; H, 4.30; N, 11.96; S, 6.84. Found: C, 56.33; H, 4.48; N, 12.00; S, 6.71.

***N*-(1,1-Dimethyl-2-methoxyethyl)-*p*-toluenesulfonamide.** A solution of 17.8 g (0.2 mol) of 2-amino-2-methyl-1-propanol in 150 mL of anhydrous diethyl ether was added dropwise to a cooled (0 °C) suspension of 0.2 mol of sodium hydride (17 g as 57% dispersion in oil) in 500 mL of dry ether during the course of 1 h and stirring was continued for an additional 2 h at room temperature. A solution of 31.2 g (0.22 mol) of methyl iodide in 100 mL of dry ether was added dropwise and the mixture stirred for 10 h at room temperature. The solid was removed by filtration and the solution was distilled at ambient pressure through a 50-cm Vigreux column. The fraction distilling (10.0 g) at 95–105 °C (lit.[24] 101 °C (744 Torr)), which was about 90% pure amine by NMR, was converted to the sulfonamide by reaction with *p*-toluenesulfonyl chloride and triethylamine. The *p*-toluenesulfonamide was obtained in 42% yield based on starting alcohol: mp 64–65 °C (from benzene–hexane); NMR ($CDCl_3$) δ 1.18 (6 H, s), 2.42 (3 H, s), 3.11 (2 H, s), 3.27 (3 H, s), 5.00 (1 H, br s), 7.27 and 7.78 (4 H, AA′BB′ system). Anal. Calcd for $C_{12}H_{19}NSO$: C, 56.01; H, 7.44; N, 5.44; S, 12.46. Found: C, 56.22; H, 7.37; N, 5.51; S, 12.27. The other sulfonamides used in this work, $C_7H_7SO_2NHR$ (R = $CH_2C_6H_5$, $CH(CH_3)_2$, and $CH(CH_3)C_6H_5$), were synthesized by conventional methods. Their melting points agreed with those reported in the literature.[25]

***N*-Alkyl-*N*-*p*-toluenesulfonylarenesulfenamides.** To an ice-cold solution of 10 mmol of an *N*-alkyl-*p*-toluenesulfonamide in 20 mL of methanol was added 10 mL of 1 N aqueous sodium hydroxide and the mixture stirred for 2 h. A solution of 10 mmol of silver nitrate in 3 mL of water and 10 mL of methanol was added dropwise. By the end of the addition a white to slightly gray powdery precipitate had formed. The reaction mixture was allowed to stir for a further 30 min and the silver salt isolated by filtration and dried in vacuo over $CaCl_2$ (yield 95–99%). Infrared spectra indicated the absence of the N–H group.

A solution of 3.5 mmol of arenesulfenyl chloride in 10 mL of benzene was added to a stirred suspension of 4 mmol of the silver salt in 30 mL of benzene and allowed to react at room temperature for 48 h. After filtration, removal of solvent in vacuo, and chromatography on silica gel (benzene–hexane (2:1) eluent) the products were recrystallized from tetrahydrofuran–hexane. **2d:** 49%, mp 185–186 °C. Anal. Calcd for $C_{20}H_{17}N_3O_6S_2$: C, 52.28; H, 3.73; N, 9.15; S, 13.97. Found: C, 51.97; H, 3.73; N, 9.03; S, 14.17. **2g:** 40%, mp 106–108 °C. Anal. Calcd for $C_{18}H_{21}N_3O_7S_2$: C, 47.46; H, 4.65; N, 9.23; S, 14.08. Found: C, 47.73; H, 4.62; N, 9.34; S, 14.17. **5b:** 58%, mp 87–88 °C. Anal. Calcd for $C_{16}H_{14}NO_2F_5S_2$: C, 46.71; H, 3.43; N, 3.40; S, 15.59; F, 23.09. Found: C, 46.85; H, 3.41; N, 3.42; S, 15.58; F, 23.31. **5c:** 27%, mp 82–83 °C. Anal. Calcd for $C_{18}H_{18}NO_3F_5S_2$: C, 47.47; H, 3.98; N, 3.08; S, 14.08; F, 20.86. Found: C, 47.59; H, 4.13; N, 3.10; S, 14.38; F, 21.08. **5d:** 54%, mp 105–106 °C. Anal. Calcd for $C_{21}H_{16}NO_2F_5S_2$: C, 53.27; H, 3.41; N, 2.96; S, 13.54; F, 20.06. Found: C, 53.50; H, 3.38; N, 2.93; S, 13.58; F, 19.87. **4c:** 36%, mp 148–150 °C. Anal. Calcd for $C_{18}H_{18}NO_3Cl_5S_2$: C, 40.21; H, 3.37; N, 2.61; S, 11.93; Cl, 32.97. Found: C, 40.47; H, 3.38; N, 2.52; S, 12.24; Cl, 33.17.

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(16) (a) Independent evidence against d-orbital involvement in the polar substituent effect has been reported by Kost and co-workers,[16b,c] who also argue that the polar substituent effect involves conjugation of the aromatic π system with the sulfur p lone pair but choose to interpret the effect in terms of changes in the four-electron interaction. (b) D. Kost and A. Zeicher, *Tetrahedron Lett.*, 3239 (1975); (c) D. Kost and M. S. Sprecher, *ibid.*, 1089 (1977).

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