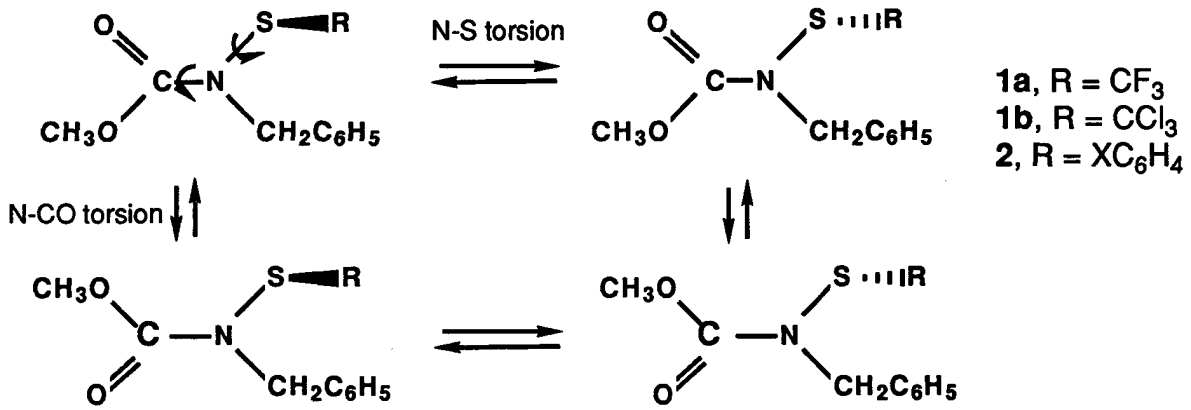
MEASUREMENT OF TWO ROTATIONAL BARRIERS, ABOUT S-N AND N-CO BONDS, IN SULFENAMIDES. EVIDENCE FOR HYPERCONJUGATION.

Daniel Kost, Hana Egozy and Gila Elhanati*

Department of Chemistry, Ben Gurion University of the Negev
Beer Sheva 84105, Israel.



Compounds **1** and **2** have two conformational changes requiring substantial activation energies: rotation about the SN and the N-CO bonds (Scheme). The rotations are stereochemically different, and can be distinguished by virtue of their different NMR consequences. Incorporation of the prochiral $CH_2C_6H_5$ group enables simultaneous observation and straightforward assignment of the torsional processes. Rotation about the S-N bond constitutes a *chiral torsion*. It interconverts enantiomers generated by the S-N chiral axis, whereas rotation about the amide bond is an *achiral torsion* and interconverts *syn,anti* diastereoisomers.[1]

At elevated temperature both rotations are fast on the NMR time scale, and the CH_2 protons give rise to a singlet. When the temperature is lowered, either S-N or N-CO torsion can be first to slow down, relative to the NMR time scale, and show exchange phenomena in the NMR spectrum. This can be followed readily in the signals due to the CH_2 protons (Figure 1): In the present case S-N torsion slows down first. As a result, the molecule becomes chiral, and the CH_2 protons become diastereotopic (*i.e.*, chemical shift different) when they sense chirality. Consequently *symmetrical* line broadening occurs and an AB-quartet develops. Upon further cooling, eventually also amide rotation becomes slow relative to the NMR time scale. This results in nonequivalence of the benzyl groups in each diastereomer, accompanied by further splitting of the initial AB-quartet into two *unequally intense* quartets corresponding to each of the *syn, anti* amide isomers.

The opposite situation, in which amide rotation slows down first followed by "freezing out" of sulfenamide rotation, has also been observed.[2] In this case, cooling of the sample (**2**, X = *m*-NO_2) resulted in *unsymmetrical* broadening of the initial high temperature CH_2 singlet, and splitting into two unequally intense singlets, corresponding to the *syn, anti* amide isomers. At lower temperatures S-N torsion also becomes slow on the NMR

