JOC*Article*

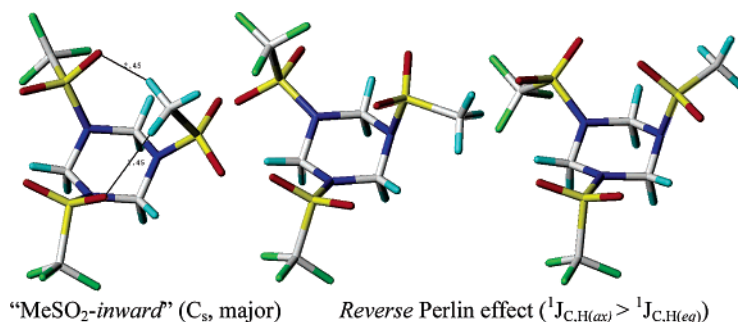# Stereodynamics of 1-(Methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane: Experimental and Theoretical Analysis

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"MeSO₂-*inward*" (C_s, major)   *Reverse* Perlin effect ($^1J_{C,H(ax)} > {}^1J_{C,H(eq)}$)

Dynamic NMR of 1-(methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane reveals the existence of three conformers and two dynamic processes: ring inversion and rotation about the N−S bond, both processes having $\Delta G^{\ddagger} = 13.5$ kcal/mol. An unprecedented large reverse Perlin effect ($J_{CHax} > J_{CHeq}$) was found experimentally and calculated theoretically.

Introduction

Conformational behavior of substituted cyclohexanes as well as heterocyclohexanes has been the subject of numerous studies.[1−3] The ring normally adopts the chair conformation unless specific intramolecular interactions stabilize the twist (ref 3b and references therein) or boat conformers.[3d−f] Substituents in the ring normally prefer the sterically favored equatorial over the more strained axial position,[1] although exceptions may exist provided that the 1,3-syn interactions with the axial substituent are attractive (like in thiane S-oxides)[4] or absent (like in 1,3,5-

trialkyl-1,3,5-triazinanes with two alkyls equatorial and one axial).[5,6] Recently, the stereodynamic behavior of 1,3,5-tris-(trifluoromethylsulfonyl)-1,3,5-triazinane (**1**) obtained by the reaction of trifluoromethanesulfonamide with formaldehyde[7] has been investigated by the use of ^{1}H, ^{13}C, and ^{19}F NMR low-temperature spectroscopy as well as quantum chemical calculations.[8] To the best of our knowledge, no other stereochemical

