

N-Allyl and *N*-Propargyl Trifluoromethanesulfonimides. Theoretical Analysis

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Received May 10, 2017

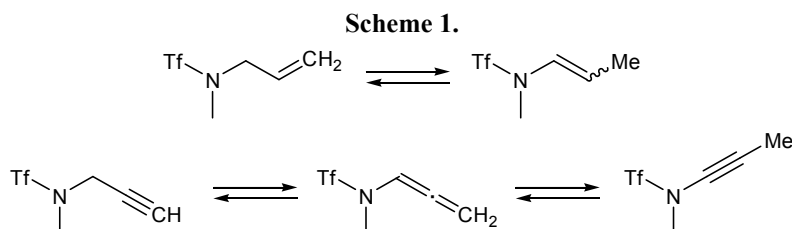
Abstract—Tautomers of *N*-allyl- and *N*-propargyl-substituted trifluoromethanesulfonimides (CF₃SO₂)₂NR (R = CH₂CH=CH₂, *Z/E*-CH=CHMe, CH₂C≡CH, CH=CH=CH₂, C≡CCH₂) were calculated by the DFT (B3LYP, wB97XD, PBE1PBE), MP2, and CBS-QB3 methods. The results were compared with the theoretical data for the corresponding amines and amides NHRR¹ (R¹ = H, CF₃SO₂). It was shown that there is no conjugation between the nitrogen atom and C=C bond and that conjugation exists with the C≡C bond with electron density displacement toward the nitrogen atom. The calculations of anions derived from *N*-allyl- and *N*-propargyl-trifluoromethanesulfonimides revealed the possibility of their rearrangement with elimination of trifluoromethanesulfonate anion and formation of its H-complex with *N*-(prop-2-en-1-ylidene)trifluoromethanesulfonamide or *N*-(prop-2-yn-1-ylidene)trifluoromethanesulfonamide.

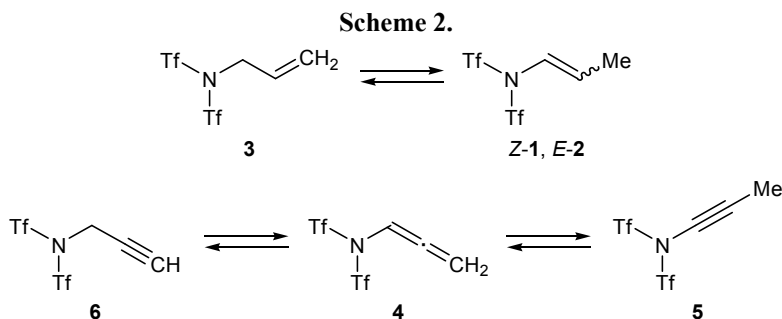
DOI: 10.1134/S1070428017100037

Chemical properties of unsaturated derivatives of trifluoromethanesulfonamide containing double, cumulated double, or triple carbon–carbon bonds were described previously [1–7]. If an unsaturated substituent consists of more than two carbon atoms, tautomerism related to the position of the multiple bond is possible (Scheme 1). In some cases, such tautomers were detected experimentally [5–7], and theoretical analysis of unsaturated derivatives of trifluoromethanesulfonamide was performed at the DFT and MP2 levels of theory [8].

Prototropic tautomerism of unsaturated heteroatom compounds plays an important role in organic chemistry. Theoretical studies of prototropic rearrangement in RCH₂CH=CH₂ systems (R = H, Me, NMe₂, OMe, PMe₂, SMe) accompanied by double bond migration were reported in [9, 10].

Theoretical analysis of unsaturated derivatives of trifluoromethanesulfonamide [8] led to the conclusion that conjugation effects in their molecules are of secondary importance since the basicity of the nitrogen atom is considerably reduced due to strong electron-withdrawing effect of the trifluoromethanesulfonyl group. It seemed reasonable to continue this analysis by passing to unsaturated derivatives of trifluoromethanesulfonimide Tf₂NH in which the basicity of the nitrogen atom is even lower due to the presence of two trifluoromethanesulfonyl groups. In this work we performed a theoretical study of *N*-allyl- and *N*-propargyl-substituted trifluoromethanesulfonimides Tf₂NR, anions derived therefrom, and possible tautomers, and the results were compared with the data for the corresponding primary amines N₂NR and trifluoromethanesulfonamide analogs TfNHR (R =





$\text{CH}_2\text{CH}=\text{CH}_2$, $Z/E-\text{CH}=\text{CHCH}_3$, $\text{CH}_2\text{C}\equiv\text{CH}$, $\text{CH}=\text{C}=\text{CH}_2$, $\text{C}\equiv\text{CCH}_2$.

