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Variable temperature NMR and theoretical study of the stereodynamics of 5-trifluoromethylsulfonyl-1,3,5-dioxaazinane: Perlin effect subject to heteroatom substitution

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ABSTRACT

Multinuclear dynamic NMR spectroscopy of 5-trifluoromethylsulfonyl-1,3,5-dioxaazinane (**4**) revealed the existence of two close in energy *chair* conformers with differently oriented CF_3 groups with respect to the ring. Of the two alternative routes for their interconversion, the ring inversion path with intermediate formation of the corresponding 2,5-*twist*-conformer is preferred, with the energy barrier of 11.2 kcal/mol in excellent agreement with the experimental value (11.7 kcal/mol). The Perlin effect is studied experimentally and calculated theoretically for all CH_2 groups and found to be subject to the nature of the adjacent heteroatoms O and N, respectively.

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1. Introduction

Substituted cyclohexanes and heterocyclohexanes have been the subject of extensive conformational studies.[1–3] The six-membered rings normally adopt a *chair* conformation unless specific intramolecular interactions stabilize the *twist*[3b] or *boat* conformers.[3d–f] The substituents usually occupy the equatorial position,[1] although there may be exceptions if the 1,3-*syn* interactions with the axial substituent are attractive (like in thiane *S*-oxides)[4] or absent (like in 1,3-dialkyl-1,3-diazinanes[5] and 1,3,5-trialkyl-1,3,5-triazinanes[6,7] with two alkyls equatorial and one axial). Recently, we have reported the stereodynamic behavior of 1,3,5-tris(trifluoromethylsulfonyl)-1,3,5-triazinane **1**, 3,5-bis(trifluoromethylsulfonyl)-1,3,5-oxadiazinane **2**, and 1-(methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane **3** as studied by low-temperature ^1H, ^{13}C, ^{15}N, and ^{19}F NMR spectroscopies and theoretical calculations.[8–10] Compounds **2** and **3** were obtained by the reaction of trifluoromethanesulfonamide with paraformaldehyde[11] or isolated from the three-component condensation of trifluoromethanesulfonamide, paraformaldehyde, and methanesulfonamide.[12] To the best of our knowledge, no other stereochemical studies were performed on 1,3,5-triheterocyclohexanes containing N and O heteroatoms and bearing an electron withdrawing group at a nitrogen atom. At the same time, the presence of strong acceptors, like the trifyl group, may impart the nitrogen atom, it is attached to, with the properties of an sp^2 rather than sp^3-hybridized atom. This may cause specific stereochemical behavior, different from that for *N*-alkyl substituted analogs as well as result in interesting stereoelectronic effects, similar to what we have found for compounds **2** and **3** (Scheme 1).[8–10]

In this paper, we report the conformational analysis of 5-(trifluoromethylsulfonyl)-1,3,5-dioxaazinane **4**, which was isolated from the product mixture formed upon condensation of trifluoromethanesulfonamide with paraformaldehyde in ethyl acetate.[13] The relative stability of the possible conformers of **4** is calculated theoretically and assessed experimentally by the use of ^1H, ^{13}C, and ^{19}F dynamic NMR measurements. The Perlin effects, both calculated theoretically and measured experimentally, are also discussed.

2. Results and discussion

B3LYP/6-311+G(d,p) calculations of **4** revealed two conformational minima. The more stable conformer **4a** has the triflyl group directed inward with respect to the ring, whereas conformer **4b** (both of C_S symmetry) is 0.46 kcal/mol higher in energy and has the triflyl group directed outward from the ring (Fig. 1). The ring

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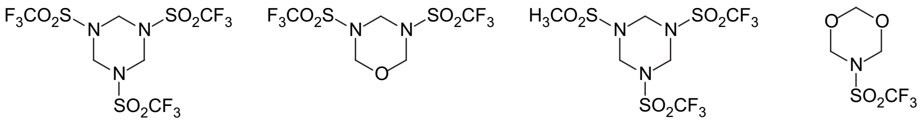

Scheme 1. Structure of compounds studied.

