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Trifluoromethanesulfonic Anhydride Induced Cleavage of a Bis(iminomethane) Compound: A New Access to a 1,3-Diaryl-2-azaallenium Triflate and a *N*-((Trifluoromethyl)sulfonyl)methanimine. Synthesis, Structures, and Quantum Chemical Calculations[†]

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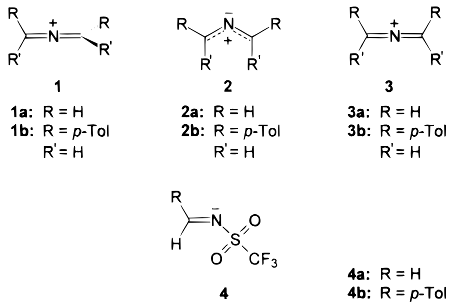
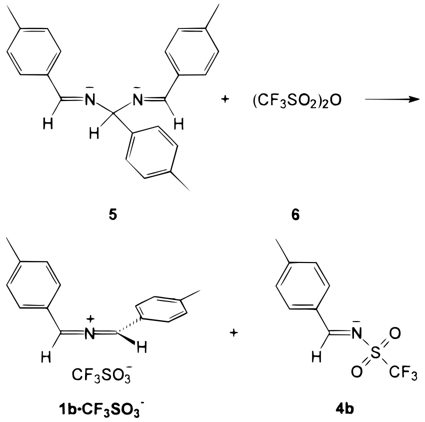
The term 2-azapropenylium ion combines two valence isomeric classes of reactive intermediates: (a) the linear-orthogonal 2-azaallenium ions (2-azoniaallene ions) (**1**) (Chart 1) and (b) the bent-planar 2-azaallylium ions (**2**).[3] A third possible linear-planar structure (**3**) may also be considered. The preferred structural type of the cation depends very sensitively on the respective substitution pattern. Thus, electron donor groups favor the geometry **2**, whereas aliphatic substituents and aryl groups seem to shift the valence isomeric equilibrium toward the side of the 2-azaallenium geometry **1**.[4] Due to their interesting structural and reactive properties both classes of compounds have been subject of intense experimental, spectroscopic, and theoretical investigations.[4−19]

In this paper we report a new preparative route to aryl-substituted derivatives of **1**. Furthermore we give complete structural information about the products obtained, based on X-ray, IR, and NMR data. These results are discussed in comparison with high level *ab initio* and DFT (density functional theory) calculations, also including chemical shift calculations with special emphasis on the valence isomerism 2-azaallenium ion (**1**)−2-azaallylium ion (**2**) of 1,3-diaryl derivatives. Furthermore, we describe the synthesis and the structure of a *N*-sulfonylimine (**4**), which is produced along with **1**.

Chart 1



Scheme 1



Several routes for the synthesis of 2-azapropenylium salts have been disclosed.[4−19] In contrast to the less reactive 2-azaallylium salts $\mathbf{2{\cdot}X^-}$, which may be isolated as chlorides or iodides, e.g., due to their higher reactivity the 2-azaallenium salts $\mathbf{1{\cdot}X^-}$ require nonnucleophilic counterions for their isolation. In the past, mainly hexachloroantimonates have been used, although the oxidative (chlorinating) properties make this counterion not best suited for synthetic purposes. In this paper we report the first preparation of a 2-azapropenylium trifluoromethanesulfonate ($\mathbf{1b{\cdot}CF_3SO_3^-}$) (triflate). Triflates such as $\mathbf{1b{\cdot}CF_3SO_3^-}$ are expected to have significant preparative advantages over the usually employed hexachloroantimonates. Indeed, preliminary results indicate the possibility of reacting even sensitive nucleophiles (e.g., alkenes) with the triflate $\mathbf{1b{\cdot}CF_3SO_3^-}$ without side reactions.[1,2]

The salt $\mathbf{1b{\cdot}CF_3SO_3^-}$ is produced (53%) together with *N*-((trifluoromethyl)sulfonyl)methanimine **4b** (16%) by cleavage of the bis(iminomethane) derivative (2,4-diazapentadiene-1,4) **5** with trifluoromethanesulfonic anhydride (**6**) (triflic anhydride) (Scheme 1). We assume initial electrophilic attack of the anhydride on one of the two nitrogen atoms of **5**. The adduct fragments immediately into $\mathbf{1b{\cdot}CF_3SO_3^-}$ and **4b**. Earlier we reported cleavage of bis(iminomethane) compounds with acylium salts.[7]

Simple addition of triflic anhydride (**6**) at low temperature to a solution of **5** in chlorinated hydrocarbons delivers the salt $\mathbf{1b{\cdot}CF_3SO_3^-}$ as a colorless precipitate, which can be purified by recrystallization. For the very moisture sensitive salt a correct combustion analysis

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[†] Dedicated to Professor J. C. Jochims of the University of Konstanz, Germany, on the occasion of his 65th birthday.