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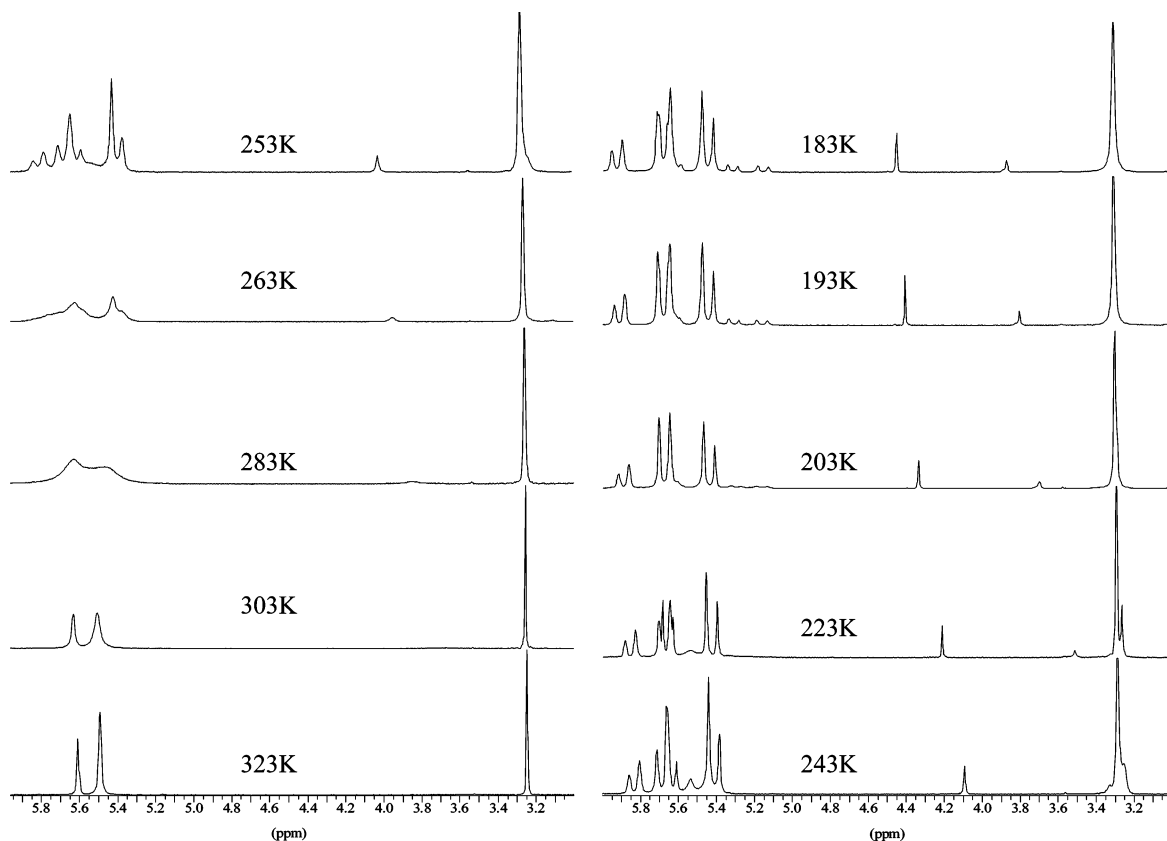
FIGURE 1. Temperature dependence of the ^{1}H NMR spectra of 1-methylsulfonyl-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane in $(CD_3)_2CO$. Small signals from δ 4.5−3.5 are an impurity and/or solvent signals.

studies were performed on 1,3,5-triazinanes bearing electron-withdrawing groups on nitrogen atom(s). At the same time, the presence of strong acceptors, like the trifyl group, may impart the nitrogen to which it is attached the properties of the sp^2- rather than sp^3-hybridized atom that, in turn, may result not only in specific stereochemical behavior different from that for *N*-alkyl substituted analogues but also to interesting stereoelectronic effects in these heterocycles. This was found to be the case for 1-(methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane (**2**), which was investigated in the present study. Compound **2** was prepared by the acid-catalyzed three-component reaction of methanesulfonamide, trifluoromethanesulfonamide, and formaldehyde.

$$CF_3SO_2NH_2 + CH_3SO_2NH_2 + CH_2O \xrightarrow{H_2SO_4} (CF_3SO_2NH)_2CH_2 \; +$$

2
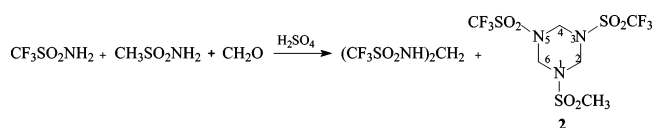
As compared to the symmetrically substituted compound **1**, compound **2** has the MeSO$_2$ group that might serve as a convenient NMR indicator in both ^{1}H and ^{13}C spectra for monitoring the conformational behavior at different temperatures. We report here the relative stability of possible conformers of **2**; ^{1}H, ^{13}C, ^{15}N, and ^{19}F dynamic NMR measurements; and unusually large reverse Perlin effects for the most stable conformer of **2**. The presence of two different sulfonyl groups,

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MeSO$_2$ and CF$_3$SO$_2$, in **2** may provide additional information as compared to the previously studied symmetrically substituted analogue.[8]

