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The C–Br bond as a main reason for conformational isomerism

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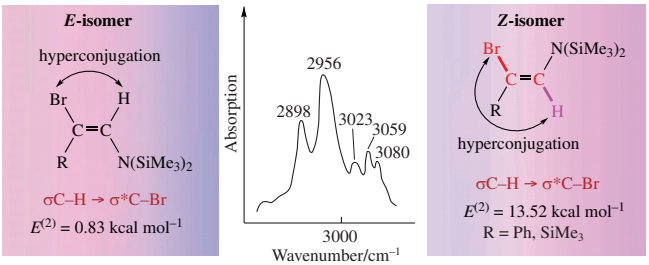
The conformational isomerism and orbital interactions of *N*-(2-bromo-2-phenylethenyl)-*N*,*N*-bis(trimethylsilyl)amine and *N*-(2-bromo-2-trimethylsilylethenyl)-*N*,*N*-bis(trimethylsilyl)amine were examined using NMR technique and quantum-chemical calculations. The IR criterion characterizing σ→σ* hyperconjugation is considered, and the linear dependence of σC–H→σ*C–X (X = F, Cl, Br) interaction energy on the polarizability of X is discussed.



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Hyperconjugation is defined as the redistribution of electron density involving σ-bonds. These orbital interactions lead to a change in geometry, electron density, molecular orbital energies, and play an important role in conformational isomerizm.[1] The preference of staggered conformation of ethane relative to the eclipsed form is due to hyperconjugation between the occupied σC–H orbitals of one methyl group and the antibonding σ*C–H orbitals of the other methyl group.[2,3] Evaluation the hyperconjugative stabilization energy of staggered and eclipsed structures of 1,1,1-trihaloethane by block-localized wave function (BLW) method showed that hyperconjugative interaction σCH → σ*CX is crucial for stabilization of the staggered conformation (Figure 1). The hyperconjugation energy in the staggered structures (7.25 kcal mol^{-1}, X = F) is higher than that in the eclipsed ones (5.90 kcal mol^{-1}).[4]

The eclipsed conformation of propylene is more stable than the staggered one by about 2 kcal mol^{-1} owing to the hyperconjugation interaction between methyl and vinyl groups.[5,6] The natural bond orbital (NBO) study has established that hyperconjugation between Me bonding orbital and adjacent vinyl C–H antibonding orbital σ(C–H)–σ*(C–H) also significantly contributes to conformational preference of propylene (Figure 2).[7]

In the present work, we report on the factors affecting the conformational isomerism of the adducts formed *via* the reaction between *N*-bromohexamethyldisilazane **1** with phenylacetylene **2a** and trimethylethynylsilane **2b**. The main data on reactivity of

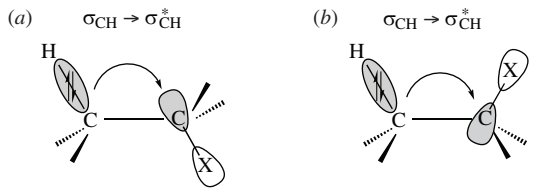


Figure 1 (*a*) Hyperconjugative interaction in the staggered conformation of trihaloethanes. (*b*) Hyperconjugative interaction in the eclipsed conformation of trihaloethanes.

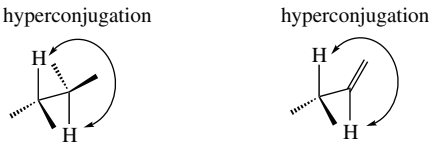
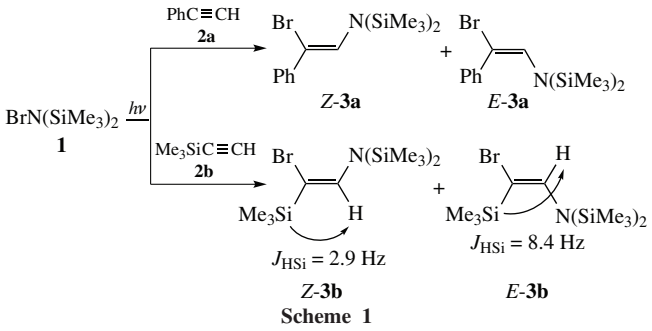


Figure 2 σ(C–H)–σ*(C–H) hyperconjugation in the staggered structure of ethane and eclipsed structure of propylene.

