

Structure and Stereodynamics of *N,N*-Bis(silyloxy)enamines

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Received April 16, 2002

Abstract: The structure and stereodynamics of *N,N*-bis(silyloxy)enamines (**1**), a new class of enamines with extraordinary reactivity, have been simulated by the DFT PBE/TZP method. The computed pattern of dynamic behavior and structural peculiarities of **1** was shown to reflect adequately the results of the studies by a series of physical methods including X-ray analysis and dynamic NMR and UV spectroscopies, which provided evidence of a rather low barrier for rotation around the C,N single bond, a negligible contribution of the $n-\pi$ -conjugation, a high barrier of inversion, and high pyramidalicity of the nitrogen atom.

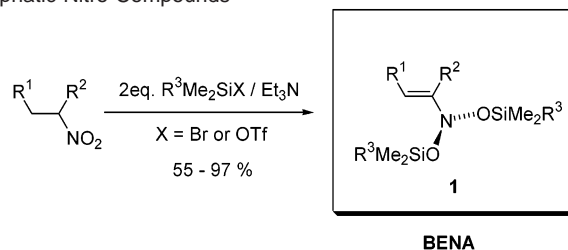
Introduction

N,N-Bis(silyloxy)enamines (BENAs) (**1**) are readily available derivatives of aliphatic nitro compounds with a very promising synthetic potential (Scheme 1).¹ Among the wide range of recently discovered reactions of BENAs, of particular interest is their intriguing ability to play roles of both β -C-electrophiles and β -C-nucleophiles in C,C-bond-forming processes with carbanions or carbocations, respectively.²

This unprecedented reactivity pattern coupled with some other properties of BENAs³ provokes a question about the peculiar structural features of this new class of organic compounds.

One might have suggested that two important structural peculiarities determine the chemical properties of BENAs, namely, the $n-\pi$ -conjugation of the nitrogen lone pair with the C,C double bond and the pyramidalicity of the sp^3 -hybridized nitrogen atom. Both factors refer to the static state of BENAs and act in opposite directions; i.e., the $n-\pi$ -conjugation strives

Scheme 1 Synthesis of *N,N*-Bis(silyloxy)enamines by Silylation of Aliphatic Nitro Compounds



to flatten the nitrogen atom, whereas the inherent pyramidalicity of the nitrogen atom tends to reduce the efficiency of the conjugation.⁴

It is well established that the classical *N,N*-dialkyl enamines (enamines), the closest relatives to BENAs, prefer to adopt a conformation securing a rather efficient $n-\pi$ -conjugation with a nearly planar configuration of the nitrogen center (vide infra).⁵ At the same time, the presence of a $N(OSi)_2$ fragment in BENAs makes the latter somehow similar to dialkoxyamines with a highly pyramidal nitrogen atom (vide infra).⁶ Therefore, the balance between the conflicting $n-\pi$ -conjugation and the nitrogen pyramidalicity effect must clearly exist to minimize the energy of BENAs. However, the extent of realization of the former or latter effect cannot be predicted with certainty.

Other important characteristics refer to the dynamic behavior of BENAs, which could be considered in terms of the activation barriers of internal rotation around the C,N bond (CN rotation) and of the nitrogen atom inversion (N inversion). The value of the activation energy for CN rotation could be taken as a