Results and Discussion

^{1}H NMR and 2-D {^{1}H−^{15}N} Measurements. The ^{1}H NMR spectrum of compound **2** in acetonitrile-d_3 at room temperature shows the singlet of the methyl group at δ 3.15 and a broadened singlet resonance at δ 5.3 with the half-width of 80 Hz belonging to all methylene groups. On heating to 323 K, the latter signal is split into two rather narrow (half-width 20 Hz) singlets at δ 5.25 and 5.35 in the 2:1 ratio of intensities, which belong to the (C^{2}H$_2$ + C^{6}H$_2$) and C^{4}H$_2$ protons, respectively. On cooling, the broadened singlet of the methylene protons decoalesced at 263 K into two broadened signals that on further cooling to 233 K formed two pairs of doublets. The first one at δ 5.65 and 5.12 (each of ^{1}H, ^2J 13.7 Hz) belongs to the C^{4}Heq and C^{4}Hax protons, respectively, whereas the second one at δ 5.58 and 5.03 (each of ^{2}H, ^2J 14.4 Hz) belongs to the (C^{2}Heq + C^{6}Heq) and (C^{2}Hax + C^{6}Hax) protons, correspondingly. Besides, at 273 K, the methyl group signal at δ 3.15 broadens, and upon further cooling, the second resonance of the MeSO$_2$ group of low intensity appears. At 233 K, this signal of a minor conformer is observed at δ 3.05, the relative intensities of the two methyl signals being 4:1. The methylene groups' resonance corresponding to this minor conformer is represented at 233 K by a very broad singlet at δ 5.2.

The similar dynamic behavior of the ^{1}H NMR spectrum of compound **2** is observed in acetone-d_6 (Figure 1).
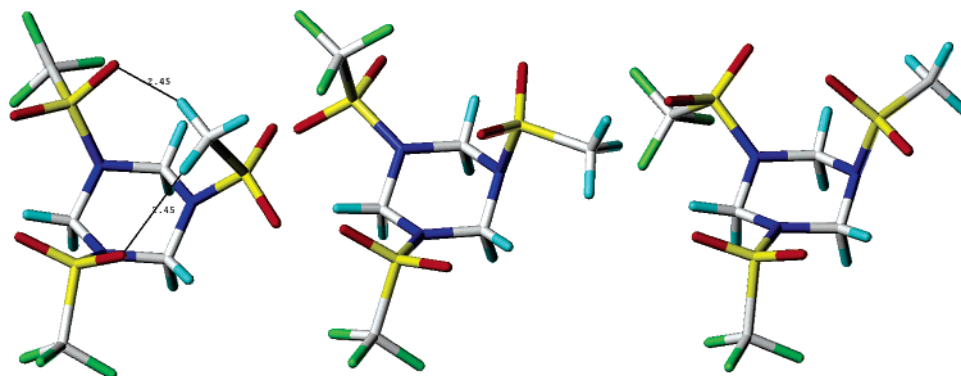
FIGURE 2. MeSO$_2$-inward (**2a**, C_S symmetry), CF$_3$SO$_2$-inward (**2b**, C_1 symmetry), and all-outward (**2c**, C_1 symmetry) rotamers of 1-methylsulfonyl-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane

At 323 K, the spectrum shows three singlets at δ 3.25, 5.5, and 5.6 in the ratio of 3:4:2 corresponding to the CH$_3$, (C^{2}H$_2$ + C^{6}H$_2$), and C^{4}H$_2$ protons, respectively. On cooling, the signals of the methylene groups decoalesce, and below 253 K, the spectrum contains four doublets that are best resolved at 223 K (Figure 1). Their assignment to the axial or equatorial protons in the 2(6)- or 4-positions in the ring was based on the relative intensities, the values of chemical shifts, and the broadening of the downfield signal due to nonresolved long-range W-coupling for equatorial protons (Figure 1) similar to ref 8. It is also proved by heteronuclear {^{1}H$-$^{15}N} spectra. The 2-D {^{1}H$-$^{15}N} spectrum of **2** in acetone-d_6 at 183 K shows cross-peaks with two ^{15}N signals at δ −273.8 and −285.5 for an upfield doublet signal of ^{2}H intensity at δ 5.4, whereas a doublet signal of ^{1}H intensity at δ 5.6 has a cross-peak with only one of the ^{15}N signals, namely, with that at δ −285.5. This implies that the ^{15}N signals at δ −273.8 and −285.5 belong to the CH$_3$SO$_2$N and CF$_3$SO$_2$N groups, respectively, and that the 2,6-Hax signals are coupled with the adjacent two nonequivalent ^{15}N nuclei, whereas the 4-Hax signal is coupled with two equivalent ^{15}N nuclei of the CF$_3$SO$_2$N groups.