bromoamine **1** were reviewed.[8] Under free radical conditions (UV irradiation or radical initiators), this compound almost selectively brominates linear and cyclic saturated hydrocarbons, but does not react with arenes.[9–12] In contrast to conventional halogenating agents (halogens, *N*-halo amides, *N*-halo imides), in case of bromoamine **1** the abstraction of hydrogen atom from the substrate involves N-centered hexamethyldisilazanyl radical $(Me_3Si)_2N^{\bullet}$ (not $Br^{\bullet}$ as it usually occurs), which changes selectivity of the reaction. This fact is confirmed by the comparison of selectivity of hydrogen abstraction in isobutane, pentane, isopentane, 1-chlorobutane, cyclohexane or their mixtures with $(Me_3Si)_2N^{\bullet}$ and with radicals $Br^{\bullet}$, $Cl^{\bullet}$, $MeCO^{\bullet}$. The reactivity of $(Me_3Si)_2N^{\bullet}$ and $(MeCO)^{\bullet}$ is close, while their regioselectivity strongly differs from those of $Cl^{\bullet}$ and $Br^{\bullet}$.[11] The data on the addition of *N*-bromohexamethyldisilazane **1** to the triple carbon–carbon bonds is almost lacking in literature.

We have studied the reactions of bromoamine **1** with phenylacetylene **2a** and trimethylethynylsilane **2b** (Scheme 1) to deliver the corresponding adducts, *N*-(2-bromo-2-phenylethenyl)-*N*,*N*-bis(trimethylsilyl)amine **3a** and *N*-(2-bromo-2-trimethylsilylethenyl)-*N*,*N*-bis(trimethylsilyl)amine **3b**, respectively. The NMR spectra of compound **3a** manifest signals for two isomers, *Z* and *E*, in a 1.2 : 1 ratio. Their structure was assigned using 2D homonuclear NOESY spectra where the cross-peaks between the olefin and *ortho*-phenyl protons (for the major isomer) and, alternatively, between Si–Me and *ortho*-phenyl protons were observed. This unambiguously evidences that the major isomer is *Z*-configured.



Scheme 1

The NMR spectrum of adduct **3b** also contains signals for two, *Z* and *E*, isomers in a 1.6 : 1 ratio. The location of substituents in these compounds has been proven by the HMBC ^{13}C–^{1}H and ^{29}Si–^{1}H experiments.[13,14] In the 2-D ^{13}C–^{1}H HMBC spectrum, protons for the methyl groups Me_3Si–C= give correlation peaks with quaternary olefinic carbon in both isomers, which proves that bromine atom is geminally located relative to the $SiMe_3$ group. The correlation HMBC ^{29}Si–^{1}H spectrum contains a peak with $^{3}J_{H–Si}$ = 8.4 Hz for the minor isomer, while the peak for the major isomer is associated with spin–spin coupling constant $^{3}J_{H–Si}$ = 2.9 Hz. Thus, the major isomer is *Z*-configured.

The geometry of compounds **3a**,**b** was optimized by DFT [B3PW91/6-311+G(d,p)] method using the GAUSSIAN 09 package.[15] The NBO energies[16] were studied using the Gaussian 09 software package at DFT/B3LYP [6-311G(d,p)] level of theory. These delocalization energies are the stabilizing energies calculated by second order perturbation theory. The gas phase calculation results are consistent with the NMR data and indicate the presence of two isomeric forms (*Z* and *E*) in compounds **3a**,**b** (Figure 3). The assignment of the structures to minima of potential energy surface (PES) is confirmed by the positive eigenvalues of the corresponding Hessians. The geometrical parameters are given in Table 1.

The relative stability of the isomers was estimated as difference between their total energies with ZPE correction (ΔE^{ZPE}). According to Table 1, *Z*-**3a** is more stable (by 2.51 kcal mol^{-1}) than *E*-**3a**. When the phenyl group is replaced by the trimethylsilyl fragment (compound **3b**), relative energy of the *Z*-isomer increases to 4.57 kcal mol^{-1} (*cf.* ref. 17). The electron density delocalization in the isomers of compounds

Table 1 Bond lengths (Å), bond angles (degree) and relative energies ΔE^{ZPE} (kcal mol^{-1}) for the *Z*- and *E*-isomers of compounds **3a**,**b**.