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- (1) For the discovery of BENAs see: (a) Feger, H.; Simchen, G. *Liebigs Ann. Chem.* **1986**, 1456. For the improved procedure for the preparation of BENAs, see: (b) Dilman, A. D.; Tishkov, A. A.; Lyapkalo, I. M.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovsky, V. A. *Synthesis* **1998**, 181. (c) Dilman, A. D.; Tishkov, A. A.; Lyapkalo, I. M.; Ioffe, S. L.; Kachala, V. V.; Strelenko, Yu. A.; Tartakovsky, V. A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2926. For the methodology of the synthetic application of BENAs, see: (d) Ioffe, S. L.; Lyapkalo, I. M.; Makarenkova, L. M. *J. Org. Chem. Russ.* **1998**, *34*, 1141 (in Russian); *Russ. J. Org. Chem.* **1998**, *34*, 1085 (English translation). (e) Tartakovsky, V. A.; Ioffe, S. L.; Dilman, A. D.; Tishkov, A. A. *Russ. Chem. Bull.* **2001**, 1850 (in Russian); **2001**, 1936 (English translation).
- (2) (a) Dilman, A. D.; Lyapkalo, I. M.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovsky, V. A. *Synthesis* **1999**, 1767. (b) Dilman, A. D.; Lyapkalo, I. M.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovsky, V. A. *J. Org. Chem.* **2000**, *65*, 8826.
- (3) For example, BENAs are prone to rearrangement into α -silyloxy oximes upon the influence of a catalytic amount of acid (see ref 1a). At the same time, some of the BENAs readily decompose at contact with Et_3N in the absence of the silylating reagent (see ref 1b).

- (4) The angle between the lone pair and the π -system increases along with an increase of the nitrogen's pyramid heights.
- (5) The structure of enamines is discussed in the following review: Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975.
- (6) The structure of saturated *N,N*-bis(alkoxy)amines is discussed in the following review: Rudchenko, V. F. *Chem. Rev.* **1993**, *93*, 725.

measure of the efficiency of the $n-\pi$ -conjugation, while the pyramidalicity of the nitrogen atom may be indirectly evaluated by the activation energy of N inversion. Thus, in enamines, CN rotation is usually hindered by a relatively high activation energy ($\Delta G^{\ddagger}_{298} = 40-80$ kJ/mol)⁷ and N inversion is very fast ($\Delta G^{\ddagger}_{298} = 4-6$ kJ/mol).⁸

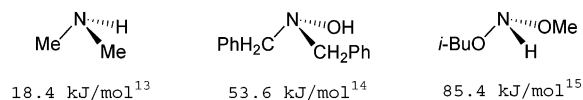
Previous studies of the dynamic behavior of a model BENA derivative revealed the occurrence of a single dynamic process, but the latter could not have been identified definitely as either CN rotation or N inversion.⁹

Here we report the results of the structural studies of BENAs by DFT PBE/TZP calculations and by X-ray analysis and dynamic NMR and UV spectroscopies.

Results and Discussion

The extremely high β -C-nucleophilicity of enamines (according to Mayr's nucleophilicity scale, for model enamines $N \approx 11-16$)¹⁰ can be explained by an efficient contribution of $n-\pi$ -conjugation to the electronic properties of their C,C double bond. The high barrier of internal rotation around the C,N bond ($\Delta G^{\ddagger}_{298} = 40-80$ kJ/mol)⁷ reflects the efficiency of this interaction. However, despite the apparently unsaturated character of the C,N bond, X-ray analysis and microwave spectroscopy reveal that the nitrogen atom in enamines is slightly pyramidal.

The substitution of alkyl groups in enamines by electronegative OSi fragments should increase the s-character of the nitrogen lone pair and increase thereby the activation energy of N inversion.¹¹ Indeed, the activation energy for N inversion goes up significantly as is shown in the series of amines.¹²



The efficiency of the $n-\pi$ -conjugation in BENAs should therefore be lower than in enamines.¹⁶ This consideration was corroborated by the recently measured β -nucleophilicity of