[§] X-ray diffraction crystal structure determinations.

(1) Böttger, G. Taken in part from the planned Ph.D. Thesis, University of Münster, 1997.

(2) (a) Geisler, A. Taken in part from Ph.D. Thesis, University of Münster, 1996. (b) Geisler, A.; Würthwein, E.-U. *Tetrahedron Lett.* **1994**, *35*, 77−80.

(3) Würthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2971−2978.

(4) Samuel, B.; Wade, K. *J. Chem. Soc. A* **1969**, 1742−1745.

(5) Barton, D. H. R.; Bracho, R. D.; Gunatilaka, A. A. L.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 579−588.

(6) Reetz, M. T.; Stephan, W.; Maier, W. F. *Synth. Commun.* **1980**, *10*, 867−871.

(7) Würthwein, E.-U. *Angew. Chem.* **1981**, *93*, 110−111; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 99−100.

(8) Al-Talib, M.; Jochims, J. C. *Chem. Ber.* **1984**, *117*, 3222−3230.

(9) Al-Talib, M.; Jibril, I.; Würthwein, E.-U.; Jochims, J. C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3365−3373.

(10) Würthwein, E.-U.; Kupfer, R.; Budzelaar, P. H. M.; Strobel, C.; Beck, H. P. *Angew. Chem.* **1985**, *97*, 327−328; *Angew. Chem., Int. Ed. Engl.* **1985**, *25*, 340−341.

(11) Müller, E.; Jochims, J. C. *Synthesis* **1986**, 465−468.

(12) Hamed, A.; Müller, E.; Jochims, J. C. *Tetrahedron* **1986**, *42*, 6645−6656.

(13) Frey, H.; Mehlhorn, A.; Rühlmann, K. *Tetrahedron* **1987**, *43*, 2945−2954.

(14) Weidner, R.; Würthwein, E.-U. *Chem. Ber.* **1989**, *122*, 1095−1106.

(15) Abu-El-Halawa, R.; Jochims, J. C. *Synthesis* **1992**, 871−874.

(16) (a) Kupfer, R.; Würthwein, E.-U. *Tetrahedron. Lett.* **1985**, *26*, 3547−3550. (b) Kupfer, R.; Meier, S.; Würthwein, E.-U. *Chem. Ber.* **1992**, *125*, 2487−2492 and references therein.

(17) Gold, H. *Angew. Chem.* **1960**, *72*, 956−959.

(18) Jochims, J. C.; Abu-El-Halawa, R.; Jibril, I.; Huttner, G. *Chem. Ber.* **1984**, *117*, 1900−1912.

(19) Liebscher, J. *Synthesis* **1988**, 655−669.

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Table 1. Geometrical Parameters for 1,3-Di-*p*-tolyl-2-azaallenium Trifluormethanesulfonate ($1b{\cdot}CF_3SO_3^-$) as Obtained by X-ray Crystallography. For Comparison, *ab Initio* Data for the Cations 1b and 2b and for the Transition State TS (See Figure 3) Are Included[a]

	$1b{\cdot}CF_3SO_3^-$	1b		2b		TS	
	X-ray	RHF/6-31G*	B3LYP/6-31G*	RHF/6-31G*	B3LYP/6-31G*	RHF/6-31G*	B3LYP/6-31G*
N−C1	1.258(2)	1.252	1.270	1.314	1.329	1.288	1.313
N−C2	1.257(2)	1.252	1.270	1.314	1.329	1.288	1.313
C2−N−C1	172.2(2)	176.82	175.81	116.54	116.62	133.93	127.66
N−C1−C11	123.7(2)	126.23	126.48	123.66	123.19	124.39	123.73
N−C2−C21	124.7(2)	126.23	126.48	123.66	123.19	124.39	123.73
C1−N−C2−C21	145.96(1.2)	−135.09	−134.89	180.00	180.00	−150.99	−156.92
C2−N−C1−C11	−55.0(1.3)	−135.09	−134.89	180.00	180.00	−151.00	−156.92
N−C1−C11−C16	175.1(0.2)	179.85	−179.44	180.00	180.00	−178.12	−179.53
N−C2−C21−C26	174.3(0.2)	0.0	0.78	180.00	180.00	−178.12	179.53