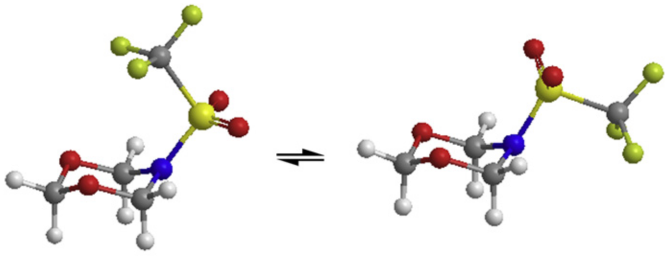

Figure 1. The 'inward' (**4a**) and 'outward' (**4b**) conformers of 5-(trifluoromethylsulfonyl)-1,3,5-dioxaazinane.

conformation corresponds to an ideal *chair* with the sum of the bond angles at the nitrogen atom being equal to 354.1° in conformer **4a** and 349.0° in conformer **4b**.

2.1. ^{1}H NMR measurements

The ^{1}H NMR spectrum of compound **4** in acetone-d_6 at 298 K or at higher temperatures shows two narrow singlets at δ 5.24 and 5.36 in the 1:2 ratio belonging to the OCH_2O and NCH_2O methylene protons, respectively. Upon cooling, the signals broaden and below 233 K they start to decoalesce to become fully resolved below 213 K (Fig. 2a). The signals are grouped into two AB spin systems with markedly different J_{AB} values (Table 1); note the appearance of a small doublet at δ 5.4 ppm (Fig. 2a), which belongs to the NCH_2O group in the minor conformer **4b**. Both the OCH_2O chemical shifts and the $^1J_{CH}$ values in conformer **4b** should be considered as approximate since the signals are overlapped with those of the major conformer **4a** and were discriminated only by the use of 2D{^{1}H–^{13}C} spectra.

2.2. ^{13}C NMR measurements

The ^{13}C chemical shifts and $^1J_{CH}$ coupling constants were obtained from cross sections of 2D heteronuclear {^{1}H–^{13}C} HSQC[14] 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. At 298 K, the ^{13}C NMR spectrum of compound **4** in acetone-d_6 contains two singlets at δ 78.66 and 94.95 ppm corresponding to the NCO and OCO carbons, respectively. At 193 K, they are shifted to δ 78.09 and 94.34 ppm and, in addition, small singlets at δ 78.53 and 94.67 ppm appear. The latter signals correspond to the minor conformer **4b** and, as in the case of 3,5-bis(trifluoromethylsulfonyl)-1,3,5-oxadiazinane **2**,[10] they are shifted downfield by ca. 0.4 ppm with respect to the corresponding signals of the major conformer **4a**.

2.3. ^{19}F NMR measurements

At 323 K, the ^{19}F NMR spectrum of compound **1** in acetone-d_6 contains one singlet with δ_F −77.77 ppm. Upon cooling, it reversibly broadens and decoalesces (T_c 263 K) to two singlets, which at 193 K resonate at δ_F −76.89 and −80.78 ppm. According to our previous work, the upfield signal at δ_F −80.78 ppm belongs to the outward CF_3 group in **1b**. The ratio of the signals is 84:16 and corresponds to a free energy difference of 0.64 kcal/mol, which nicely correlates with the aforementioned calculated value of ΔE of 0.46 kcal/mol.

As for the conformational barrier, the presence of only one bulky group at the ring nitrogen atom makes compound **4** conformationally

