Nuclear Magnetic Resonance Study of the Effect of Hyperconjugation on Amide and Sulfenamide Rotational Barriers in Methyl *N*-Benzyl-*N*-(trihalomethanesulfenyl)carbamates

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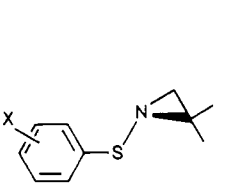
The title compounds $CH_3OCON(CH_2C_6H_5)SCX_3$ have two conformational changes requiring substantial activation energies: rotation about the SN and the N–CO bonds. Both of these changes have been observed simultaneously and assigned by utilizing the ^1H NMR signals of the prochiral benzyl methylene protons, which behave differently toward the stereochemically distinct processes. Since SN torsion is a T_C process and amide rotation is a T_A process, slow rotation of the former renders the methylene protons diastereotopic, giving rise to an AB quartet, while slow rotation about the N–CO bond gives rise to two unequally intense singlets representing the syn and anti amide isomers. Activation free energies for both processes were determined: **6a**, X = Cl, $\Delta G^{\ddagger}_{CN}$ = 11.6 kcal/mol, $\Delta G^{\ddagger}_{SN}$ = 14.3 kcal/mol; **6b**, X = F, $\Delta G^{\ddagger}_{CN}$ = 11.6 kcal/mol, $\Delta G^{\ddagger}_{SN}$ = 12.5 kcal/mol. The syn and anti equilibrium constants at 210 K are 7.0 and 6.9, respectively. The strong σ-acceptor groups CX_3 cause an increase in sulfenamide barriers and a decrease in amide barriers, relative to phenyl-substituted analogues, indicating the effect of hyperconjugation in this system, which was not observed in the phenyl analogues.

Introduction

The valence bond concept of hyperconjugation,[1] in its various manifestations (the Baker–Nathan effect,[1b] the anomeric effect,[2] organic fluorine chemistry[3]), has been a fundamental tool in structural and mechanistic organic chemistry. Its energetic, geometric, and charge delocalization implications have been discussed frequently, in connection with experimental[4] and theoretical[5] studies. In this paper we report on the effect of hyperconjugation on amide and sulfenamide rotations in the title compounds.

Barriers to rotation about the N–S bond in sulfenamides (1, RSNR′R″) have attracted considerable attention over the years,[6] since they represent a large class of compounds with neighboring heteroatoms, and perhaps to a great extent due to a peculiar substituent effect. It had been found and confirmed in several experiments that torsional barriers increased markedly with increasing electron demand by the substituents R on the sulfur side, particularly in arenesulfenamides (1, R = XC_6H_4), where correlations were found between barriers ($\Delta G^{\ddagger}$) and Hammett-type substituent constants.[7] However, when nitrogen inversion barriers were measured in suitably substituted sulfenamides [*N*-(arenesulfenyl)aziridines (**2**),[8] *N*-(arenesulfenyl)imines (**3**),[9] and *N*-(arenesulfenyl)iminocarbonates (**4**)[10]], no substituent effect was found. In the latter three sulfenamide systems, only nitrogen inversion barriers were observed, and SN torsional barriers could not be observed.



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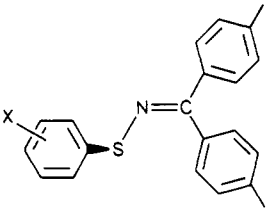

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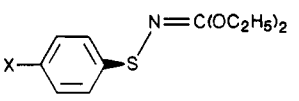

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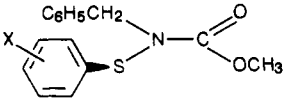

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In a previous study we were able to measure both sulfenamide and amide torsional barriers within the same molecules, methyl *N*-benzyl-*N*-(arenesulfenyl)carbamates (**5**).[11] We found the usual substituent effect (negative Hammett reaction constant) on sulfenamide rotational barriers, while no significant effect on amide torsional barriers could be detected, in agreement with the lack of substituent effect on nitrogen inversion in systems **2**–**4**. We now report on measurements of sulfenamide and amide torsional barriers in the analogous system **6**, in which for the first time substituent effects on *both* conformational changes are found, providing evidence for a hyperconjugation effect between nitrogen and sulfur.