Parameters	3a		Parameters	3b	
	Z	*E*		*Z*	*E*
r[C(5)–C(8)]	1.472	1.473	*r*[Si(1)–C(3)]		
r[C(8)–Br(7)]	1.914	1.927	*r*[C(3)–Br(6)]	1.926	1.946
r[C(8)=C(9)]	1.344	1.344	*r*[C(3)=C(7)]	1.342	1.340
r[C(9)–H(24)]	1.094	1.091	*r*[C(7)–H(26)]	1.094	1.094
r[C(9)–N(10)]	1.404	1.412	*r*[C(7)–N(8)]	1.411	1.424
Br(7)C(8)C(9)	119.851	115.692	Br(6)C(3)C(7)	119.683	114.186
Br(7)C(8)C(5)	116.542	115.697	Br(6)C(3)Si(1)	114.441	110.905
N(10)C(8)C(9)	128.705	126.471	N(8)C(7)C(3)	129.896	125.316
C(8)C(9)H(24)	114.116	116.680	C(3)C(7)H(26)	114.350	117.880
ΔE^{ZPE}	2.51	0.00	ΔE^{ZPE}	4.57	0.00

3a,**b** was studied by the NBO analysis. The delocalization energies [$E^{(2)}$] were calculated by second order perturbation theory analysis. The most intense orbital interactions are shown in Table 2.

The strongest interactions that stabilize isomers *Z*,*E*-**3a** are realized in the ring: π[C(3)=C(4)] → π*[C(5)=C(6)], π[C(1)=C(2)] → π*[C(5)=C(6)].

The hyperconjugations LP(N8) → π*[C(8)=C(9)] and LP(N8)) → σ*[C(9)–H(24)] significantly contributes to stabilization of the isomers. These interactions do not change when passing from *Z*- to *E*-form. The secondary hyperconjugation σ[C(9)–H(24)] → σ*[C(8)–Br(7)], leading to stabilization energy of 13.52 kcal mol^{-1} in the *Z*-form, is almost absent in the *E*-form. This interaction plays a crucial role in the prevalence of total stabilization energy of the *Z*-isomer over the *E*-isomer in compound **3a** (see Table 2).

In case of compound **3b** depriving phenyl substituent, the energy of hyperconjugation does not exceed 15 kcal mol^{-1} (see Table 2). The *Z*-isomer of compound **3b** is characterized not only by the secondary hyperconjugation σ[C(9)–H(24)] → → σ*[C(8)–Br(7)], but also σ[Si(1)–C(3)] → σ*[C(7)–N(8)] hyperconjugation, which are absent in the *E*-isomer. The total energy of both orbital interactions is 25.26 kcal mol^{-1}.

The hyperconjugation σ[C(9)–H(24)] → σ*[C(8)–Br(7)] in the *Z*-isomer weakens the C–H bond. Consequently, in the IR

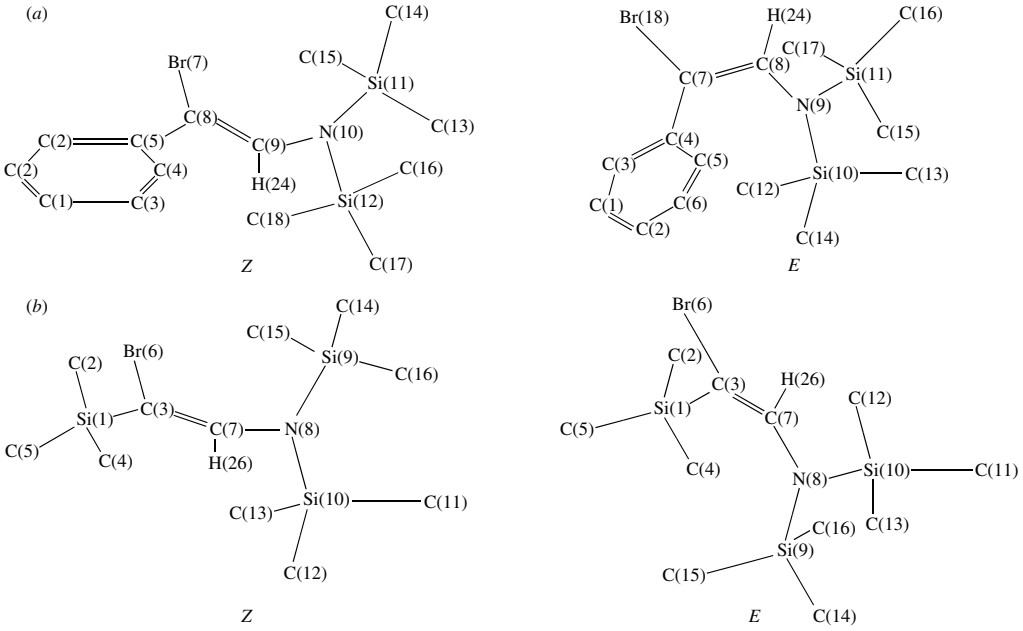


Figure 3 *Z*,*E*-Isomers of compounds (*a*) **3a** and (*b*) **3b** according to quantum chemical calculations.

Table 2 Main interaction energies $E^{(2)}$ (kcal mol^{-1}) for *Z*- and *E*-isomers of compounds **3a**,**b**.