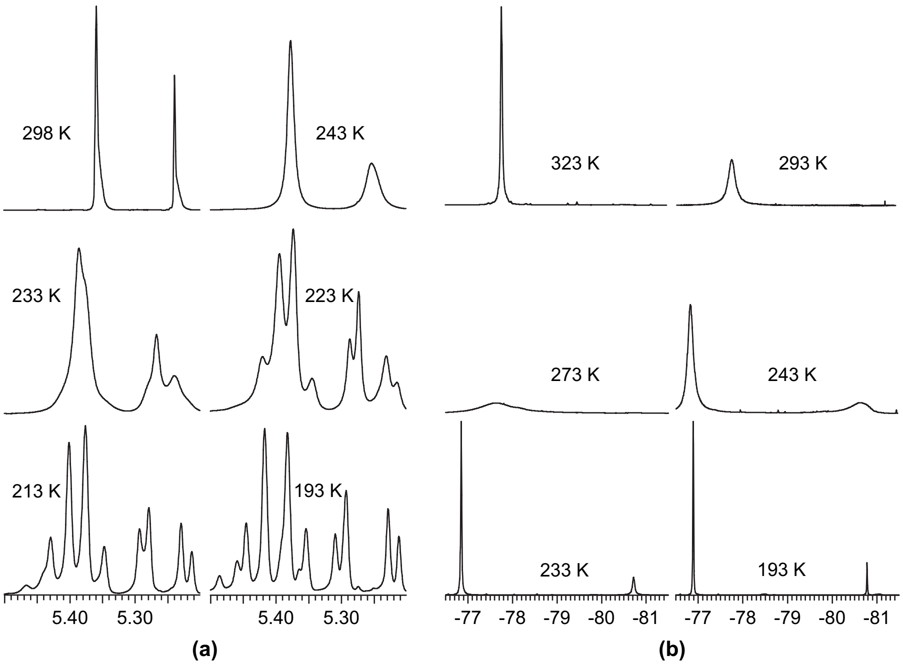

Figure 2. (a) ^{1}H NMR spectra of **4** in acetone-d_6; (b) ^{19}F NMR spectra of **4** in acetone-d_6.

Table 1

Experimental (193 K, acetone-d_6) and calculated [GIAO/B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)] ^{1}H and ^{13}C chemical shifts (ppm) and $^1J_{CH}$ and $^2J_{HH}$ coupling constants (Hz) in conformers **4a** and **4b**

Group	Experimental						Calculated			
	δ_C	Atom	δ_H	$^2J_{HH}$	$^1J_{CH}$	Perlin effect	δ_H	$^2J_{HH}$	$^1J_{CH}$	Perlin effect
OCH_2O in **4a**	94.34	H_{ax}	5.19	6.6	162.0	+13.2	5.05	6.2	149.4	+17.8
		H_{eq}	5.27		175.2		5.27		167.2	
NCH_2O in **4a**	78.09	H_{ax}	5.34	11.2	165.7	+2.4	4.89	11.1	151.0	+9.1
		H_{eq}	5.40		168.1		5.42		160.1	
OCH_2O in **4b**	94.67	H_{ax}	5.26	—	165.3	+7.1	5.04	6.2	148.6	+18.5
		H_{eq}	5.26		172.4		5.26		167.1	
NCH_2O in **4b**	78.53	H_{ax}	5.34	10.8	164.8	+4.3	4.87	10.4	150.5	+10.2
		H_{eq}	5.45		169.1		5.45		160.7	

more flexible and lowers the temperature of decoalescence to 238 K from 263 K for compounds **1** and **3** (three RSO_2 groups in the ring)[8,10] or 243 K for compound **2** (two CF_3SO_2 groups in the ring).[9]

2.4. Theoretical calculations

Our previously studied 1,3,5-triheterocyclohexanes **1**–**3**[8–10] contained two or three trifyl groups, and the ring inversion proved to be not the only dynamic process determining their stereodynamics since it led to conformers with two or even three trifyl groups directed inward that are sterically impossible. Therefore, the ring inversion and internal N–S rotation in those systems are interwined and one cannot occur without the other. As distinct from that, compound **4** has only one trifyl group and, hence, the question arises as to how the interconversion between **4a** and **4b**, depicted in Figure 1 occurs? Since nitrogen atom inversion can be excluded (close to planar arrangement), two processes, the ring inversion and internal N–S rotation, are feasible; so, we calculated transition states for these two routes of interconversion of conformers **4a** and **4b**.

For the internal rotation about the N–S bond, the B3LYP/6-311+G(d,p) vibrational frequency calculations verified the existence of the transition state [**TS-1**]‡, which lies 14.4 kcal/mol higher than **4a** and has one imaginary frequency of $-74\ cm^{-1}$. The vibrational mode corresponds mainly to rotation about the N–S bond, so that the transition state [**TS-1**]‡ indeed connects conformers **4a** and **4b** (Fig. 3).