Method and Results

The title compounds **6a** and **6b** were synthesized ac-

(1) (a) We use the term hyperconjugation in a general sense to denote any σ–π conjugation, i.e., both positive and negative hyperconjugation. (b) Baker, J. W.; Nathan, W. S. *J. Chem. Soc.* **1935**, 1840, 1844. (c) Baker, J. W. *Hyperconjugation*; Oxford University Press: Fair Lawn, NJ, 1952. (d) Mulliken, R. S. *Tetrahedron* **1959**, *6*, 68.

(2) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer Verlag: Berlin, 1983.

(3) Sheppard, W. A.; Sharts, C. M. *Organic Fluorine Chemistry*; W. A. Benjamin: New York, 1969. Holtz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 1.

(4) Among many others: Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095. Kornberg, N.; Kost, D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1661.

(5) (a) Hoffman, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221. (b) Radom, L. *Prog. Theor. Org. Chem.* **1981**, *3*, 1. (c) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362. (d) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1. (e) Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1982**, *104*, 2960. (f) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141. (g) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700.

(6) (a) For a review on sulfenamide rotation, see: Raban, M.; Kost, D. *Tetrahedron* **1984**, *40*, 3345. (b) General reviews on sulfenamide chemistry: Davis, F. A. *Int. J. Sulfur Chem.* **1973**, *8*, 71. Craine, L.; Raban, M. *Chem. Rev.* **1989**, *89*, 689.

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(8) Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1976**, *98*, 8333.

(9) (a) Davis, F. A.; Slegeir, W. A. R.; Kaminski, J. M. *J. Chem. Soc., Chem. Commun.* **1972**, 634. (b) Davis, F. A.; Kluger, E. W. *J. Am. Chem. Soc.* **1976**, *98*, 302. (c) Brown, C.; Hudson, R. F.; Grayson, B. T. *J. Chem. Soc., Chem. Commun.* **1978**, 156.

(10) Meese, C. O.; Walter, W. *Chem. Ber.* **1976**, *109*, 3129. In this study, equal barriers were measured for **3** when X = NO_2 and when X = H.

(11) Kost, D.; Zeichner, A.; Sprecher, M. S. *J. Chem. Soc., Perkin Trans. 2*, **1980**, 317. Kost, D.; Zeichner, A. *Tetrahedron Lett.* **1975**, 3239.

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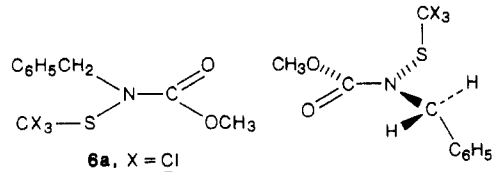

6a, X = Cl
6b, X = F

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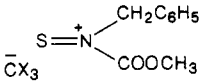

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cording to the following sequence:

$$C_6H_5CH_2NH_2 + CH_3OCOCl \rightarrow C_6H_5CH_2NHCOOCH_3$$

$$C_6H_5CH_2NHCOOCH_3 + CX_3SCl \rightarrow \mathbf{6}$$

6a, X = Cl; **6b**, X = F

Compounds **6** exhibit two conformational changes that require substantial activation energies, rotation about the S–N (sulfenamide) and CO–N (amide) bonds. Since these torsional processes belong to two different stereochemical classes, chiral torsion (T_C) and achiral torsion (T_A),[6a,12] respectively, they have different NMR consequences and can readily be distinguished by the spectral shape of the prochiral methylene protons. The detailed stereochemical and kinetic analysis can be found in ref 11 and is only briefly outlined below.

Scheme I shows the conformational changes associated with torsion about the S–N and N–CO bonds in **6**. At the fast exchange limit temperature, when both processes are fast on the NMR time scale, the benzyl methylene protons are enantiotopic and give rise to a singlet. Upon cooling, this singlet broadens and decoalesces. The shape of the resulting spectral band is dominated by the torsional process with the higher barrier, i.e., with that which first becomes slow on the NMR time scale when the sample is cooled. If the T_C process is the first to become slow, chirality develops due to the S–N chiral axis, and the prochiral methylene protons become diastereotopic. As a result, *symmetrical* line broadening should occur with eventual splitting of the methylene signal into an AB quartet.[13] Further cooling eventually renders also the amide torsion slow on the NMR time scale, resulting in the formation of syn and anti diastereomers, in which the benzyl groups are diastereotopic by external comparison. The spectral consequence is further splitting of the AB quartet due to the methylene protons into two quartets of unequal intensities, one for each amide isomer. The relative intensities of the quartets reflect the equilibrium constant for the syn ⇄ anti interconversion. The ability to observe both rotations depends critically on the magnitude of this equilibrium constant: only when it is within the range of ca. $0.05 \leq K \leq 20$ is the intensity of signals due to the minor isomer sufficient so that both of the processes can be observed.