The molecular structures were optimized, and their thermodynamic parameters were calculated, using DFT functionals B3LYP, wB97XD, and PBE1PBE (PBE0) and the Møller–Plesset perturbation theory with the 6-311G(*d,p*) basis set, as well as using the precision CBS-QB3 composite method. All calculations were performed using Gaussian 09 software package [11].

Table 1 contains the calculated differences in the total energies corrected for zero-point vibrations (ΔE) and free energies (ΔG) for tautomeric equilibria shown in Scheme 2. Some geometric parameters of the calculated molecules and charges on the nitrogen atom are given in Table 2. *N*-Substituted trifluoromethanesulfonimides lack NH group; therefore, they cannot isomerize to imines which, as shown previously for trifluoromethanesulfonamide analogs [8], are most stable isomerization products.

***N*-Allyltrifluoromethanesulfonimide.** 1,3-Proton migration in *N*-allyltrifluoromethanesulfonimide (**3**) by the action of a base could lead to the formation of

Z and *E* isomers of *N*-(prop-1-en-1-yl)trifluoromethanesulfonimide, *Z*-**1** and *E*-**2**, respectively. The exothermic effect of this isomerization varies from ~ 2.1 (CBS-QB3) to 4.3 kcal/mol (B3LYP). The B3LYP and PBE1PBE calculations showed insignificant preference of *E*-**2** ($\Delta\Delta G = -0.65$ and -0.12 kcal/mol, respectively), whereas the wB97XD functional including the empirical dispersion correction, as well as more precise MP2 and CBS-QB3 methods, predict higher stability of *Z*-**1** with a $\Delta\Delta G$ value of 0.38 (CBS-QB3) to 0.88 kcal/mol (wB97XD).

The sum of the bond angles at the nitrogen atom in molecule **3** is close to 180° , and molecules *Z*-**1** and *E*-**2** are even flatter (Table 2), indicating sp^2 -hybridization of the nitrogen atom therein. In going from *N*-allyl derivative **3** to *N*-vinyl derivatives **1** and **2**, the C–N bond shortens by ~ 0.07 Å, which, however, is the result of reduction of the covalent radius of C_{sp^2} compared to C_{sp^3} rather than of possible conjugation between the nitrogen atom and double bond. There is no such conjugation in molecules **1** and **2**, as follows from almost orthogonal orientation of the nitrogen *p*-orbital and π -bond plane therein in contrast to the amino

Table 1. Differences in the total energies corrected for zero-point vibrations (ΔE , kcal/mol) and free energies (ΔG , kcal/mol) of isomeric trifluoromethanesulfonimides **1–6** and amines **7–9**, calculated by different methods

Compound	B3LYP/ 6-311G(d,p)		wB97XD/ 6-311G(d,p)		PBE1PBE/ 6-311G(d,p)		MP2/ 6-311G(d,p)		CBS-QB3	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$\text{Tf}_2\text{N}-\text{CH}=\text{CH}-\text{CH}_3$ (<i>Z</i> - 1)	0.43	0.65	0	0	0.09	0.12	0	0	0	0
$\text{Tf}_2\text{N}-\text{CH}=\text{CH}-\text{CH}_3$ (<i>E</i> - 2)	0	0	0.66	0.88	0	0	0.51	0.58	0.52	0.38
$\text{Tf}_2\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ (3)	4.28	4.89	4.04	4.14	4.27	4.79	3.48	4.37	2.65	2.95
$\text{Tf}_2\text{N}-\text{CH}=\text{C}=\text{CH}_2$ (4)	0	0	0	0	0	0	1.54	2.27	0	0
$\text{Tf}_2\text{N}-\text{C}\equiv\text{C}-\text{CH}_3$ (5)	3.37	2.27	4.67	4.80	3.59	2.88	0.60	0	4.65	3.41
$\text{Tf}_2\text{N}-\text{CH}_2-\text{C}\equiv\text{CH}$ (6)	6.51	6.98	4.73	4.02	6.36	6.87	0	1.36	1.92	2.38
$\text{H}_2\text{N}-\text{CH}=\text{CH}-\text{CH}_3$ (<i>Z</i> - 7)	0.14	0	0	0.28	0	0	0	0.46	0	0
$\text{H}_2\text{N}-\text{CH}=\text{CH}-\text{CH}_3$ (<i>E</i> - 8)	0	0.23	0.03	0	0.01	0.4	0.03	0	0.24	0.61
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ (9)	8.44	8.56	8.08	7.94	8.93	9.21	7.01	7.37	6.69	6.96