- (7) Data for enamines with a functional group at the β -carbon atom of the C,C double bond: (a) Shvo, Y.; Taylor, E. C.; Bartulin, J. *Tetrahedron Lett.* **1967**, 3259. (b) Mannschreck, A.; Koelle, U. *Tetrahedron Lett.* **1967**, 863.
- (8) (a) Meyer, R. *Chimia* **1977**, 31, 55. (b) Meyer, R. *Helv. Chim. Acta* **1978**, 61, 1418.
- (9) We detected a broadening and splitting of the Me₃SiO signal when the sample of BENA **1j** was studied by ²⁹Si NMR at low temperature. A further broadening of the split lines down to 180 K has not been observed.
- (10) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, 123, 9500.
- (11) Bent, H. A. *Chem. Rev.* **1961**, 61, 275.
- (12) One has to be careful in comparing the values of activation energy presented in this paper for different processes. Most of the literature data were obtained using different methods and procedures that may strongly affect certain values.
- (13) Wollrab, J.; Laurie, V. *J. Chem. Phys.* **1968**, 48, 5058.
- (14) (a) Fletcher, J. R.; Sutherland, I. O. *Chem. Commun.* **1970**, 687. (b) Kost, D.; Raban, M. *J. Org. Chem.* **1976**, 41, 1748.
- (15) Rudchenko, V. F.; Ignatov, S. M.; Chervin, I. I.; Nosova, V. S.; Kostyanovskii, R. G. *Izv. Acad. Nauk. SSSR, Ser. Khim.* **1986**, 1153; *Chem. Abstr.* **1987**, 106, 175847r.
- (16) P. W. Hickmott in 1980 formulated the opposite point of view: Ahmed, M. G.; Ahmed, S. A.; Hickmott, P. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2383. He suggested that the introduction of a σ -electronegative group (e.g., OAlk) to the nitrogen atom has to increase the efficiency of $n-\pi$ -conjugation due to the decrease of the electrostatic repulsion of the lone pairs. However, the stereoelectronic effects in the studied structure (substituted *N*-vinylhydroxylamine) prevented the conjugation of the nitrogen lone pair and C,C double bond. Thus, opposite the expected increase of nucleophilicity, he observed a low activity of the substituted *N*-vinylhydroxylamine toward some strong electrophiles.

BENAs, which turned out to be 6–10 orders of magnitude lower than that of standard enamines (according to Mayr's nucleophilicity scale, for the model BENAs $N \approx 5-6$).¹⁷

However, these considerations alone do not allow one to conclude which of the two dynamic processes, N inversion or CN rotation, has been observed in a model BENA by NMR at variable temperatures.⁹

DFT PBE Calculations. To evaluate the pattern of dynamic behavior and to reveal the static structural peculiarities of BENAs as compared with enamines, we have performed DFT PBE/TZP calculations¹⁸ of the most favorable conformations and of the transition states for CN rotation and N inversion using a set of models: vinylamine (**2**),¹⁹ *N,N*-dimethylvinylamine (**3**), hypothetical *N,N*-bis(oxy)enamines CH₂=CHN(OH)₂ (**4**) and CH₂=CHN(OSiH₃)₂ (**5**), and existing BENA CH₂=CHN(OSiMe₃)₂ (**1a**) (Table 1). The CN rotation potentials for vinylamine (**2**) and *N,N*-bis(oxy)enamines **4**, **5**, and **1a**, the typical representatives of enamines and BENAs, respectively, are compared in Figure 1.²⁰

All curves exhibit two symmetrical minima that correspond to two enantiomeric "conjugated" conformations, **A** and **A***. In conformation **A*** the geometrical parameters for enamines **2** and **3** differ significantly from those for *N,N*-bis(oxy)enamines **4**, **5**, and **1a** (cf. entries 1 and 5 with 6, 11, and 16, Table 1). For enamines **2** and **3** conformation **A*** is characterized by an almost planar nitrogen atom (the sum of the valency angles at N is 341–350°), a shorter C,N single bond ($r(\text{C-N})$ is 1.387–1.396 Å), and a longer C,C double bond ($r(\text{C=C})$ is 1.344–1.350 Å). In the case of *N,N*-bis(oxy)enamines **4**, **5**, and **1a**, the sum of the valence angles at N is 321–322°, $r(\text{C-N})$ is 1.422–1.426 Å, and $r(\text{C=C})$ is 1.331–1.337 Å. The difference in the calculated geometrical parameters of conjugated conformation **A*** for model enamines and *N,N*-bis(oxy)enamines can be interpreted as the result of much weaker $n-\pi$ -conjugation and much higher pyramidalicity of the nitrogen atom in BENAs than in enamines.