The opposite order of events is also possible, whereby initially, upon cooling, amide torsion slows down relative to the NMR time scale, accompanied by *unsymmetrical* line broadening to form two unequal singlets corresponding to the methylene groups of the syn and anti amide isomers. Further cooling brings about "freezing out" of S–N torsion, resulting in symmetrical splitting of each of the methylene singlets into an AB quartet.

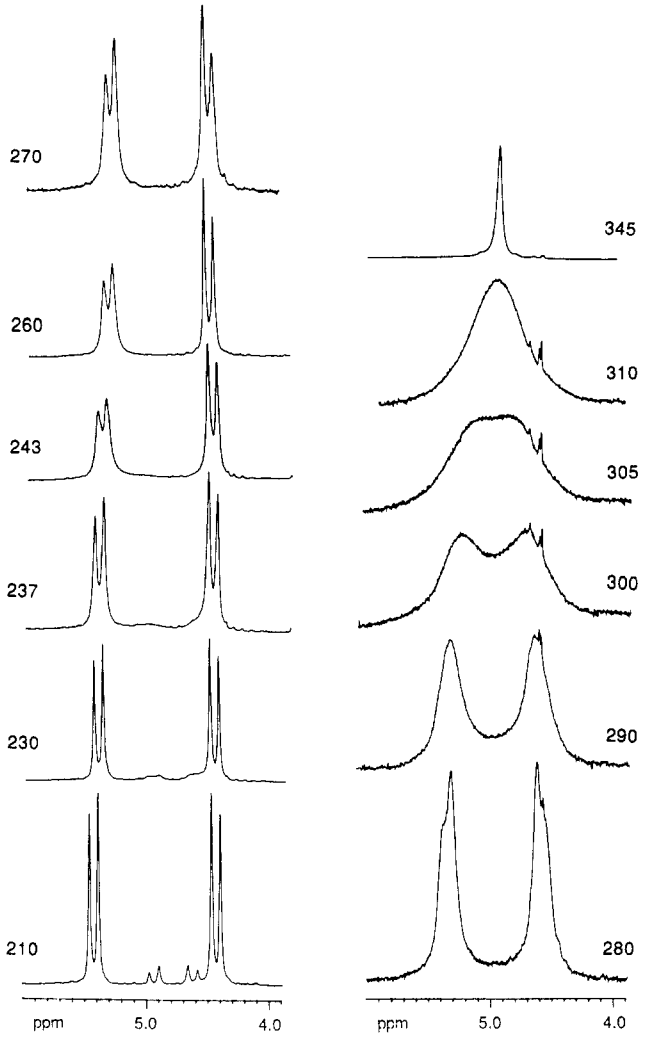
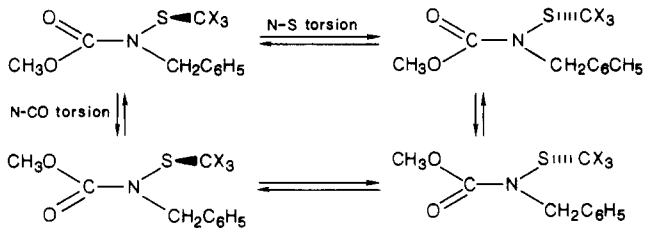


Figure 1. ^1H NMR (200 MHz) variable-temperature spectra of **6a**, showing the CH_2 resonance region. Temperatures are in kelvins.