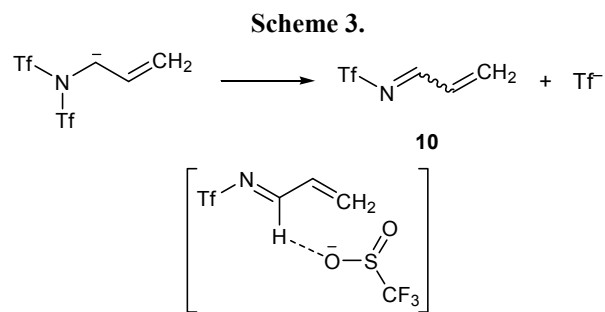
Table 2. Mulliken charges on the nitrogen atom (q_N), sums of bond angles at the nitrogen atom [$\Sigma(N) = S^1NC + S^2NC + S^1NS^2$], and C–N bond lengths in isomeric trifluoromethanesulfonimides **1–6** and amines **7–9**, calculated by different methods

Compound	B3LYP/6-311G(d,p)			MP2/6-311G(d,p)		
	q_N , a.u.	$\Sigma(N)$, deg	C–N, Å	q_N , a.u.	$\Sigma(N)$, deg	C–N, Å
Tf ₂ N–CH=CH–CH ₃ (Z-1)	–0.758	359.9	1.445	–0.911	359.7	1.441
Tf ₂ N–CH=CH–CH ₃ (E-2)	–0.742	359.8	1.444	–0.889	359.7	1.440
Tf ₂ N–CH ₂ –CH=CH ₂ (3)	–0.744	356.9	1.514	–0.909	355.2	1.501
Tf ₂ N–CH=C=CH ₂ (4)	–0.732	359.1	1.447	–0.876	358.8	1.443
Tf ₂ N–C≡C–CH ₃ (5)	–0.944	359.1	1.353	–1.165	359.0	1.362
Tf ₂ N–CH ₂ –C≡CH (6)	–0.737	356.4	1.504	–0.894	354.0	1.493
H ₂ N–CH=CH–CH ₃ (Z-7)	–0.428	341.8	1.40	–0.485	336.9	1.402
H ₂ N–CH=CH–CH ₃ (E-8)	–0.423	339.8	1.40	–0.467	334.7	1.405
H ₂ N–CH ₂ –CH=CH ₂ (9)	–0.461	327.1	1.47	–0.495	324.3	1.469

analogs, isomeric prop-1-en-1-amines **7** and **8** (Table 1), where the lone electron pair on the nitrogen atom is collinear to the π -bond plane. This difference is also confirmed by the decrease in energy in going from allyl derivatives to vinyl, which is almost twice as large for unsaturated amines **7–9** as for trifluoromethanesulfonimide derivatives **1–3**. Analysis of the charge distribution (calculated at the MP2 level of theory; charges on heavy atoms were summed with those on the hydrogen atoms attached thereto) confirms the fundamental difference in the electronic structure of alkenylamines **7–9** and *N*-alkenyltrifluoromethanesulfonimides **1–3**. The total charge on the R substituent in *Z* and *E* isomers **7** and **8** is 0.085 and 0.071 *e*, respectively, and the double bond polarization toward the β -carbon atom, $\Delta = q(C_\alpha) - q(C_\beta) = 0.358$ and 0.334 *e*. In contrast, the charge on the R substituent in **Z-1** and **E-2** is much higher (0.446 and 0.420 *e*, respectively), all carbon atoms are charged positively, and the double bond is less polarized ($\Delta = 0.110$ and 0.028 *e*, respectively). Thus, there is no conjugation between the imide nitrogen atom and the double bond, and the structure of **Z-1** and **E-2** is determined by the strong electron-withdrawing inductive effect of the Tf₂N group.

Taking into account that the isomerization is initiated by deprotonation by the action of a base, we made an attempt to calculate the [Tf₂N–CH–CH=CH₂][–] anion and estimate the possibility of stabilization of the negative charge on the α -carbon atom by the electron-withdrawing Tf₂N group. However, geometry optimization by all used computational methods (DFT, MP2, CBS-QB3) led to the same result, i.e., elimination of CF₃SO₂[–] (Tf[–]) anion with formation of *N*-(prop-2-

en-1-ylidene)trifluoromethanesulfonamide (**10**) as an H-complex with trifluoromethanesulfinate anion (Scheme 3).



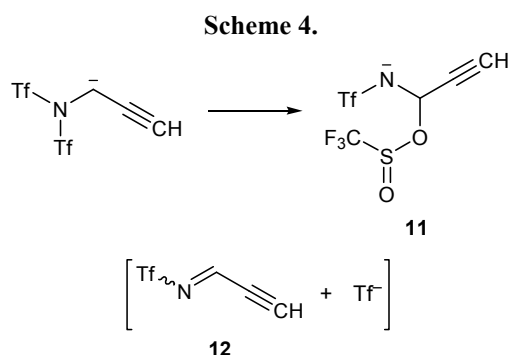
***N*-Propargyltrifluoromethanesulfonimide.** As shown previously for *N*-propargyltrifluoromethanesulfonamide, *N*-allenyltrifluoromethanesulfonamide is the most stable among the NH isomers [8]. All computational methods, except MP2, also predict allenyl isomer **4** to be the most stable among those possible, allenyl (**4**), prop-1-yn-1-yl (**5**), and prop-2-yn-1-yl (**6**) (Table 1). According to the MP2 calculations, the energy differences between the isomers are the smallest among those calculated by the other methods; propargyl isomer **6** is characterized by the lowest total energy, and the most stable (with respect to the free energy) is propynyl isomer **5**. Similar inconsistency between the ΔE and ΔG values calculated by the MP2 method was noted by us previously [8]. Like all DFT method, the most precise CBS-QB3 composite method predicts the highest stability for allenyl isomer **4**; however, the DFT and CBS-QB3 methods gave opposite results for the relative stabilities of isomers **5** and **6**. As in molecules **1–3**, the nitrogen atom in **4–6** has almost planar environment, and the C–N bond