Theoretical analysis of an alternative option of interconversion, occurring by ring inversion, revealed the existence of the two transition states, [**TS-2**]‡ and [**TS-3**]‡, as well as the intermediate *twist* conformer **4c** (Fig. 3). The transition states [**TS-2**]‡ and [**TS-3**]‡ have very close energies, 10.9 and 11.2 kcal/mol with respect to **4a**, and imaginary frequencies of −269 and $-267\ cm^{-1}$, respectively. The latter values are much larger than that for [**TS-1**]‡, which is indicative of narrower barriers at the saddle points [**TS-2**]‡ and [**TS-3**]‡ on the potential energy surface. The calculated displacement vectors at −269 and $-267\ cm^{-1}$ suggest that the corresponding transition states [**TS-2**]‡ and [**TS-3**]‡ are, indeed, the transition states connecting the intermediate 2,5-*twist* conformer **4c** with the chair conformers **4a** and **4b**, respectively, via the intermediate 2,5-*twist* conformer **4c**. The potential energy diagram in Figure 3 via the transition states [**TS-2**]‡ and [**TS-3**]‡ is very similar to that of silacyclohexane.[15]

The calculated barrier via the transition states [**TS-2**]‡ and [**TS-3**]‡ of 11.2 kcal/mol is in excellent agreement with the experimental value of 11.7 kcal/mol found for compound **4** from the temperature of coalescence T_c=238 K, taking into account the distance between the $OCH_{ax}O$ and $OCH_{eq}O$ signals $\Delta\nu$=34 Hz and the value of coupling constant J_{HH}=6.6 Hz.

NMR computations of absolute shieldings and spin–spin coupling constants were performed at the GIAO/B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory. The ^{1}H and ^{19}F chemical shifts were calculated using the corresponding absolute shieldings calculated for Me_4Si and $CFCl_3$ at the same level of theory. Excellent coincidence of the calculated and measured $^2J_{HH}$ coupling constants as well as of the chemical shifts for the equatorial protons can be seen in Table 1. The calculated chemical shifts for the axial protons are notably smaller than the experimental ones, the deviations $\Delta\delta_H$ being 0.14 and 0.45 ppm for the OCH_2O and NCH_2O groups, respectively (Table 1). The same trend with $\Delta\delta_{Hax}$ even reaching 1.4 ppm was observed in our previous work.[9] According to calculations, the fluorine nuclei in conformer **4a** are less shielded by 5.5 ppm than those in conformer **4b**, which is in good agreement