Scheme I



6a, X = Cl; **6b**, X = F

Clearly, these two different modes of spectral changes enable straightforward and unequivocal assignment of barrier types. Both modes of spectral changes had been observed for the carbamates **5**.[11] In the present study, sulfenamide torsional barriers are higher than amide barriers, and hence only the first mode of spectral changes described above has been observed (Figure 1). Two separate coalescence temperatures are observed for amide rotation in each compound: one for the coalescence of the low-field halves of the AB quartets and the other for the high-field doublets. Since the chemical shift differences ($\Delta\nu$) are substantially different, the corresponding temperatures at which they coalesce are not the same.

The spectra shown in Figure 1 are sufficiently well resolved to enable observation of both the major and the

(12) Kost, D.; Aviram, K.; Raban, M. *Isr. J. Chem.* **1983**, *23*, 124. Kost, D.; Aviram, K.; Raban, M. *J. Org. Chem.*, previous paper in this issue.

(13) Some of the AB patterns observed and reported in this paper have exceedingly large chemical shift differences ($\Delta\nu_{AB}$) and may more appropriately be termed AX systems. We have used "AB" throughout to mean both types of spin systems, since "AX" is often reserved for heteronuclear systems.

Table I. Dynamic ^{1}H NMR (200 MHz) Data for 6a and 6b[a]

	amide rotation										sulfenamide rotation		
compd	$\Delta\nu_1$[b]	$\Delta\nu_2$[b]	T_c^1	T_c^2	$\Delta G_1^{\neq}$	$\Delta G_2^{\neq}$	$\Delta\nu_{Me}$	T_c^{Me}	$\Delta G_{Me}^{\neq}$	K_{eq}	$\Delta\nu_{AB}$	T_c	$\Delta G_{SN}^{\neq}$
6a	91	33	243	234	11.6	11.6	8	220	11.5	7.0[c]	166	305	14.3
6b	85	18	240	230	11.5	11.6	21	231	11.6	6.9[c]	218	271	12.5

[a] Chemical shifts are expressed in hertz, temperatures in kelvins, and free energies of activation in kilocalories per mole. [b] $\Delta\nu_1$ is the chemical shift between the exchanging low-field doublets due to the major and minor amide isomers; $\Delta\nu_2$ is the corresponding shift for the high-field doublets. [c] At 210 K.

minor AB quartets, at low temperature, and follow the changes through coalescence to the high exchange limit spectra. As a result, accurate coalescence temperatures could be located (±2 °C), and the corresponding rate constants were calculated by using the equations[14] $k_c = (\pi/2^{1/2})\Delta\nu$ for the exchange of uncoupled signals[15] (amide rotation) and $k_c = (\pi/2^{1/2})(\Delta\nu^2 + 6J^2)^{1/2}$ for the exchange of AB quartets[16] (sulfenamide rotation). In fact, the remarkably large chemical shift differences ($\Delta\nu_{AB}$) between exchanging sulfenamide sites make the use of the latter equation unnecessary, as both equations yield nearly equal rate constants.

Additional confidence in calculated rate constants is gained by comparing $\Delta\nu$ values at various slow-exchange temperatures with those obtained from $W_{1/2}$, the width at half-height of the coalescence spectrum, by subtracting from it the coupling constant J. We find that the various shifts are essentially temperature independent and correspond closely to $W_{1/2}$.

Amide torsional barriers, which could not be as accurately determined from the coalescence of the two AB quartets, have also been measured and evaluated separately from the coalescence of the methoxy singlets. At low temperature, the methoxy signal is split only due to amide rotation, into two singlets. The ratio of the areas under these singlets was calculated and represents the syn and anti equilibrium constants (Table I). The barriers measured from this coalescence process agree very well with those obtained from the benzyl methylene proton signals.

Activation free energies were calculated by using Eyring's equation and are listed in Table I, along with the coalescence temperatures, chemical shifts of exchanging signals, and equilibrium constants for **6a** and **6b**.