[a] Bond lengths are given in angstroms, bond angles and torsional angles in degrees.

could not be obtained. Compound $\mathbf{1b{\cdot}CF_3SO_3^-}$ may be stored at low temperature under an inert atmosphere. The sulfonylimine **4b**, isolated from the mother liquor of the crystallization of $\mathbf{1b{\cdot}CF_3SO_3^-}$, also proved to be moisture sensitive. Only a few examples of such highly electron deficient imines are known.[20−22] Yagupolskii and Taft et al. have argued that the $=NSO_2CF_3$ unit is more electron withdrawing than a =O unit in organic and inorganic acids, thus leading to the prediction of new superacids which are much stronger than any known acids.[21,23]

X-ray Diffraction Studies

The structures of both compounds $\mathbf{1b{\cdot}CF_3SO_3^-}$ and **4b** were solved by X-ray diffraction analysis.[24] Only two X-ray studies of 2-azaallenium salts without hetero substituents have previously been reported, a fluorenone derivative[9] and the aliphatically substituted bis(2-adamantylidene)ammonium hexachloroantimonate.[10] Both of these tetrasubstituted salts are relatively stable and are not characteristic of the less substituted derivatives of synthetic interest.

The triflate $\mathbf{1b{\cdot}CF_3SO_3^-}$ crystallizes in a monoclinic lattice with four ion pairs per unit cell (space group $P2_1/c$).[24a] Figure 1 shows an almost ideal 2-azaallenium structure (**1**) (approximately C_2 symmetry of the cation). Table 1 summarizes the observed and calculated geometrical parameters (vide infra). The C=N bonds are found to be very short (1.257(2) Å, 1.258(2) Å), compared to literature data for iminium C=N bonds (1.279 Å,[25] 1.30 Å[26]). This observation is in line with the sp hybridization of the central nitrogen atom, inducing short bonds to the adjacent carbon atoms. The deviation of the central C−N−C bond angle (172.2(2)°) from 180° is partially due to the reduced symmetry of the ion (C_2 instead of D_{2d}). It indicates also a rather flexible arrangement around nitrogen allowing perceptible deviations from linearity. Both carbon atoms C1 and C2 are sp^2 hybridized (sum of angles: 359.9°/360.1°). The two planes stretched out by these two carbon atoms and their neighbors intersect with an interplanar angle of 94.9(0)°. Both aromatic substituents seem to conjugate significantly with the respective C=N bonds as it is concluded from the dihedral angles C26−C21−C2−N (−174.3(2)°) and C16−C11−C1−N (175.1(2)°). Some weak interactions between cations and anions in the solid state are indicated by the distances H1−O1, 2.45 Å; H2−O3. 2.54 Å; and H2'−O2, 2.37 Å.

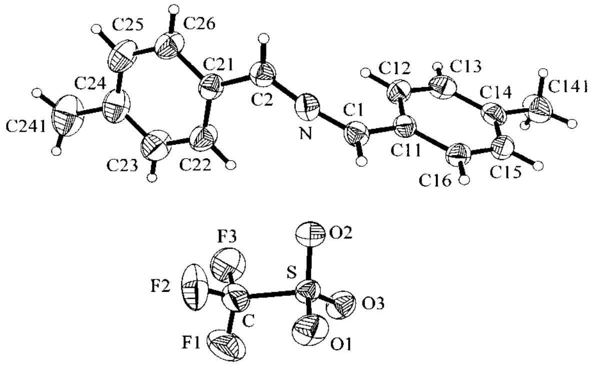

Figure 1. Molecular structure of 1,3-di-*p*-tolyl-2-azaallenium trifluormethanesulfonate ($\mathbf{1b{\cdot}CF_3SO_3^-}$) as obtained by X-ray crystallography. For geometrical parameters, see Table 1.

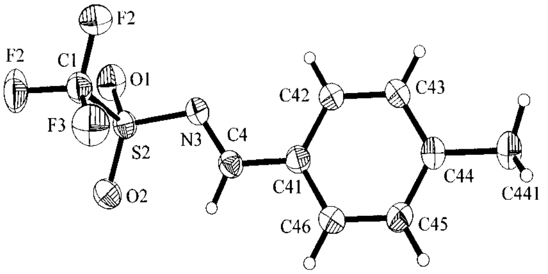

Figure 2. Molecular structure of *N*-((trifluormethyl)sulfonyl)-*p*-tolylmethanimine (**4b**), as obtained by X-ray crystallography. For geometrical parameters, see Table 2.