In contrast to vinylamine, the CN rotation curves for *N,N*-bis(oxy)enamines **4**, **5**, and **1a** contain additional minima corresponding to conformation **B**, in which the lone pair of nitrogen is orthogonal to the π -bond.²¹

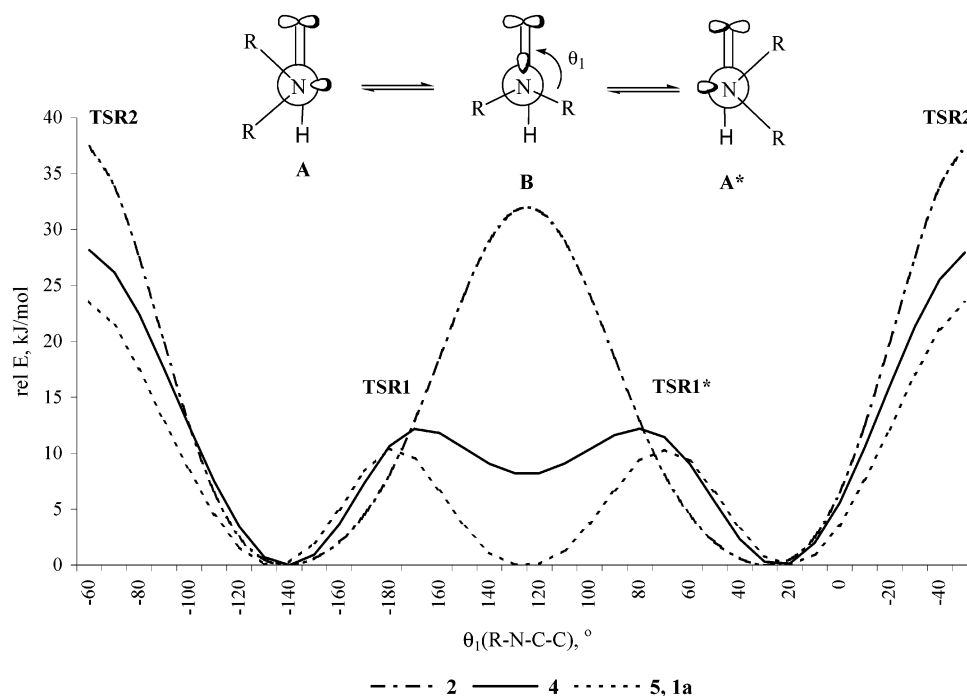
The geometrical parameters of *N,N*-bis(oxy)enamines **4**, **5**, and **1a** in conformation **B** and of transition state **B** for vinylamine are almost the same except for the pyramidalicity of the nitrogen atom. For enamine **2** in transition state **B** the sum of the valence angles at N is 324°, while that for *N,N*-bis(oxy)enamines **4**, **5**, and **1a** is 310–312°. This difference is the

- (17) Dilman, A. D.; Ioffe, S. L.; Mayr, H. *J. Org. Chem.* **2001**, 66, 3196.
- (18) All calculations that are discussed throughout the text were performed using the quantum chemical program PRIRODA: Laikov, D. N. *Chem. Phys. Lett.* **1997**, 281, 151.
- (19) The CN rotation potential curve as well as the inversion transition state for ethylenamine (**2**) have been previously computed by both ab initio and DFT methods: Pugh, J. K.; Streitwieser, A. *J. Org. Chem.* **2001**, 66, 1334. Our results are consistent with these data.
- (20) The presented CN rotation curves for *N,N*-bis(oxy)enamines **4** and **5** were obtained by scanning the PES (36 points). The CN rotation curves for **2** and **1a** were plotted using the saddle points that were computed taking into account the zero-point vibration energy (Table 1). The shape of the CN rotation curve for **2** is known from the literature (ref 19), while that for **1a** is supposed to be similar to the shape of the CN rotation curve for **5**. For the model enamine **3** only one conformation (minimum **A***) has been computed taking into account the zero-point vibration energy (Table 1).
- (21) The AM1-calculated potential energy curve for CN rotation in *N,N*-bis-(hydroxy)enamine **4** has no minimum **B**.