Assignment of syn and anti configurations to the major and minor amide diastereomers is facilitated by the great difference between the corresponding AB quartets: the signals due to the methylene protons of the major isomer have an unusually large difference in chemical shifts for diastereotopic protons [**6a**, $\Delta\nu_{AB}$ = 205 Hz (1.03 ppm) at 202 K; **6b**, $\Delta\nu_{AB}$ = 261 Hz (1.31 ppm) at 200 K]. This large difference must be due to a substantial magnetic influence which operates on *one* of the methylene protons only. Such an influence can only come from the anisotropic carbonyl group, suggesting that in the major isomer the latter is adjacent to the benzyl group in the *E* conformation, as shown in **7**. The exceptionally large chemical shift difference is understood as follows: the phenyl group avoids the bulky trihalomethyl group by orienting itself predominantly on the opposite side of the amide plane. As a result, one of the geminal protons points toward the carbonyl group and is located in its deshielding region and, hence, is shifted substantially downfield. The other proton points largely in the direction of the trihalomethyl group and is little exposed to the carbomethoxyl group. For this reason, the chemical shift of that proton (the high-field doublet) changes only slightly from one amide isomer to the other. By contrast, the low-field doublet is shifted dramatically upfield upon amide rotation from major to minor isomer, as it loses the deshielding influence of the carbonyl. It is the rigidity of the molecule, having substantial barriers for both SN and N–CO rotations, that fixes this conformation and causes each of the geminal protons to spend most of its time in the locations shown, resulting in the large chemical shift differences.

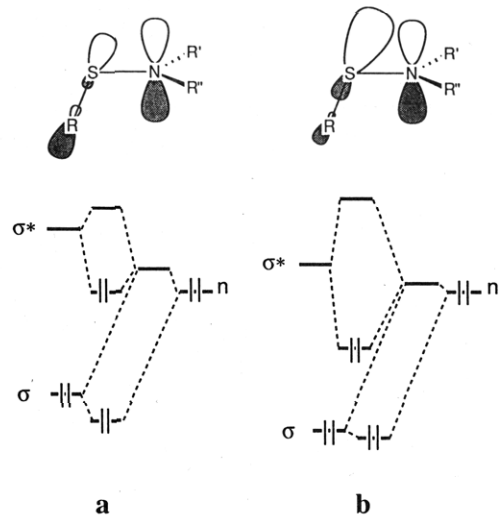


Figure 2. Schematic illustration of the n → σ* hyperconjugation. (a) With a nonelectronegative substituent R, the n,σ* energy gap is relatively large, the interaction weak. The n,σ gap is such that the four-electron (repulsive) interaction is significant and partly offsets the n,σ* stabilization. (b) With an electronegative R group, both σ and σ* orbitals are lowered, resulting in (i) weaker n,σ repulsive interaction, (ii) stronger stabilizing n,σ* interaction, due to a smaller gap, and due to (iii) a more polarized σ* orbital with a greater coefficient on S and hence better overlap.

Discussion

Torsional barriers about single bonds between heteroatoms in sulfenamides and analogues are generally attributed to the presence of adjacent lone pairs on sulfur and nitrogen,[17] and hence one might expect electron withdrawal from either atom to result in a *decrease* in barrier height, rather than the observed increase.

Several rationales had been suggested for this substituent effect and eventually discarded with the accumulation of new evidence.[18] The earliest of these mechanisms in-

(14) This procedure was shown to yield reliable rate constants and barriers whenever $\Delta\nu > J$: Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

(15) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(16) Kurland, R. J.; Rubin, M. B.; Wise, M. B. *J. Chem. Phys.* **1964**, *40*, 2426.

(17) A theoretical study on the hydrazyl (NH_2NH) model system demonstrated the connection between π-electron occupancy and torsional barriers in analogous systems.[12]

(18) The current explanation that seems to best accommodate all of the available data on aromatic substituent effects on SN torsional barriers is the so-called "electrosteric effect", according to which steric crowding at the torsional transition state forces the aromatic ring out of conjugation with the sulfur lone pair. The energetic cost of this loss of conjugation depends upon the substituent, increasing with its electron demand: Raban, M.; Yamamoto, G. *J. Am. Chem. Soc.* **1979**, *101*, 5890.