At 243 K, a small singlet appears upfield to the main MeSO$_2$ signal, suggesting the appearance of the second conformer of **2**, and below 203 K, the corresponding ring protons of this conformer emerge (Figure 1). The approximate relative intensities of the not fully resolved MeSO$_2$ signals are ∼1:6.

^{13}C NMR Measurements. The ^{13}C NMR spectrum of compound **2** in CD$_3$CN at room temperature contains three singlets at δ 41.42, 61.24, and 61.86 and a quartet at δ 120.18 ppm (J = 320.3 Hz), which belong to the CH$_3$, C$^{2(6)}$, C^4, and CF$_3$ groups, respectively. The spectrum in acetone-d_6 at 183 K shows two sets of these signals: 39.96 (major) and 39.55 (minor), 60.71 (major) and 68.93 (minor), and 61.40 (major) and 69.05 (minor) and two quartets at δ 119.17 (J 319.4 Hz, major) and δ 119.41 (J 321.8 Hz, minor). Note a substantial downfield shift, δ > 8, of the methylene group signals in the minor conformer with respect to the major conformer.

Since acquisition of 1-D ^{13}C NMR spectra at low temperatures was complicated by the limited solubility of compound **2**, the ^{13}C chemical shifts as well as coupling constants $^1J_{CH}$ were obtained from cross-sections of 2-D heteronuclear {^{1}H$-$^{13}C} HSQC[9] spectra recorded without wide band decoupling from ^{13}C by a GARP pulse sequence. Digital resolution for the proton channel in HSQC experiments was 0.2 Hz. NMR parameters for the two conformers **2a** and **2b** are given in Table 1.

TABLE 1. ^{1}H Chemical Shifts δ and $^1J_{CH}$ and $^2J_{HH}$ Coupling Constants (Hz) in Conformers 2a and 2b

conformer	position	acetone-d_6 (193 K)			CD$_3$CN (233 K)		
		δ	$^2J_{HH}$	$^1J_{CH}$	δ	$^2J_{HH}$	$^1J_{CH}$
2a (major)	2,6-Hax	5.43	14.7	169.2	5.03	14.4	167.5
	2,6-Heq	5.65		158.6	5.58		158.9
	4-Hax	5.68	13.8	169.8	5.12	13.7	168.2
	4-Heq	5.90		160.2	5.65		159.5
2b (minor)	2-Hax	5.29	13.1		a		
	2-Heq	5.65					
	6-Hax	5.13	14.7				
	6-Heq	5.60					
	4-Hax,eq	b					

^{a} At 233 K (the lowest possible temperature for acetonitrile), only a very broad signal centered at δ 5.2 is detected. Further decrease of the temperature leads to solidification of the solution. ^{b} Hidden under 4-Hax,eq of the major conformer **2a**.

Theoretical Calculations. Quantum chemical calculations performed for **1**[7] proved the conclusion based on the NMR and X-ray studies on the planarity of the nitrogen atom surroundings in the CF$_3$SO$_2$NR$_2$ fragment.[10] To verify whether this is true for the nonfluorinated group MeSO$_2$NR$_2$ in **2** and therefore whether the inversion at the nitrogen atom could be responsible for the observed dynamic behavior of **2**, we have calculated possible isomers of **2** at the DFT level of theory. As compared to calculations of **1**, the basis set was extended and augmented with polarization functions on heavy atoms, so all calculations were performed at the B3LYP/6-311+G(d,p) level of theory. Because of lower symmetry of molecule **2** than **1**, the former has three conformational minima, namely, **2a** with the MeSO$_2$ group directed inward toward the ring (C_S symmetry), **2b** with the CF$_3$SO$_2$ group inward (C_1 symmetry), and **2c** with all three substituents directed outward from the ring (C_1 symmetry) (Figure 2).