Table 1. DFT PBE Calculated Geometric Parameters and Relative Energies for Conformational Minima and Transition States of Compounds **1a** and **2–5** ($R_2NCH=CH_2$)^a

entry	compd	R	conformation ^{a,b}	rel E , ^c kJ/mol	θ_1 (RNCC), deg	θ_2 (RNCC), deg	r (C–N), Å	r (C=C), Å	sum of angles at N, deg
1	2	H	A*	0	18.8	150.4	1.396	1.344	341.4
2	2	H	B	30.3	122.9	–122.7	1.442	1.334	323.7
3	2	H	TSR2	37.0	–58.0	58.0	1.447	1.336	325.5
4	2	H	N inversion TS	4.5 ^d	0	180.0	1.378	1.347	360.0
5	3	Me	A*	0	7.5	151.0	1.387	1.350	349.7
6	4	OH	A*	0	23.7	139.4	1.422	1.337	322.4
7	4	OH	B	6.5	125.8	–124.3	1.442	1.331	312.3
8	4	OH	TSR1*	10.3	79.9	–167.5	1.439	1.333	317.3
9	4	OH	TSR2	25.9	–56.3	55.4	1.458	1.331	315.7
10	4	OH	N inversion TS	51.7	3.8	178.5	1.372	1.350	359.8
11	5	OSiH ₃	A*	0.3	20.4	134.4	1.426	1.335	321.5
12	5	OSiH ₃	B	0	126.0	–125.4	1.441	1.332	312.3
13	5	OSiH ₃	TSR1*	9.3	69.9	–177.8	1.441	1.334	318.0
14	5	OSiH ₃	TSR2	23.9	–55.3	55.0	1.461	1.331	318.1
15	5	OSiH ₃	N inversion TS	65.0	0.6	–177.7	1.371	1.351	360.0
16	1a	OSiMe ₃	A*	0.3	21.2	134.6	1.425	1.337	321.0
17	1a	OSiMe ₃	B	0	127.2	–125.5	1.445	1.332	309.7
18	1a	OSiMe ₃	TSR1*	8.8	70.8	–177.6	1.441	1.335	317.6
19	1a	OSiMe ₃	TSR2	23.9	–52.3	56.8	1.465	1.331	314.7
20	1a	OSiMe ₃	N inversion TS	65.3	7.0	–174.6	1.366	1.355	358.9

^a See Figure 1. ^b **TSR1** and **TSR2** = transition states for rotation, N inversion TS = transition state for inversion. ^c The values were calculated taking into consideration the zero-point vibration energy. ^d The experimental value of the activation energy for N inversion is 4.2 kJ/mol (by microwave spectroscopy).^{8a}

**Figure 1.** Potential energy curves for internal rotation around the C,N bond for *N,N*-bis(oxy)enamines **4**, **5**, and **1a** and vinylamine (**2**).²⁰

consequence of the increased s-character of the nitrogen lone pair in *N,N*-bis(oxy)enamines as compared with enamines.

The discrepancy in geometrical parameters for the “conjugated” **A** and “nonconjugated” **B** is different for enamine **2** and *N,N*-bis(oxy)enamines **4**, **5**, and **1a** (cf. entries 1 and 2, and entries 6, 11, and 16 with 7, 12, and 17, Table 1). In the case of enamine **2**, the conjugation affects these parameters stronger, which also testifies to the weaker $n-\pi$ -conjugation in BENAs.