Table II. Amide and Sulfenamide Rotational Barriers for (Arenesulfenyl)carbamates 5[a]

substituent X	$\Delta G^{\ddagger}_{SN}$[b]	$\Delta G^{\ddagger}_{CN}$[b]
4-MeO	8.7	12.1
4-Me	9.1	12.1
H	9.4	12.1
4-Cl	9.5	12.0
3-NO_2	9.9	12.0
4-NO_2	10.9	12.0
2,4-$(NO_2)_2$	16.2	12.3

[a] Taken from ref 11. [b] In kilocalories per mole.

voked π conjugation between the nitrogen lone pair and a vacant sulfur orbital at the torsional ground state.[7] The vacant orbital on sulfur could either be a low-lying d orbital, in which case the ground state would be stabilized by (p–d)π conjugation, or it could be a S–C σ^* orbital, engaged in a stabilizing hyperconjugation (Figure 2). In both cases, partial double bonding between sulfur and nitrogen should be formed and could lead to substantial barriers to torsion about the SN bond. Substituent dependence of the barrier is due to the effect of substituents on the energy of the vacant orbital on sulfur: electron-withdrawing substituents lower the energy of the d (or σ^*) orbital and, hence, decrease the HOMO–LUMO energy gap and intensify the ground-state stabilization. In the case of hyperconjugation, a second stabilizing factor operates, namely, an electronegative substituent R *polarizes* the S–R bond, such that much of the electron density in the σ orbital is located near R. The reverse polarization occurs in the σ^* orbital, producing a large coefficient on sulfur, capable of better overlap with the n lone-pair orbital on nitrogen and hence in stronger N–S π bonding (Figure 2). As a result, the torsional barrier is increased.

A subsequent study on nitrogen inversion barriers in **2** showed no similar substituent dependence of barriers. Since involvement of the nitrogen lone pair in **2** in partial double bonding to sulfur is expected to *stabilize* the planar transition state for nitrogen inversion, and hence to lower nitrogen inversion barriers,[19] and since no decrease of the barriers was observed in the presence of electron-withdrawing groups, it was concluded that neither (p–d)π bonding nor n–σ^* hyperconjugation is important in this system. If hyperconjugation is absent from the arenesulfenamide functionality, it cannot be responsible for the substituent effect on SN torsional barriers observed in various other systems as well. However, the effect of substituents on SN torsional barriers could *not* be measured directly in either **2**, **3**, or **4**. One system which *does* allow simultaneous measurement of the SN torsional barrier and a second barrier for an adjacent conformational change is **5**. The conclusion that N–S double bonding was not significantly involved in the system was thus verified directly in **5**, where the usual increase of SN torsional barriers with increasing electron demand by para substituents was observed, while no substituent effect on amide barriers was found. Table II reproduces the barriers for amide and sulfenamide rotations in **5** for comparison.[11] Like in **2**, the absence of a substituent effect on amide torsion in **5** excluded the possibility of significant hyperconjugation in this series. The fact that a substantial substituent effect on SN torsional barriers was observed in **5**, despite the absence of hyperconjugation, is evidence that the latter is *not* the cause for substituent dependence of SN barriers, in this as well as other arenesulfenamides.

While essentially equal nitrogen inversion barriers had been measured for the differently substituted aziridines **2**, a substantial decrease in barriers was observed when the arenesulfenyl group was replaced by CCl_3S or CF_3S. It was argued that the trihalomethyl group, a much better σ-acceptor, can effect n–σ^* hyperconjugation, unlike the *S*-aryl group in **2**, which is a poor σ-acceptor (though an efficient π-acceptor!). Thus the lowering of nitrogen inversion barriers was attributed in this case to hyperconjugation, which increases SN double bonding and hence stabilizes the planar nitrogen inversion transition state. This behavior of the nitrogen inversion barrier in aziridines is in accord with the results of a theoretical study[5e] and has been observed in other aziridines.[20] This should also be accompanied by a parallel *increase* in SN torsional barriers, as a result of the additional ground-state stabilization. However, here again the direct effect of hyperconjugation on SN torsional barrier could not be assessed, for the latter could not be observed in the aziridine system.

In the present study, the effect of hyperconjugation on SN torsion could be observed. The existence of significant hyperconjugation in the presence of the trihalomethyl group was demonstrated in **2**. Attachment of this group to the sulfenylcarbamate system to form **6** thus enables simultaneous observation of the effect of n–σ^* hyperconjugation on the amide and sulfenamide rotational barriers. Examination of Tables I and II reveals that indeed the presence of the trihalomethyl group results in changes in amide *and* sulfenamide rotational barriers, which are best accommodated by invoking hyperconjugation: On the one hand, SN torsional barriers are higher than those measured for monosubstituted **5**. This indicates added ground-state stabilization in **6**, which might be due to hyperconjugation. On the other hand, the change in substitution brings about also a substantial decrease in the N–CO torsional barrier. This is in agreement with the view that the nitrogen lone pair is more intensively involved in the SN bond and, therefore, is less effective in stabilizing the planar amide ground state.