The lowest energy minimum corresponds to conformer **2a**, which is stabilized by two H···O interactions ($l_{H···O}$ 2.45 Å), conformer **2b** is 4.42 kcal/mol higher in energy, and conformer **2c** is 5.57 kcal/mol higher than **2a**. The energy difference between **2b** and **2c** (1.15 kcal/mol) is close to that calculated for the inward and all-outward conformers of **1** at the same level of theory [1.44 kcal/mol, B3LYP/6-311+G(d,p)]. The most stable conformer **2a** has the lowest dipole moment (4.33 D), conformer **2b** is more polar (7.44 D), and the most polar conformer **2c** has a dipole moment of 8.45 D. The sum of the

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TABLE 2. Relative Bond Lengths [$\Delta l = l(\text{C}-\text{Hax}) - l(\text{C}-\text{Heq})$], Atomic Charge Differences ($\Delta q = q_{\text{Heq}} - q_{\text{Hax}}$), Dihedral Angles $H_{\text{Eq}}-\text{C}-n-x$ (θ), Planarity of Nitrogen Atom (Sum of Bond Angles, Σ_{N}), and Perlin Effect ($\Delta J = J_{\text{CHeq}} - J_{\text{CHax}}$) in Molecules 2−4

molecule	position	Δl (Å)	$\Delta q \times 10^4$	θ (deg)	Σ_{N} (deg)	ΔJ_{clcd} (Hz)	$\Delta J_{\text{expl}}{}^{a}$ (Hz)
2a	2-CH$_2$	0.009	252	3.8	359.4 (N1)	−4.4	−10.6 (−8.6)
	4-CH$_2$	0.007	455	13.0	356.3 (N3)	−5.3	−9.6 (−8.7)
	6-CH$_2$	0.009	252	3.8	356.3 (N5)	−4.4	−10.6 (−8.6)
2b	2-CH$_2$	0.008	135	35.0	345.0 (N1)	−5.7	
	4-CH$_2$	0.011	104	31.8, 0.3	354.1 (N3)	−3.0	
	6-CH$_2$	0.010	483	37.6	359.4 (N5)	4.7	
2c	2-CH$_2$	0.009	585	34.8	345.3 (N1)	2.6	
	4-CH$_2$	0.009	381	5.3, 21.6	359.8 (N3)	−3.1	
	6-CH$_2$	0.010	149	35.9	358.6 (N5)	−4.8	
3	2,6-CH$_2$	0.010	193	37.5	350.1	4.9	
	3,5-CH$_2$	0.001	7			−1.1	
	4-CH$_2$	0.005	150			5.5	
4	2,6-CH$_2$	0.002	−163	2.9	360.0	−4.5	
	3,5-CH$_2$	0.000	162			2.3	
	4-CH$_2$	0.005	301			8.8	

^{a} In acetone-d_6. The values in parentheses refer to solution in acetonitrile-d_3.

bond angles at nitrogen in the $\text{CF}_3\text{SO}_2\text{N}<$ fragment in all conformers is equal or very close to 360°, that is, the nitrogen atom bearing the trifyl group is virtually planar. The nitrogen atom with the less electronegative methylsulfonyl group (the $\text{CH}_3\text{SO}_2\text{N}<$ fragment) is also planar in conformer **2a**, but in **2b** and **2c**, it is somewhat pyramidal: the sum of the angles around nitrogen is 345°. Although formally the energy difference of ≥2 kcal/mol must virtually rule out **2b** and the more so **2c** from the equilibrium at low temperatures, in solution, ΔE should be substantially lower due to different polarities of the conformers. Calculated geometrical parameters and atomic charges as well as the calculated and experimental values of the Perlin effect ($J_{\text{CHeq}} - J_{\text{CHax}}$) in **2** are given in Table 2.