As is known from the chemistry of enamines, the steric interactions between the substituent at the nitrogen atom and the substituent at the β -position of the C,C double bond can destabilize conformations such as **A**.⁵ Thus, conformation **B** is the most favorable by steric requirements. The appearance of

these deep minima **B** on the CN rotation curve for *N,N*-bis(oxy)enamines **4**, **5**, and **1a** can be interpreted also as a result of diminishing the conjugative stabilization in conjugated conformation **A**.

We have estimated the contribution of both “conjugative” and “steric” interactions in the energy of equilibrium conformations for vinylamine **2** and *N,N*-bis(oxy)enamines **4**, **5**, and **1a** by approximating their rotation potentials through Fourier series and decomposing them into steric and conjugative functions (Table 2).^{22a} These constituents have the same shape for **1a** and **2**, **4**, and **5**. The typical couple of steric and conjugative functions for **5** is presented in Figure 2.^{22b} The nitrogen lone pair in conformation **B** is orthogonal to the π -bond, and the

Table 2. Steric and Conjugative Contributions to the Energy of Conformation **A**^{a,b}

entry	R	compd	steric energy, kJ/mol	conjugative energy, kJ/mol
1	H	2	2.6	-34.2
2	OH	4	7.4	-15.4
3	OSiH ₃	5	8.7	-8.5
4	OSiMe ₃	1a	9	-8.2

^a Both steric and conjugative energies are supposed to equal zero for conformation **B**. ^b The positive and negative energies correspond to the destabilizing and stabilizing interactions, respectively.

stabilizing conjugative energy is therefore equal to zero. The steric interactions are obviously the least in conformation **B**; thus, we can equate the destabilizing steric energy to zero.²³

The values of the destabilizing steric and stabilizing conjugative energies for the vinylamine **2** and *N,N*-bis(oxy)enamines **4**, **5** and **1a** studied herein are presented in Table 2. These values describe how much energy the molecule gains or loses upon the transformation from conformation **B** to conformation **A**, respectively.

The *n*- π -conjugation in vinylamine **2** is the most efficient in the series of compounds **2**, **4**, **5**, and **1a** since the rotation **B** \rightarrow **A** gives the largest gain in conjugative energy (entry 1, Table 2). In the series of models of BENAs **4**, **5**, and **1a**, the conjugative energy is smaller as compared to that of enamine **2** (cf. entries 1 and 2–4, Table 2). The efficiency of the *n*- π -conjugation in this series is the largest for *N,N*-bis(hydroxy)-enamine **4**, which may be the consequence of the higher electronegativity of the OSiH₃ and OSiMe₃ groups as compared to the OH group. The *p*-character of the nitrogen lone pair in **4** is larger, and the *n*- π -conjugation in it is therefore stronger.

The loss in energy due to the steric interactions upon the rotation **B** \rightarrow **A** is negligible in vinylamine **2** and the largest in **5** and **1a** (cf. entries 1 with 3 and 4, Table 2). In the latter case, the conjugative and steric interactions obviously neutralize each other to result in the equality of energies of conformations **A** and **B** (cf. entries 11 and 16 with 12 and 17, Table 1). The difference in the stabilities of conformations **A** and **B** for **4** (cf. entries 6 and 7, Table 1) can be explained by the higher stabilizing conjugative interactions and lower destabilizing steric repulsion in **4** with respect to **5** and **1a**.

Thus, according to DFT PBE /TZP calculations, BENAs exist in two conformations, **A** and **B**, while only one conformation, **A**, is favorable for enamines.

The barriers for interconversion of equilibrium conformations are different for BENAs and enamines. In the former case, the CN rotation should proceed mainly via **TSR1** (**TSR1***) with the activation barrier 8.8–9.2 kJ/mol, since reaching the other transition state, **TSR2**, requires overcoming a much higher barrier (23.9 kJ/mol). The CN rotation in vinylamine **2** should proceed via transition state **B** with a high activation energy of 30.3 kJ/mol. The realization of the CN rotation via the second

transition state, **TSR2** (37.0 kJ/mol), is also possible for vinylamine **2**.