The fact that in **6a** the SN torsional barrier is 1.8 kcal/mol higher than in **6b** suggests that steric factors also play an important role: eclipsing of the bulkier trichloromethyl group with one of the other nitrogen ligands in the torsional transition state for **6a** causes more congestion than that of the trifluoromethyl group in **6b**. It might be argued that the increased barriers in **6a** and **6b** are due only to the steric bulk of the trihalomethyl groups. However, this can be ruled out when the steric bulk of the groups is compared with that of a phenyl group: Taft's steric parameters (E_s) for the phenyl and trifluoromethyl groups are nearly equal,[21] and yet the SN torsional barrier for **6b** is 3.1 kcal/mol *higher* than that of a phenyl-substituted carbamate **5**, by far more than the difference in barriers between **6a** and **6b**. If steric factors alone were responsible, the barriers should also be nearly equal. Thus an additional electronic effect must be involved. Furthermore, no steric effect was found for amide rotation

(19) The expectation that nitrogen inversion barriers in aziridines be decreased by increased conjugation between the nitrogen lone pair and the ligand is based on similar findings in a series of para-substituted *N*-phenylaziridines: Andose, J. D.; Lehn, J.-M.; Mislow, K.; Wagner, J. *J. Am. Chem. Soc.* **1970**, *92*, 4050.

(20) Inversion-barrier lowering in α-fluoro aziridines and in (hydroxymethyl)- and (methoxymethyl)aziridines was observed and attributed to hyperconjugation by: (a) Kostyanovsky, R. G.; Samojlova, Z. E.; Tchervin, I. I. *Tetrahedron Lett.* **1968**, 3052. (b) Bystrov, V. F.; Kostyanovsky, R. G.; Panshin, O. A.; Stepanyants, A. U.; Iuzhakova, O. A. *Opt. Spectrosc. (Engl. Transl.)* **1965**, *19*, 122, 217.

(21) E_s values for CF_3 and phenyl groups differ from each other by 0.2 units or less, depending on which estimate is chosen.[8,18] By any type of estimate, the difference in steric parameters is by far *smaller* than that of CF_3 and CCl_3, and yet the difference in barrier heights is greater.

(equal barriers for **6a** and **6b**), due to the distance of substituents from the reaction center, and yet amide rotational barriers are lower in this study than in series **5**, indicating the operation of an additional electronic effect. Thus, although a steric origin for the greater $\Delta G^{\ddagger}_{SN}$ in **6** relative to **5** cannot be absolutely ruled out, the combination of both increased S–N and decreased N–CO barriers is best understood in terms of a hyperconjugation effect.

The question of whether the effect on barriers that has been demonstrated in this experiment is due to conjugation of the nitrogen lone pair with a vacant d or σ^* orbital cannot easily be answered on the basis of the present results. The experimental manifestations of both types of interactions are essentially indistinguishable: both are expected to produce a partial SN double bond, with all the associated geometrical and energetic implications. We prefer n–σ^* hyperconjugation for the following reasons: Firstly, several recent theoretical studies show that the chemistry of second-row elements can be reproduced almost equally well with and without the inclusion of 3d orbitals in the basis set.[22] Secondly, the similar trends found in various aziridine series substituted with first-row elements at nitrogen[20] and in series **2** indicate that a second-row element is *not* necessary for the phenomenon and, hence, that d orbitals are not involved. Finally, the different behavior of phenyl- vs trihalomethyl-substituted sulfenamides (in series **2**, and in **5** vs **6**) also points toward hyperconjugation rather than d-orbital conjugation: the former requires a charge-separated canonical structure **8**; the trihalomethyls form much more stable anions than the aryl groups, and hence, their effectiveness in raising SN and lowering amide barriers relative to aryl groups can be associated with their stabilizing influence on structure **8**, i.e., with hyperconjugation.