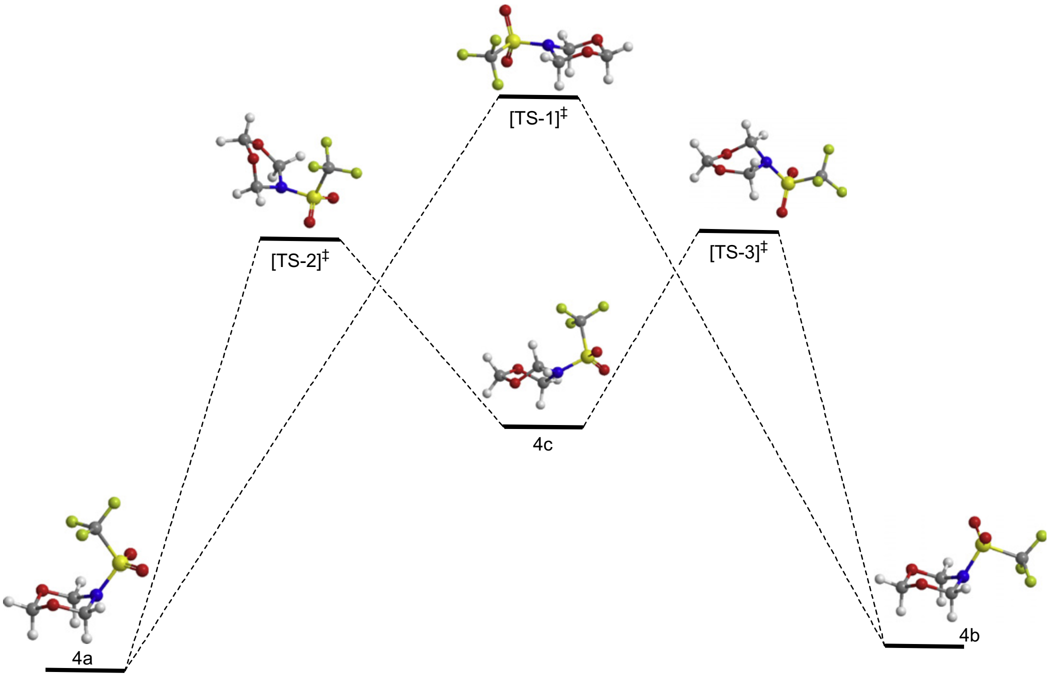

Figure 3. Interconversion of conformers **4a** and **4b** via internal rotation (route **4a**⇆[**TS-1**]‡⇆**4b**) and ring inversion (route **4a**⇆[**TS-2**]‡⇆ **4c**⇆[**TS-3**]‡⇆**4b**).

Table 2

Elongation of axial bonds [$\Delta l = l(C{-}H_{ax}) - l(C{-}H_{eq})$], Mulliken atomic charge differences ($\Delta q = q_{Heq} - q_{Hax}$), dihedral angles H_{eq}–C–N–S (θ), planarity of the nitrogen atom (sum of the bond angles, ΣN) in conformers **4a** and **4b** and transition state [**4-TS**]$^{\neq}$

Molecule	Position	Δl, Å	$\Delta q \times 10^3$	θ, deg	ΣN, deg
4a	2-CH$_2$	0.016	46	18.2	354.1
	4,6-CH$_2$	0.012	40		
4b	2-CH$_2$	0.017	49	26.5	349.0
	4,6-CH$_2$	0.012	40		

with the experimental 3.9 ppm upfield shift of the ^{19}F NMR signal of the minor conformer **4b** with respect to **4a** (Fig. 1b).

Some calculated geometrical parameters and atomic charges for both conformers **4a** and **4b** are given in Table 2. The sum of the bond angles at nitrogen (ΣN) deviates from 360° by 6° and 11° for **4a** and **4b**, respectively, which is notably larger than the deviations from planarity in molecules **1**–**3**, where they were insignificant.[9,10] The axial C–H bonds are by 0.014±0.002 Å longer than the corresponding equatorial C–H bonds mainly due to $n_O \rightarrow \sigma^*(C{-}H_{ax})$, vide infra, which is proved by larger Δl values for OCH$_2$O than for NCH$_2$O groups.

2.5. Perlin effect

Unlike the previously studied compounds **1**–**3**, all the CH$_2$ groups in molecule **4** show the normal Perlin effect.[16,17] Detailed analysis of the normal and the reverse Perlin effects was given previously[3b,9,18] The normal Perlin effect ($J_{CHax} < J_{CHeq}$) is usually ascribed to weakening of the C–H$_{ax}$ bond adjacent to a heteroatom X due to hyperconjugation $n_x \rightarrow \sigma^*(C{-}H_{ax})$. Experimental evidence was found for this interaction by varying the proton-donating ability of the solvent.[19] However, the same authors noted that for some X the $\sigma(C{-}X) \rightarrow \sigma^*(C{-}H_{eq})$ and $\sigma^*(C{-}X) \rightarrow \sigma(C{-}H_{eq})$ orbital interactions in the –C–X–C–H fragment may outweigh the lone pair effect $n_x \rightarrow \sigma^*(C{-}H_{ax})$. The experimental and calculated values of the Perlin effect presented in Table 1 prove that the presence of oxygen atom in the α-position to a CH$_2$ group in the ring decreases J_{CHax} with respect to J_{CHeq}, whereas the NSO$_2$CF$_3$ group has the opposite effect. This results in the reverse Perlin effect when the CH$_2$ group is between the two NSO$_2$CF$_3$ groups, like in compounds **1**–**3**,[9,10] or leads to attenuation of the normal Perlin effect of the NCH$_2$O group with respect to the OCH$_2$O group, as can be seen in Table 1. Note that for all methylene groups in molecule **4**, the equatorial hydrogens are more positively charged (Table 2), similar to what was observed for molecules **1**–**3**.[8–10] That means that the charge on the atom does not correlate with the sign of the Perlin effect, as we noticed previously.[9]