^{19}F NMR Measurements. A low-temperature dynamic ^{19}F NMR spectroscopic study of compound **2** in acetone-d_6 proves the theoretically predicted structure and relative stability of conformers **2a** and **2b**. At 333 K, the spectrum contains one sharp singlet at δ −77.9 with a half-width $\Delta\nu_{1/2}$ of 11 Hz. Lowering of temperature to 293 K is followed by an upfield shift of the signal and its broadening to $\Delta\nu_{1/2}$ 90 Hz. At 283 K, two signals appear with the relative intensities of 4:1, that is, equal to those of the two methyl group signals in the ^{1}H NMR spectrum. The first signal at δ −78.4 ($\Delta\nu_{1/2}$ 83 Hz) is due to two equivalent trifyl groups of **2a**, whereas the second broadened signal at δ −77.7 ($\Delta\nu_{1/2}$ ∼300 Hz) belongs to trifyl groups of **2b**. At 203 K, the latter signal is split into two narrow signals of equal intensity with δ_{F} −76.4 ($\Delta\nu_{1/2}$ 33 Hz) and −78.9 ($\Delta\nu_{1/2}$ 25 Hz). Equal intensity of the signals and comparison of their chemical shifts to those of the inward and outward directed trifyl groups in **1**[8] allow us to conclude that the split signals belong to the trifyl groups of conformer **2b** that become nonequivalent under the conditions of slow rotation.

Therefore, judging from both theoretical calculations and experimental ^{1}H and ^{19}F NMR low-temperature spectroscopic studies, we may conclude that compound **2** exists as the equilibrium mixture of at least two conformers, **2a** and **2b**.

The estimation of the energy of activation at the coalescence temperatures for the two dynamic processes, that is, for the ring inversion and rotation about the N−S bonds, gives for both processes $\Delta G^{\ddagger} = 13.5$ kcal/mol. This value coincides with the values obtained in ref 8.

Reverse Perlin Effect. The most intriguing result is the reverse Perlin effect experimentally observed for all three

methylene groups in **2**. Normal Perlin effect ($^1J_{\text{CHax}} < {}^1J_{\text{CHeq}}$) reflects elongation and weakening of the C−Hax bond adjacent to a heteroatom and was for a long time attributed to hyperconjugation of the $n_X \rightarrow \sigma^*(\text{C}-\text{H})$ type.[11] Lately, this concept was rejected as primarily responsible for the $^1J_{\text{CH}}$ (the Perlin effect)[14] and $^1J_{\text{CC}}$ coupling constants,[12] although the authors specially emphasized that their conclusion is not necessarily general.[12,13] Recently, a reverse Perlin effect ($J_{\text{CHax}} > J_{\text{CHeq}}$) was found for some 4-silathiane S-oxides and was interpreted in terms of the buttressing effect of the SO group on the C−Hax bonds.[14] The experimentally observed large reverse Perlin effect in **2** requires an alternative explanation.

A normal Perlin effect reflects elongation of the C−Hax versus C−Heq bond due to the previous hyperconjugation effect. However, Table 2 clearly demonstrates that there is no correlation of the Perlin effect with the C−H bond length or the atomic charge on the corresponding hydrogen atom. In all cases, the C−Hax bonds are by ∼0.01 Å longer than the corresponding C−Heq bonds, and Heq are more positive than Hax. Through-space interactions between the nonbonded atoms, like O···H or F···H, cannot explain the observed results either since the reduced contacts between these atoms exist in all conformers of **2** and for all CH$_2$ groups despite the calculated sign of the Perlin effect.

Since, apparently, there are no effects that could strengthen the C−Hax bonds with respect to C−Heq in **2b,** it may be alternatively suggested that the observed large reversed Perlin effect is the result of weakening the C−Heq bonds due to their interactions with the syn-periplanar (or close to it, cf. angles θ in Table 2) vicinal N−S bonds of the [$\sigma(\text{C}-\text{Heq}) \rightarrow \sigma^*(\text{N}-\text{S})$] type. With this, the residual effect of the [$n(\text{N}) \rightarrow \sigma^*(\text{C}-\text{Hax})$] hyperconjugation still results in some elongation of the C−Hax bonds.

To clarify whether the reverse Perlin effect could be reproduced theoretically in the six-membered nitrogen-containing heterocycles with the nitrogen lone pair being strongly

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conjugated with the substituent, we have calculated 1-cyano-piperidine **3** and 1-carbonyl piperidinium cation **4**, the isocyanate cation analogue of piperidine.
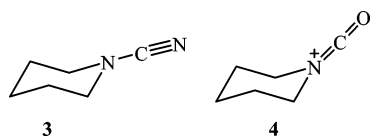
Molecule **3** has a normal Perlin effect for the 2,6- and 4-CH_2 groups and a very slight reverse Perlin effect for the 3,5-CH_2 groups. Note that the nitrogen atom is rather pyramidal in **3** and that the H_{eq}−C−N−CN dihedral angle is rather large, 37.5°. Molecule **4** has an ideally planar nitrogen atom, a close to zero H_{eq}−C−N−CO dihedral angle, and shows a large reverse Perlin effect for the 2,6-CH_2 groups, that is, at the α-position to the formally positive nitrogen (Table 2). Remarkably, the C−Hax bonds are still longer than the corresponding C−Heq bonds.