Experimental Section

^{1}H NMR spectra were measured on a Bruker WP-200-SY spectrometer operating at 200 MHz. Temperatures were controlled by a Bruker variable-temperature unit and calibrated by the spectra of methanol.[23] They are believed to be accurate to within ±2 °C on an absolute scale and possibly much better relative to one another. DNMR measurements were done on ca. 10% solutions in toluene-d_8. Elemental analyses were performed at the Weizman Institute Microanalytical Laboratory.

Trifluoro- and trichloromethanesulfenyl chlorides were obtained from commercial sources. The latter was distilled before use. Methyl *N*-benzylcarbamate was prepared as described previously by using method B and had mp 60–61 °C.[11]

Methyl *N*-Benzyl-*N*-(trichloromethanesulfenyl)carbamate (6a). To an ice-cold solution of 2.6 g (0.016 mol) of methyl *N*-benzylcarbamate in dry benzene (100 mL) under a stream of nitrogen was added dropwise from a syringe 7.5 mL of a 2.5 N solution of *n*-butyllithium (0.019 mol) in hexane over 10 min, with stirring. Upon addition, the initially turbid emulsion turned clear. Addition of butyllithium was continued until a distinct change of color was observed, to pale yellow. The solution was stirred for 10 min, after which a solution of 3.0 g (0.016 mol) of trichloromethanesulfenyl chloride in 50 mL of dry benzene was added. The mixture was left to react overnight under nitrogen with stirring and was then filtered. The filtrate was washed successively with 0.5 N H_2SO_4, 10% $NaHCO_3$, and three times with saturated NaCl solutions and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed over silica gel with a 10% acetone solution in 60–80 °C petroleum ether, to yield 61% of **6a**, a viscous liquid: ^{1}H NMR ($CDCl_3$, 310 K) δ 3.16 (s, CH_3), 4.28 (br s, CH_2), 7 (m, C_6H_5); ^{1}H NMR (toluene-d_8, 202 K) δ 3.16 (s, minor CH_3), 3.20 (s, major CH_3), 4.39 (d, J = 14.7 Hz, major CH_2, high-field half), 4.59 (d, J = 16.0 Hz, minor CH_2, high-field half), 4.89 (d, J = 16.0 Hz, minor CH_2, low-field half), 5.42 (d, J = 14.7, major CH_2, low-field half), 7 (m, C_6H_5).

Anal. Calcd for $C_{10}H_{10}Cl_3NO_2S$: C, 38.18; H, 3.17; N, 4.45; S, 10.19. Found: C, 38.66; H, 3.05; N, 4.20; S, 9.81.

Methyl *N*-Benzyl-*N*-(trifluoromethanesulfenyl)carbamate (6b). The preparation is essentially analogous to that of **6a**, with minor modifications resulting from the low boiling point of trifluoromethanesulfenyl chloride (–4 °C). The reaction is run in ether rather than benzene solvent, in an ice–salt bath. An ethereal solution of trifluoromethanesulfenyl chloride was prepared by passing the gas through 50 mL of ether in an acetone–dry ice bath. Five grams of the gas was passed as determined by weighing the cylinder before and after the process. This solution was then placed in a dropping funnel and added quickly into the reaction mixture, containing the *N*-benzylcarbamate (2.6 g, 0.016 mol) and butyllithium (6.4 mL of a 2.5 N solution in hexane, 0.016 mol) in an ice–salt bath and under nitrogen. The mixture was left to react overnight under nitrogen, while the temperature was allowed to rise slowly to room temperature. Workup and purification were as described for **6a**, and the yield with respect to the carbamate was 70% of a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 3.15 (s, CH_3), 4.26 (br s, CH_2), 7 (m, C_6H_5); ^{1}H NMR (toluene-d_8, 200 K) δ 3.07 (s, minor CH_3), 3.17 (s, major CH_3), 3.85 (d, J = 14.7 Hz, major CH_2), 3.98 (d, J = 16.0 Hz, minor CH_2), 4.62 (d, J = 15.9 Hz, minor CH_2), 5.15 (d, J = 14.7 Hz, major CH_2), 7 (m, C_6H_5).

Anal. Calcd for $C_{10}H_{10}F_3NO_2S$: C, 45.28; H, 3.80; N, 5.28; S, 12.09. Found: C, 45.46; H, 3.77; N, 4.89; S, 11.80.

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