The *N*-sulfonylimine **4b** crystallizes in a triclinic lattice with two molecules per unit cell (space group $P\bar{1}$) (Figure 2, Table 2).[24b] Figure 2 shows the C=N bond laying in the plane with the aromatic system and having the CF_3 group perpendicular to the aromatic moiety. In spite of the strongly electron withdrawing sulfonyl group, the C=N bond length (1.291(3) Å) is close to the standard value (1.279 Å[25]) observed for simple imines. However,

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(20) (a) Behrend, E.; Haas, A. *Chem. Ztg.* **1971**, *95*, 1009−1010. (b) Behrend, E.; Haas, A. *J. Fluorine Chem.* **1974**, *4*, 83−98.

(21) Yagupolskii, L. M.; Popov, V. I.; Pavlenko, N. V.; Maletina, I. I.; Mironova, A. A.; Gavrilova, R. Yu.; Orda, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1986**, *22*, 1947−1950.

(22) (a) Zhu, S.-Z; Chen, Q.-Y. *J. Chem. Soc., Chem. Commun.* **1991**, *10*, 732−733. (b) Zhu, S. Z.; Li, A.-W.; Zhu, Y.-H.; Dai, J.-N.; Ming, X.-M.; Yuan, X.-W. *J. Fluorine Chem.* **1993**, *60*, 283−288.

(23) Burk, P.; Koppel, I. A.; Koppel, I.; Yagupolskii, L. M.; Taft, R. W. *J. Comput. Chem.* **1996**, *17*, 30−41.

(24) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U.K. (a) Compound $\mathbf{1b{\cdot}CF_3SO_3^-}$, CSD-405674. (b) Compound **4b**, CSD-405675.

(25) International Tables of Crystallography, Vol. C, IUCR, 1995.

(26) Trefonas, L. M.; Flurry, R. L., Jr.; Majeste, R.; Meyers, E. A.; Copeland, R. F. *J. Am. Chem. Soc.* **1966**, *88*, 2145−2149.

Table 2. Geometrical Parameters for *N*-((Trifluormethyl)sulfonyl)-*p*-tolylmethanimine (4b) as Obtained by X-ray Crystallography. For Comparison, *ab Initio* Data (See Figure 4) Are Included[a]

	X-ray	RHF/6-31G*	B3LYP/6-31G*
N3−C4	1.291(3)	1.272	1.292
N3−S2	1.633(2)	1.640	1.699
S2−O 1	1.423(2)	1.421	1.467
S2−O2	1.427(2)	1.429	1.459
S2−C1	1.835(2)	1.820	1.873
C1−F1	1.323(2)	1.308	1.333
C1−F2	1.316(2)	1.306	1.336
C1−F3	1.328(2)	1.311	1.331
N3−C4−C41	122.1(2)	122.41	122.23
C4−N3−S2	116.9(14)	117.63	115.21
N3−S2−O1	108.78(9)	109.44	108.36
N3−S2−O2	114.73(9)	112.22	112.94
N3−S2−C1	100.06(9)	99.40	98.10
N3−C1−F1	108.3(2)	108.42	108.08
N3−C1−F2	111.39(14)	110.71	110.45
N3−C1−F3	111.00(14)	110.00	109.72
N3−S2−C1−F1	176.5(0.1)	−179.50	−179.38
N3−S2−C1−F2	56.9(0.2)	60.52	60.68
N3−S2−C1−F3	−64.3(0.2)	−60.19	−60.09
N3−C4−C41−C42	−6.7(0.3)	−1.27	−1.44
S2−N3−C4−C41	−179.0(0.1)	179.07	178.21
C4−N3−S2−C1	106.5(0.2)	120.65	123.85
C4−N3−S2−O1	−146.6(0.2)	−127.86	−124.98
C4−N3−S2−O2	−5.5(0.2)	8.82	12.12

[a] Bond lengths are given in angstroms, bond angles and torsional angles in degrees.

the N−S bond is short (1.633(2) Å), as compared to published data (1.656 Å).[25]

Quantumchemical Calculations

The unusual structural and dynamic properties of the system **1**, **2** observed experimentally have additionally been investigated by high-level *ab initio* and DFT (density functional theory) calculations. To study the 2-azaallylium−2-azaallenium equilibrium in the gas phase and to evaluate the influence of aryl substituents on energies and structures, we present theoretical data for the cations **1a,b** and **2a,b**.