2.6. NBO analysis

To quantitatively assess the relative contribution of different interactions involving the C–H$_{ax}$ and C–H$_{eq}$ bonds we employed NBO analysis,[20] as implemented into the Gaussian03 package.[21] The results presented in Table 3 are not much different for the major **4a** and the minor **4b** conformers, so, the discussion will be focused on the former. For the NC–H$_{eq}$ bond in **4a** the resultant interaction {[σ(C–H)→all σ^*-orbitals]−[all σ-orbitals→σ^*(C–H)]} amounts to 1.0 kcal/mol, whereas the same value for the NC–H$_{ax}$ bond is 6.2 kcal/mol. Therefore, the energetic equivalent of the normal Perlin effect for the NCH$_2$ group is 5.2 kcal/mol. For the OCH$_2$O group in **4a**, the same analysis gives the resultant interactions of 0.5 and 10.0 kcal/mol for the C–H$_{eq}$ and C–H$_{ax}$ bonds, respectively, giving rise to the energetic equivalent of the normal Perlin effect for the OCH$_2$O group of 9.5 kcal/mol. This is in excellent agreement with much larger values of the normal Perlin effect for the OCH$_2$O group than that for the NCH$_2$ group in conformer **4a**, both experimental and calculated; the same conclusions can be drawn from the NBO analysis of the **4b** conformer (Table 1).

Table 3

Second order perturbation energies (kcal mol^{-1}) for orbital interactions of the C–H bonds in conformers **4a** and **4b** of 5-trifluoromethylsulfonyl-1,3,5-dioxaazinane from NBO calculations

4a		**4b**	
$\sigma(NC{-}H_{ax}) \rightarrow \sigma^*(N{-}S)$	4.11	$\sigma(NC{-}H_{ax}) \rightarrow \sigma^*(N{-}S)$	4.31
$\sigma^*(N{-}S) \rightarrow \sigma(NC{-}H_{ax})$	0.66	$\sigma^*(N{-}S) \rightarrow \sigma(NC{-}H_{ax})$	0.74
$n(N) \rightarrow \sigma^*(NC{-}H_{ax})$	3.17	$n(N) \rightarrow \sigma^*(NC{-}H_{ax})$	2.74
$n_1(O) \rightarrow \sigma^*(NC{-}H_{ax})$	1.19	$n_1(O) \rightarrow \sigma^*(NC{-}H_{ax})$	1.24
$n_2(O) \rightarrow \sigma^*(NC{-}H_{ax})$	5.26	$n_2(O) \rightarrow \sigma^*(NC{-}H_{ax})$	5.34
$\sigma(NC{-}H_{eq}) \rightarrow \sigma^*(C{-}N)$	3.44	$\sigma(NC{-}H_{eq}) \rightarrow \sigma^*(C{-}N)$	3.38
$\sigma(NC{-}H_{eq}) \rightarrow \sigma^*(C{-}O)$	2.89	$\sigma(NC{-}H_{eq}) \rightarrow \sigma^*(C{-}O)$	2.97
$\sigma(N{-}C) \rightarrow \sigma^*(NC{-}H_{eq})$	0.88	$\sigma(N{-}C) \rightarrow \sigma^*(NC{-}H_{eq})$	0.93
$\sigma(C{-}O) \rightarrow \sigma^*(NC{-}H_{eq})$	1.04	$\sigma(C{-}O) \rightarrow \sigma^*(NC{-}H_{eq})$	1.01
$n_1(O) \rightarrow \sigma^*(NC{-}H_{eq})$	2.46	$n_1(O) \rightarrow \sigma^*(NC{-}H_{eq})$	2.51
$\sigma^*(N{-}S) \rightarrow \sigma(NC{-}H_{eq})$	0.92	$\sigma^*(N{-}S) \rightarrow \sigma(NC{-}H_{eq})$	0.92
$\sigma(OC{-}H_{ax}) \rightarrow 2\sigma^*(C{-}O)$	1.10	$\sigma(OC{-}H_{ax}) \rightarrow 2\sigma^*(C{-}O)$	1.10
$n_1(O) \rightarrow 2\sigma^*(OC{-}H_{ax})$	2.50	$n_1(O) \rightarrow 2\sigma^*(OC{-}H_{ax})$	2.54
$n_2(O) \rightarrow 2\sigma^*(OC{-}H_{ax})$	9.56	$n_2(O) \rightarrow 2\sigma^*(OC{-}H_{ax})$	9.64
$2\sigma(C{-}O) \rightarrow \sigma^*(OC{-}H_{eq})$	1.62	$2\sigma(C{-}O) \rightarrow \sigma^*(OC{-}H_{eq})$	1.60
$\sigma(OC{-}H_{eq}) \rightarrow 2\sigma^*(C{-}O)$	6.36	$\sigma(OC{-}H_{eq}) \rightarrow 2\sigma^*(C{-}O)$	6.36
$n_1(O) \rightarrow 2\sigma^*(OC{-}H_{eq})$	5.26	$n_1(O) \rightarrow 2\sigma^*(OC{-}H_{eq})$	5.32