Orbital interaction	**3a**		Orbital interaction	**3b**	
	Z	*E*		*Z*	*E*
π[C(3)=C(4)] → π*[C(5)=C(6)]	43.80	44.65			
π[C(1)=C(2)] → π*[C(5)=C(6)]	41.93	41.07			
π[C(5)=C(6)] → π*[C(8)=C(9)]	11.53	10.08			
LP(N8) → π*[C(8)=C(9)]	22.02	19.93	LP(N8) → π*[C(8)=C(9)]	8.15	5.66
LP(N8) → σ*[C(9)–H(24)]	14.79	12.20	LP(N8) → σ*[C(9)–H(24)]	13.86	14.50
σ[C(9)–H(24)] → σ*[C(8)–Br(7)]	13.52	0.83	σ[C(9)–H(24)] → σ*[C(8)–Br(7)]	14.33	0.87
			σ[Si(1)–C(3)] → σ*[C(7)–N(8)]	10.93	0.69

spectrum, the stretching vibration frequency $\nu_{C–H}$ should undergo a bathochromic shift compared to the corresponding frequency of the *E*-isomer. The presence of two isomers leads to splitting of the stretching vibration band $\nu_{C–H}$ into two components. Indeed, in the IR spectrum of compound **3a** the stretching vibration $\nu_{C–H}$ represents a doublet with components at 3080.55 cm^{-1} and 3059.07 cm^{-1}. The former value corresponds to the *E*-isomer and is the standard value of the C–H bond stretching vibration frequency in the C=C–H fragment. The value of 3059.07 cm^{-1} can be attributed to the *Z*-isomer. In accordance with the isomer ratio of 1.2 : 1 for compound **3a**, the intensity of the band at 3059 cm^{-1} (*Z*) should be higher than the intensity of the band at 3080 cm^{-1} (*E*), which fully corresponds to the spectrum. The value of splitting $\Delta\nu_{C–H}$ is 21.63 cm^{-1}. Calculated data with visualization of vibrations also give a doublet with frequencies 3107 cm^{-1} (*E*) and 3071 cm^{-1} (*Z*). The theoretical value $\Delta\nu_{C–H}$ (34.19 cm^{-1}) exceeds the experimental one. The $\Delta\nu_{C–H}$ value can serve as an experimental criterion for σ[C(9)–H(24)] → → σ*[C(8)–Br(7)] hyperconjugation.

Energy σC–H → σ*C–X hyperconjugation is determined by the donor ability of the σC–H bonds and acceptor ability of the σ*C–X bonds. In series X, the energy will be determined mainly by the acceptor ability of σ*C–X bonds. In monosubstituted ethanes, acceptor ability of the σ*C–X bonds increases when going to the end of a period (with augmenting electronegativity of X), and when going from top to bottom of the group (with decreasing electronegativity of X).[18] Therefore, electronegativity is not a unique criterion for energy σC–H → σ*C–X hyperconjugative interaction. The effect of the polarizability X (X = Hal) on the energy of σC–H → σ*C–X in substituted ethanes and propylenes was not discussed. Table 3 shows that in the calculated analogues of compound **3b**, the energy $E^{(2)}$ of σC–H → σ*C–X interaction enhanced in the series X = F < Cl < Br both in the substituted ethanes and trifluoroethanes.[3,18] The energies of σC–H → σ*C–X interactions are proportional to the polarizability of X. The maximum value of $E^{(2)}$ at X = Br corresponding to the maximum transfer of electron density to σ*C–X is due to the high polarizability of Br.

In conclusion, NBO analysis has shown that σ → σ* interactions are the main factor stabilizing the *Z*-isomer in *N*-(2-bromo-2-phenylethenyl)-*N*,*N*-bis(trimethylsilyl)amine **3a** and *N*-(2-bromo-2-trimethylsilylethenyl)-*N*,*N*-bis(trimethylsilyl) amine **3b** obtained by the original synthesis. The IR criterion for the presence of hyperconjugation based on the stretching vibration of $\nu_{C–H}$ band is first considered. It is shown that the polarizability of X (X = Br, F, Cl) stimulates σCH → σ*CX interactions.

Table 3 The NBO energies $E^{(2)}$ (kcal mol^{-1}) of σC–H → σ*C–X interactions for the *Z*-isomers of compounds (Me)SiCXCHN(SiMe$_3$)$_2$, polarizability (σ_α, ref. 19) and electronegativity of X.

X	$E_Z^{(2)}$	σ_α	Electronegativity
F	10.24	0.55	3.98
Cl	13.55	2.18	3.16
Br	14.33	3.05	2.96

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.11.018.

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