At first, we resumed our earlier *ab initio* calculations[3] on the singlet structures of the experimentally unknown[27] parent $C_2H_4N^+$ systems **1a**, **2a**, and **3a** at higher levels of theory, now using the RHF/6-31+G* basis set of the GAUSSIAN 94 system of programs[28] for geometry optimizations. Effects of correlation were estimated using second- to fourth-order Møller−Plesset theory (MP2−MP4). The character of the stationary points was determined by frequency calculations. Furthermore, we employed the DFT method using the B3LYP/6-31+G* combination as implemented in GAUSSIAN 94. The results of these calculations are summarized in Table 3.

All methods agree in predicting the allene form **1a** to be the most stable isomer. According to the frequency calculations, the bent 2-azaallylium isomer **2a** corresponds to the transition state of the 2-azaallenium automerization reaction by simultaneous bond rotation and bending at nitrogen. This form is considerably higher in energy (ca. 41 kcal/mol) and is therefore expected to be unimportant for the ground state chemistry of **1a**. Even much higher in energy is structure **3a** with a linear, planar D_{2h} symmetry (state ^1A_G), which has a calculated relative energy of ca. 77 kcal/mol. It corresponds to a second-order transition state (NIMAG = 2). The DFT data, obtained from B3LYP/6-31+G* optimizations, produced rather similar relative energies. However, the B3LYP method gives considerable longer C=N and C−H bonds compared to the RHF values, whereas bond angles and torsional angles are similar (Table 4). The calculated geometrical parameters for **4a** are given in Table 5.

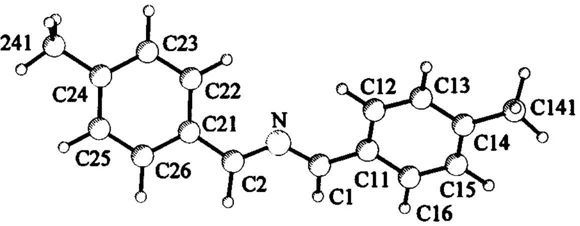

Figure 3. Molecular structure of the transition state **TS** for the interconversion **1b** → **2b** as calculated by the B3LYP/6-31G* method. For geometrical parameters, see Table 1.

Comparing the relative energies of the parent $C_2H_4N^+$ system **1a**, **2a** with those calculated for the experimentally investigated di-*p*-tolyl system **1b**, **2b**, one notices that the two aryl groups exert a strong substituent effect. The energy difference between the allene form **1b** and the allyl structure **2b** is now reduced to only about 1−3 kcal/mol (MP2, DFT) in favor of the allene type structure **1b** (RHF/6-31G* even favors the allyl form!) (Table 6). Thus, for the gas phase only a slight predominance of the allenic structure is predicted. The calculated and observed geometrical parameters agree well; small differences, possibly due to packing forces, are found for the C1−N−C2 angle and the torsional angles. Different from the parent system **2a**, the 2-azaallylium isomer **2b** is now found to correspond to a minimum on the potential energy hyperface. Figure 3 shows the transition state **TS** between the linear (**1b**) and bent (**2b**) form which is characterized by a C1−N−C2 bond angle of 127.7° (B3LYP) and a C1−N−C2−C21 torsional angles of −156.9°. With a calculated barrier of only 3−4 kcal/mol, this cationic system shows extreme structural flexibility allowing bond bending in the range of 120 to 180° with simultaneous twisting by 90° from the orthogonal linear allene type structure to the bent planar allylium type isomer within a very small energy range.

Experimentally, the X-ray diffraction investigation of $\mathbf{1b{\cdot}CF_3SO_3}^-$, presented above, confirms the predominance of the cumulenic structure in the crystalline state (Table 1). In solution the linear valence structure is realized also: thus, the IR spectrum of a CH_2Cl_2 solution of salt $\mathbf{1b{\cdot}CF_3SO_3}^-$ is dominated by a very strong absorption at 1910 cm^{-1}, assigned to the asymmetric stretching vibration of the cumulenic C=N=C bonds. In comparison, 1,3-diphenylallene shows the corresponding IR absorption at 1947cm^{-1}.[29] For an IR absorption at 1910 cm^{-1} a C=N=C bond angle of 168° is predicted, in good agreement with 172(2)° found for $\mathbf{1b{\cdot}CF_3SO_3}^-$ in the crystal.[30] Although 1,3-di-*p*-tolyl-2-azaallenium tri-

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(27) See, however, for the mass spectrum: Dammel, R.; Bock, H. *Z. Naturforsch.* **1987**, *42b*, 810−814.