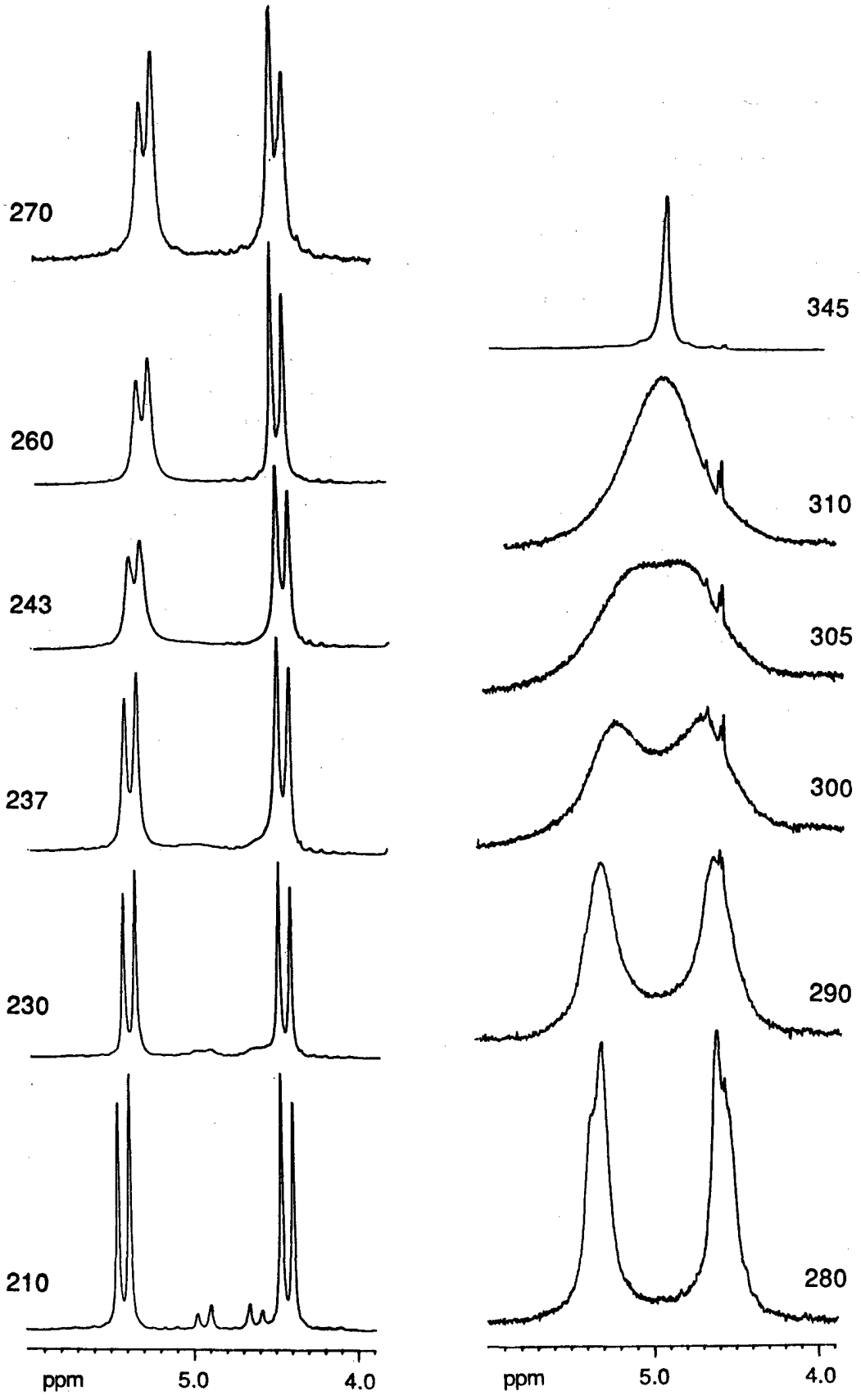


Figure 1: 200 MHz ^{1}H-NMR variable temperature spectra of **1b**, showing the CH_2 resonance region. Temperatures are in degrees Kelvin.

time scale, and each of the amide singlets splits further into an AB-quartet.

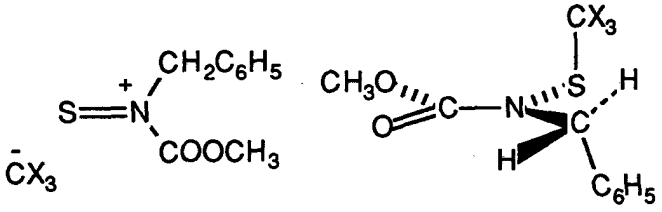
The rotational barriers for **1** were determined for both torsional processes, and are (in kcal/mole): **1a**, $\Delta G^{\neq}_{SN}$ = 12.5, $\Delta G^{\neq}_{CN}$ = 11.5; **1b**, $\Delta G^{\neq}_{SN}$ = 14.3, $\Delta G^{\neq}_{CN}$ = 11.5.

The possibility to measure at the same time both amide and sulfenamide rotational barriers in **1** offers a unique opportunity to demonstrate the effect of hyperconjugation on the barriers in these non-ionic molecules. This is achieved by comparison of the barriers in **1** to those in the closely related series **2** (Table 1). The S-N torsional barriers in **1** are generally higher, while the amide barriers are lower, than the corresponding barriers in the aromatic series **2**. This is best understood in terms of (n→σ*) hyperconjugation in the present case, facilitated by the electronegative nature of the CX_3 group.

Table 1: Amide and sulfenamide rotational barriers[a] for trihalomethanesulfenylcarbamates (**1**)[b] and arenesulfenylcarbamates (**2**).[c]

Compound	X	$\Delta G^{\neq}_{SN}$[d]	$\Delta G^{\neq}_{CN}$[d]
1a	F	12.5	11.5
1b	Cl	14.3	11.5
2a	4-MeO	8.7	12.1
2b	4-Me	9.1	12.1
2c	H	9.4	12.1
2d	4-Cl	9.5	12.0
2e	3-NO_2	9.9	12.0
2f	4-NO_2	10.9	12.0
2g	2,4-di(NO_2)	16.2	12.3

[a]Measured in toluene-d_8 solution at 200 MHz on a Bruker WP-200-SY spectrometer. [b]This work. [c]Taken from ref. 2. [d]kcal/mol.



3 **4**

The ability of the CX_3 group to stabilize a negative charge causes the canonical structure **3** to be relatively stable. As a result the contribution of **3** to the overall structure of **1a** and **1b** is substantial, causing increased double-bond character of the S-N bond. This, in turn, is evident from the high SN torsional barriers in **1**, relative to **2**. The hyperconjugation represented by **3** requires that the nitrogen lone-pair orbital interacts with the S-C σ* orbital. However, the greater involvement of the lone-pair in the S-N bond must result in reduced π-electron density in the N-CO bond, and hence in lower N-C bond order and lower amide torsional barrier. This indeed is observed in compounds **1** relative to **2**.

Assignment of the *E* configuration to the major amide isomer at low temperature is based on the substantially larger difference in chemical shifts of the CH_2 protons relative to that in the minor isomer (Figure 1). The bulky phenyl group avoids the CX_3 group, as shown in **4**; in this conformation the large chemical shift difference must arise from the proximity of the anisotropic carbonyl group, and hence the major isomer has the structure depicted in **4**.

References

[1] D. Kost, K. Aviram and M. Raban, *J. Org. Chem.*, in press.

[2] D. Kost, A. Zeichner and M. S. Sprecher, *J. Chem. Soc., Perkin Trans.* 2, 317 (1980).