Conclusion

Two dynamic processes, ring inversion and rotation about the N−S bond in 1-(methylsulfonyl)-3,5-bis(trifluoromethyl-sulfonyl)-1,3,5-triazinane, were found and investigated by multinuclear dynamic NMR in conjunction with theoretical studies. These processes lead to the existence of three conformers with different orientations of the CF_3SO_2 and CH_3SO_2 groups with respect to the triazinane ring, two of which were observed experimentally. An unprecedented large reverse Perlin effect ($J_{CHax} > J_{CHeq}$) was found experimentally and was proved by theoretical calculations. The conclusion can be made that, apart from the C−H bond length and atomic charge on hydrogen, the reverse Perlin effect in the studied system is mainly determined by the presence at the α-position of the nitrogen atom bearing a very strong electron-withdrawing group CF_3-SO_2, which makes it almost positively charged. As a result, the [σ(C−Heq) → σ*(N−S)] hyperconjugation weakens the C−Heq bonds and leads to the observed reversed Perlin effect. This conclusion is in agreement with calculations on the model compound, 1-carbonyl piperidinium cation, possessing planar nitrogen and also showing a large reverse Perlin effect.

Experimental Procedures

Synthesis of 1-(Methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane 2. A total of 3 g (0.02 mol) of $CF_3SO_2NH_2$ and 1.9 g (0.02 mol) of $MeSO_2NH_2$ was dissolved in 40 mL of concentrated H_2SO_4 at 40 °C, and 0.6 g (0.02 mol) of $(CH_2O)_n$ was added in small portions. The resulting thickened mixture was stirred for 3 h and then poured into ice, the precipitate was filtered, washed with saturated aqueous NaCl and water, and dried under vacuum. The filtrate was saturated with NaCl, extracted by ether, and the extract was dried over $MgSO_4$, evaporated, and dried under vacuum. The precipitate and the residue from the extract were combined and treated with ether/hexane (2:1) to separate compound **2** from bis(trifluoromethanesulfonylamino)methane. Finally, compound **2** was purified by flash chromatography. M.p. 204 °C. Elemental analysis: calcd for $C_6H_9F_6N_3O_6S_3$ (%):C 17.09, H 2.14, F 27.00, N 9.79, S 22.54; found: C 16.78, H 2.11, F 26.55, N 9.79, S, 22.41.

NMR Measurements. Dynamic ^1H, ^{13}C, ^{15}N, and ^{19}F NMR spectra were recorded in acetone-d_6 or CD_3CN at working frequencies 400 (^1H), 100 (^{13}C), 40 (^{15}N), and 376 (^{19}F) MHz; ^1H and ^{13}C NMR chemical shifts are reported in parts per million downfield to TMS and ^{19}F NMR in parts per million downfield to $CFCl_3$. ^{15}N NMR chemical shifts were obtained from 2-D {^1H−^{15}N} spectra recorded by the use of a gradient probe working in the *hmbcgp* mode optimized to the long-range coupling constant J_{NH} equal to 9 Hz and are reported in parts per million downfield to CH_3NO_2. The temperature was varied by the use of a BVT 3000 variable temperature unit, with a temperature stability of ±0.2°.

Theoretical Calculations. All calculations were performed with full optimization of all variables at the B3LYP/6-311+G(d,p) level of theory using the Gaussian 03 package.[15] NMR computations of absolute shieldings and spin−spin coupling constants were performed on conformers **2a**−**c** using the GIAO method.[16,17]

Supporting Information Available: Energy and geometry for the conformers **1**−**4** at the B3LYP/6-311+G(d,p) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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