(28) Gaussian 94, Revision B.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(29) Jacobs, T. L.; Dankner, D. *J. Org. Chem.* **1957**, *22*, 1424−1427.

Table 3. ***Ab Initio* Total Energies (au) and Relative Energies (kcal/mol) for the $C_2H_4N^+$ Isomeric Cations 1a, 2a, and 3a**

compd	symmetry	RHF/6-31+G*	$E_{\rm rel}$	ZPE	MP4/6-31+G*//RHF/6-31+G*	$E_{\rm rel}$	B3LYP/6-31+G*	$E_{\rm rel}$	ZPE
1a	D_{2d}	−132.21585(0)	0.00	36.65	−132.65462	0.00	−133.04996(0)	0.00	35.81
2a	C_{2v}	−132.16916(1)	29.30	37.37	−132.58966	40.76	−132.98444(1)	41.11	34.67
3a	D_{2h}	−132.11420(2)[a]	63.78	36.42	−132.53280[a]	76.44	−132.93629(1)	71.33	38.52

[a] The UHF and UMP methods were used.

Table 4. ***Ab Initio* Geometrical Parameters for the $C_2H_4N^+$ Isomeric Cations 1a, 2a, and 3a**

	1a		**2a**		**3a**	
	RHF/6-31+G*	B3LYP/6-31+G*	RHF/6-31+G*	B3LYP/6-31+G*	RHF/6-31+G*	B3LYP/6-31+G*
C=N	1.2372	1.2504	1.3060	1.3241	1.2744	1.2885
C−H	1.0777	1.0921	1.0767[a]	1.0913[a]	1.0848	1.1026
			1.0824[b]	1.0991[b]		
C−N−C	180.0	180.0	115.50	114.95	180.0	180.0
H−C−N	119.59	119.60	118.26[a]	117.94[a]	121.52	121.55
			123.26[b]	123.32[b]		

[a] Exo-H. [b] endo-H.

Table 5. ***Ab Initio* Geometrical Parameters for *N*-((Trifluormethyl)sulfonyl)methanimine (4a)[a] (B3LYP/6-31+G*)**

bond lengths (Å)		bond angles (deg)		torsional angles (deg)	
C−H	1.077/1.080	H−C−N	117.7/123.7	H−C−N−S	−1.2/178.8
C=N	1.258	C−N−S	117.0	C−N−S−C	122.8
N−S	1.661	N−S−O	111.9/108.8	C−N−S−O	11.1/−125.7
S=O	1.426/1.419	N−S−C	98.7	N−S−C−F	61.2/181.2/300.5
S−C	1.831	S−C−F	110.8/108.2/109.8		
C−F	1.307/1.305/1.311				

[a] The following total energies were obtained: RHF/6−31 + G*//6−31 + G* −976.79880 au; MP2/6−31 + G*//6−31 + G* −976.23914 au; B3LYP/6-31 + G* −980.24546 au.

Table 6. ***Ab Initio* Total Energies (au) and Relative Energies (kcal/mol) for the Cations 1b and 2b and for the Transition State TS**

compd	symmetry	RHF/6-31G*	$E_{\rm rel}$	ZPE	MP2/6-31G*//RHF/6-31G*	$E_{\rm rel}$	B3LYP/6-31G*	$E_{\rm rel}$	ZPE
1b	C_2	−669.45304	1.44	185.33	−671.62054	0.00	−673.86816	0.00	173.16
2b	C_{2v}	−669.45534	0.00	185.23	−671.61451	2.49	−673.86566	1.57	173.30
TS[a]	C_1[b]	−669.44809	4.55	184.68	−671.61334	4.52	−673.86362	2.85	173.04

[a] Transition state (NIMAG = 1). [b] As given by the QST2 method ($\sim C_2$).