length monotonically decreases in the series $6 > 4 > 5$, i.e., in going from sp^3 - to sp^2 - and then to sp -hybridized carbon atom. To answer the question whether this is the result of reduction of the covalent radius of the carbon atom or there is a contribution of conjugation with the multiple bond in molecules **4** and **5**, we have analyzed their structures. The N–C–H and S–N–S planes in allenyl isomer **4** are almost orthogonal to each other. Therefore, the p orbital of the nitrogen atom is orthogonal to the π -bond plane, and there is no conjugation in molecule **4**. By contrast, at any position of the nitrogen p -orbital, its overlap with one or both π -bonds of the C \equiv C fragment in propargyl isomer **5** will be nonzero. This is the reason why the C–N bond shortens by ~ 0.06 Å in going from compound **6** to isomer **4**, i.e., from sp^3 - to sp^2 -hybridized carbon atom, while in going from isomer **4** to **5** (from sp^2 - to sp -hybridized carbon atom) the C–N bond becomes shorter by ~ 0.08 – 0.09 Å (Table 2). In the latter case, there is some contribution of the conjugation between the p -orbital on the nitrogen atom and π -system of the triple bond.

Analysis of the charge distribution in molecules **4**–**6** (as above, according to the MP2 calculations; charges on non-hydrogen atoms were summed with those on the hydrogen atoms attached thereto) indicated unexpected polarization of bonds as a result of conjugation. The total electron density transfer from the alkynyl group to the trifluoromethanesulfonimide fragment in molecules **4** and **6** amounts to 0.386 and 0.375 e , respectively, whereas in molecule **5** it is much higher (0.642 e), and almost all additional negative charge in molecule **5** is localized on the nitrogen atom whose total charge is -0.876 , -0.894 , and -1.165 e in molecules **4**, **6**, and **5**, respectively. These findings, as well as the strong polarization of the triple bond in **5** toward the nitrogen atom [$\Delta = q(C_\beta) - q(C_\alpha) = 0.203e$], indicate electron density transfer from the triple bond to the nitrogen p -orbital. Such polarization is opposite to the classical conjugation between an amino group and multiple bond, where the amino group acts as electron donor. This is the result of strong electron-withdrawing effect of two CF₃SO₂ groups, which makes the p orbital on the nitrogen atom virtually vacant.

An attempt to calculate propargyl anion [Tf₂NCH–C \equiv CH][–] by analogy with the allenyl anion (see above) also led to its rearrangement during the geometry optimization. According to the B3LYP calculation, the rearrangement products were *N*-(prop-2-yn-1-ylidene)trifluoromethanesulfonamide (**12**) and

trifluoromethanesulfinate ion, whereas wB97XD, PBE1PBE, MP2, and CBS-QB3 methods, unlike the rearrangement shown in Scheme 3, predict formation of nitrogen-centered anion **11** rather than isomeric H-complex of imine **12** (Scheme 4). Presumably, the reason is more efficient conjugation between the double bonds in azadiene **10** than between the double and triple bonds in **12**.



Thus, theoretical analysis of the spatial and electronic structures of *N*-allyl- and *N*-propargyltrifluoromethanesulfonimides and their possible tautomers showed the lack of conjugation between the imide nitrogen atom and C=C double bond. Analogous conjugation with the C \equiv C triple bond is possible, but, unlike ynamines, it involves electron density transfer from the triple bond to the nitrogen atom whose p orbital is virtually vacant due to strong electron-withdrawing effect of two trifluoromethanesulfonyl groups on the nitrogen atom. The calculations of anions derived from *N*-allyl- and *N*-propargyltrifluoromethanesulfonimides predict the possibility of their rearrangement with elimination of trifluoromethanesulfinate ion which either adds to the α -carbon atom or forms H-complex with *N*-(prop-2-en-1-ylidene)trifluoromethanesulfonamide anion **10** or *N*-(prop-2-yn-1-ylidene)trifluoromethanesulfonamide (**12**).

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 17-03-00213).

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