3. Conclusion

Both theoretical calculations and a variable temperature dynamic multinuclear NMR study of 5-trifluoromethylsulfonyl-1,3,5-dioxaazinane revealed the existence of two close in energy conformers with the CF$_3$ groups directed inward and outward with respect to the ring. Their interconversion proceeds via ring inversion and intermediate formation of 2,5-*twist*-conformer, the calculated barrier of 11.2 kcal/mol being in excellent agreement with the experimental value of 11.7 kcal/mol. The normal Perlin effect is observed for all CH$_2$ groups in both the conformers of 5-trifluoromethylsulfonyl-1,3,5-dioxaazinane **4**. The experimental and theoretical values of ΔJ_{CH} are much larger for the OCH$_2$O than for the NCH$_2$O methylene groups corroborated by evaluating the corresponding orbital interactions of the two C–H$_{ax}$/C–H$_{eq}$ bonds obtained from a parallel NBO analysis.

4. Experimental section

4.1. Synthesis

Compound **4** was synthesized as described in Ref. 13. To the mixture of 2.5 g (0.017 mol) of trifluoromethanesulfonamide and 4 g (0.134 mol) of paraformaldehyde in 35 mL of ethyl acetate, 12 mL of concd H$_2$SO$_4$ was added dropwise and vigorously stirred at room temperature for 6 h. The mixture was pored into ice water, extracted thrice with ethyl acetate, washed with aqueous NaHCO$_3$, and dried over MgSO$_4$. The solvent was removed and the residue distilled under vacuum to give 3.14 g of compound **4** as colorless liquid with bp 73–75 °C/3 mmHg. NMR spectra in CD$_3$CN at room temperature, δ, ppm: ^{1}H: 5.16s (2H, OCH$_2$O), 5.26s (4H, OCH$_2$N); ^{13}C: 78.95 (OCN), 95.28 (OCO); ^{19}F: −77.77 br s. Mass spectrum was taken using an HP-5890 capillary column Ultra-2 (5% phenyl methyl silicone) GC-system equipped with an HP 5971A mass detector; m/z (EIMS) 220 ([M−H]$^+$, 10%), 162 ([M−C$_2$H$_3$O$_2$]$^+$, 100%), 133 (CF$_3$SO$_2^+$, 7%), 69 (CF$_3^+$, 60%).

4.2. NMR measurements

Dynamic ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 100 (^{13}C), and 376 (^{19}F) MHz; ^{1}H 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 $CFCl_3$. Temperature was varied by the use of a BVT 3000 variable temperature unit, temperature stability ±0.2°.

4.3. Theoretical calculations

All calculations were performed using the Gaussian03 suite of programs.[20] Energy calculation with full optimization of all variables as well as calculation of vibrational frequencies were performed at the B3LYP/6-311+G(d,p) level of theory with the basis set augmented with polarization functions on heavy atoms. NMR computations of absolute shieldings and spin–spin coupling constants were performed using the GIAO method[22,23] at the same level of theory B3LYP/6-311+G(d,p).

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Supplementary data

Supplementary data include the energy and geometry of the conformers **4a** and **4b** at the B3LYP/6-311+G(d,p) level of theory; ^{13}C NMR spectrum of **4** in acetone-d_6 at 193 K; 2D{^{1}H–^{13}C} spectrum of **4** in acetone-d_6 at 193 K. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.03.019.

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