Table 7. Comparison of Experimental (300 MHz) and Calculated (GIAO) ^{13}C, ^{14}N/^{15}N, and ^{1}H NMR Chemical Shifts (ppm) for 1b·$CF_3SO_3^-$, 1b, and 2b

1b·$CF_3SO_3^-$		**1b**	**2b**	**1b·$CF_3SO_3^-$**		**1b**	**2b**
atom	expt	RHF/6-311+G(2d,p)//B3LYP/6-31G*		atom	expt	RHF/6-311+G(2d,p)//B3LYP/6-31G*	
C−1	143.05	156.57	204.36	H−1	9.34	9.08	9.55
C−11	118.65	119.72	128.98	H−12	7.85	8.21	9.62
C−12	132.13	139.48	148.30	H−13	7.50	7.91	7.97
C−13	130.86	135.52	133.50	H−15	7.50	7.96	7.88
C−14	150.16	170.80	180.93	H−16	7.85	8.40	8.60
C−15	130.86	134.37	132.65	H−141	2.47	2.86	2.98
C−16	132.13	149.94	157.45	H−141	2.47	2.89	2.98
C−141	20.90	21.69	22.73	H−141	2.47	2.53	2.61
N	206[a]	231.94[b]	199.06[b]				

[a] ^{15}N-NMR chemical shift, external reference 80% $HCONH_2$/d_6-DMSO. [b] The calculated absolute ^{14}N/^{15}N shielding for $HCONH_2$ is 161.37.

flate (**1b·$CF_3SO_3^-$**) is chiral due to its axial symmetry and its substitution pattern, resolving of its enantiomers is precluded, because the barrier of racemization via an achiral 2-azaallylium intermediate is calculated to be much too low.

The dominance of the allenic structure in solution is further indicated by *ab initio* and DFT calculations of the chemical shifts using the standard GIAO method as implemented in GAUSSIAN 94, employing four different RHF and DFT methods as suggested in the literature.[31] Table 7 summarizes the calculated and experimental chemical shifts. Most significantly for the structural assignment are the iminium carbon atoms C1/C3 and their protons H1/H3. Good agreement between theory and experiment is only found for the cumulenic 2-azaallenium structure **1b**. These calculations suggest that the ^{13}C NMR shifts for the carbon atoms C1/C3 of cations **1** should be found at relatively high field, about 50 ppm higher than those for the corresponding bent isomers **2**. The corresponding ^{1}H NMR shifts are calculated to be similar for both types of cations, being therefore less valuable for structural assignment. The ^{14}N/^{15}N nucleus

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(30) Al-Talib, M.; Jibril, I.; Huttner, G.; Jochims, J. C. *Chem. Ber.* **1985**, *118*, 1876−1886.

(31) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497−5509.

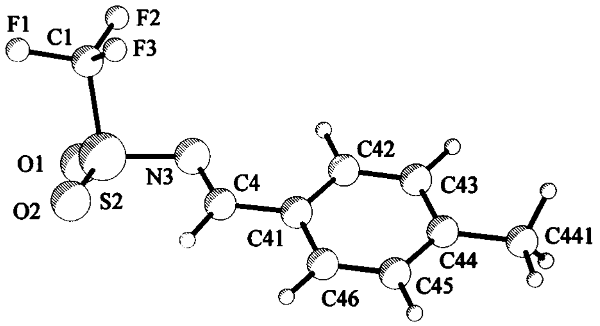

Figure 4. Molecular structure of *N*-((trifluormethyl)sulfonyl)-*p*-tolylmethanimine (**4b**), as calculated by the B3LYP/6-31G* method. For geometrical parameters, see Table 2.

Table 8. Comparison of Experimental (300 MHz) and Calculated (GIAO) ^{13}C and ^{1}H NMR Chemical Shifts (ppm) for 4b

atom	expt	RHF/ 6-311+G(2d,p)// B3LYP/6-31G*	atom	expt	RHF/ 6-311+G(2d,p)// B3LYP/6-31G*
C−1	119.19	111.72	H−4	9.11	9.56
C−4	181.37	189.18	H−42	7.95	8.12
C−41	129.17	130.90	H−43	7.40	7.57
C−42	132.77	147.05	H−45	7.40	7.59
C−43	130.31	131.75	H−46	7.95	9.02
C−44	150.49	160.41	H−441	2.50	2.66
C−45	130.31	133.48	H−441	2.50	2.71
C−46	132.77	140.33	H−441	2.50	2.26
C−441	20.96	21.16			

of the 2-azaallenium ion **1b** is calculated to be deshielded by about 30 ppm compared to the 2-azaallylium ion **2b**. However, considering the large spread of the experimental ^{14}N/^{15}N shifts and the calculated mean deviation, this small difference is of little diagnostic value.[32] The performance of the shift calculations based on RHF/6-31G* geometries is about as good as that based on B3LYP/6-31G* geometry optimizations. The agreement between theory and experiment even for the ^{1}H NMR shifts is excellent.

Similar quantum chemical calculations were also performed for the second product of the cleavage reaction, the *N*-sulfonylimine **4b** (Figure 4). In Table 2 the geometrical parameters are compared with those obtained by X-ray crystallography. The overall agreement is good (B3LYP calculates the N3−S2 bond surprisingly long), the only significant difference concerns the conformation of the SO_2CF_3 group relative to the imine moiety. This may well be due to packing forces in the crystal. The calculated chemical shifts (Table 8) are again in surprisingly good agreement with experiment, indicating that NMR spectra even of sulfur- and fluorine-containing molecules like **4b** may be simulated successfully by quantum chemical methods.

Experimental Section

General Methods. IR: NaCl cells (0.1 mm), solvent CH_2Cl_2. Laser desorption TOF-MS (LDI-MS): construction Dr. H. Luftmann, University of Münster; N_2 laser 337 nm, 3 ns pulses. Melting points: uncorrected. All solvents are rigorously dried by standard methods. All experiments are carried out with exclusion of moisture (argon; septum-syringe technique[33]) in glassware which is thoroughly dried by repeated heating under argon and subsequent evacuation.

1,3-Di-*p*-tolyl-2-azaallenium Trifluoromethanesulfonate (1b·$CF_3SO_3^-$). A total of 13.60 g (40 mmol) of 1,3,5-tri-*p*-tolyl-2,4-diazapenta-1,4-diene (**5**)[34] is dissolved in dichloromethane (40 mL) and cooled to 0 °C with stirring. The solution is treated with 11.28 g (6.7 mL) (40 mmol) of trifluoromethanesulfonic anhydride (**6**) during an interval of 20 min. The reaction mixture is stirred for 30 min at 0 °C and then at rt for 18 h. The solvent is removed in vacuo. The remaining solid is dissolved in chloroform (20 mL). The solution is treated dropwise with 50−60 mL of tetrachloromethane, until a fine cloudiness appears. To complete the precipitation, stirring is continued for 1 h at 0 °C. The pale yellow solid is filtered off and washed with tetrachloromethane. After two recrystallizations from $CHCl_3$/CCl_4, **1b·$CF_3SO_3^-$** is obtained as a colorless microcrystalline powder: yield 7.92 g (53%); mp 125 °C (dec).

^{1}H NMR (300.13 MHz, CD_3NO_2): $\delta = 2.47$ (s, 6H), 7.70 (d, $^{3}J = 8.6$ Hz, 4H), 7.85 (d, $^{3}J = 8.3$ Hz, 4H), 9.34 (s, 2H). **^{13}C NMR** (75.47 MHz, CD_3NO_2): $\delta = 20.90$ (q), 121,11 (q, ^{1}J(C,F) = 320.4 Hz), 118.65 (s), 130.86 (d), 132.13 (d), 143.05 (d), 150.16 (s). **LDI-MS**: m/z (%) = 222 (100) [M^+].

***N*-((Trifluoromethyl)sulfonyl)-*p*-tolylmethanimine (4b).** The filtrate from the preparation of **1b·$CF_3SO_3^-$** is concentrated in vacuo to $^{2}/_{3}$ of its volume. After 3 d at rt an orange viscous gum is formed, which is separated and discarded. The reaction mixture is now concentrated to $^{1}/_{2}$ of its original volume. While standing at rt for 3 d, colorless needles of **4b** are formed. They are separated by filtration, washed with tetrachloromethane, and dried in vacuo: yield 1.61 g (16%); mp 101 °C.

^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 2.50$ (s, 3H), 7.40 (d ,$^{3}J = 7.9$ Hz, 2H), 7.95 (d, $^{3}J = 8.3$ Hz, 2H), 9.11 (s, 2H). **^{13}C NMR** (75.47 MHz, CD_3NO_2): $\delta = 20.96$ (q), 119,19 (q, ^{1}J(C,F) = 320.0 Hz), 129.17 (s), 130.31 (d), 132.77 (d), 150.49 (s), 181.37 (d).

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Supporting Information Available: Full spectroscopic data for compounds **1b·$CF_3SO_3^-$** and **4b** and details of the quantum chemical calculations (GAUSSIAN 94 archive entries) (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[32] Olsson, L.; Cremer, D. *J. Phys. Chem.* **1996**, *100*, 16881−16891.

[33] Durst, T. In *Comprehensive Carbanion Chemistry*, Part B; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; pp 239−292.

[34] Ogata, Y.; Kawasaki, A.; Okumura, N. *J. Org. Chem.* **1964**, *29*, 1985−1988.