The barriers for N inversion in BENAs and enamines differ from each other significantly. In the former case, it is estimated to be 51.7–65.3 kJ/mol, while that for vinylamine **2** is 4.5 kJ/mol.

The activation barrier of N inversion in BENAs should be much higher than the barrier of CN rotation, and N inversion should be slow on the NMR time scale.

Synthesis of BENAs. While the above calculations refer to the behavior of the isolated molecules of the simplified models in the gas phase, they could be used as key leads for the interpretation of the data provided by the results of the physicochemical studies of the real compounds.

The required set of BENAs **1a**–**1o** were prepared using previously described procedures (Scheme 1, Table 3; see also the Materials and Methods). In addition we have also synthesized enamine **6**, as a model enamine, which contains an electron-withdrawing substituent in the β -position of the C,C double bond (Figure 3).

It is worthy to note that the use of Me₃SiOTf/Et₃N for the silylation of 1-(4-nitrophenyl)-2-nitroethane led to the formation of a mixture of BENA **1n** and isomeric *N,N*-bis(silyloxy)aniline **1n'** (Figure 3).²⁴ At the same time, the employment of Me₃-SiBr/Et₃N as the silylating reagent allowed us to obtain BENA **1n** as a single product.

The choice of certain objects for study was dictated by the suitability of BENAs for study by dynamic NMR (taking into account the symmetry relationships of the exchanging groups at the nitrogen atom) and by their aggregative state (for X-ray analysis). The variation of the electronic nature of the substituents at the C,C double bond of BENA was needed, since the specific influence of substitution on the structural properties and the dynamic behavior could give some information about the efficiency of the *n*- π -conjugation.

X-ray Analysis. The calculated structural parameters for BENAs are in line with the data obtained by X-ray analysis (cf. entries 1 and 2 with 3 and 4, Table 4).

The conformations of BENAs **1k** and **1o** in a crystal state are different (Figure 4). BENA **1k** may suffer stronger steric repulsion of the bulky α -substituent and OSi groups in conformation **B**; therefore, the distorted conformation **A*** becomes the most favorable. In contrast to α -substituted BENA **1k**, β -substituted BENA **1o** was found to be in conformation **B**.

Independent of the conformation, the nitrogen atom is highly pyramidal in both BENAs **1k** and **1o**. The sum of valency angles for them is close to that for dimethoxyamine **7** (cf. entries 1, 2, and 5, Table 4, Figure 5) and far from that for enamines **2**, **3**, **6**, **9**, and **10** (cf. entries 1 and 2 with 6–11, Table 4, Figure 5).²⁵ The presence of the π -electron-withdrawing substituent in the β -position of the C,C double bond in BENAs does not affect the pyramidalicity of the nitrogen atom (cf. entries 1 and 2, Table 4), while in the case of enamines, the introduction of a 4-NO₂C₆H₄ fragment to the C,C double bond in **6** or an Ac

(22) (a) The decomposition of the rotation potential into a number of functions that describe the different interactions has been previously applied: Radom, L.; Hehre W. J.; Pople J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. For details see the Supporting Information. (b) The plots of steric and conjugative constituents of the CN rotation potential for compounds **2**, **4**, and **1a** are presented in Supporting Information.

(23) We equated the value of the steric energy function to zero in the point of conformation **B**, since this procedure enables us to evaluate the steric and conjugative energies in the other points.

(24) This phenomenon will be a subject of our special studies.

(25) In the literature we failed to find the crystal structures of the enamines that would be the close structural analogues of BENAs **1k** and **1o** studied herein. The enamines **9** and **10**, presented in Table 4, were selected from the number of described structures, since they contain the most planar and the most pyramidal nitrogen atoms, respectively.

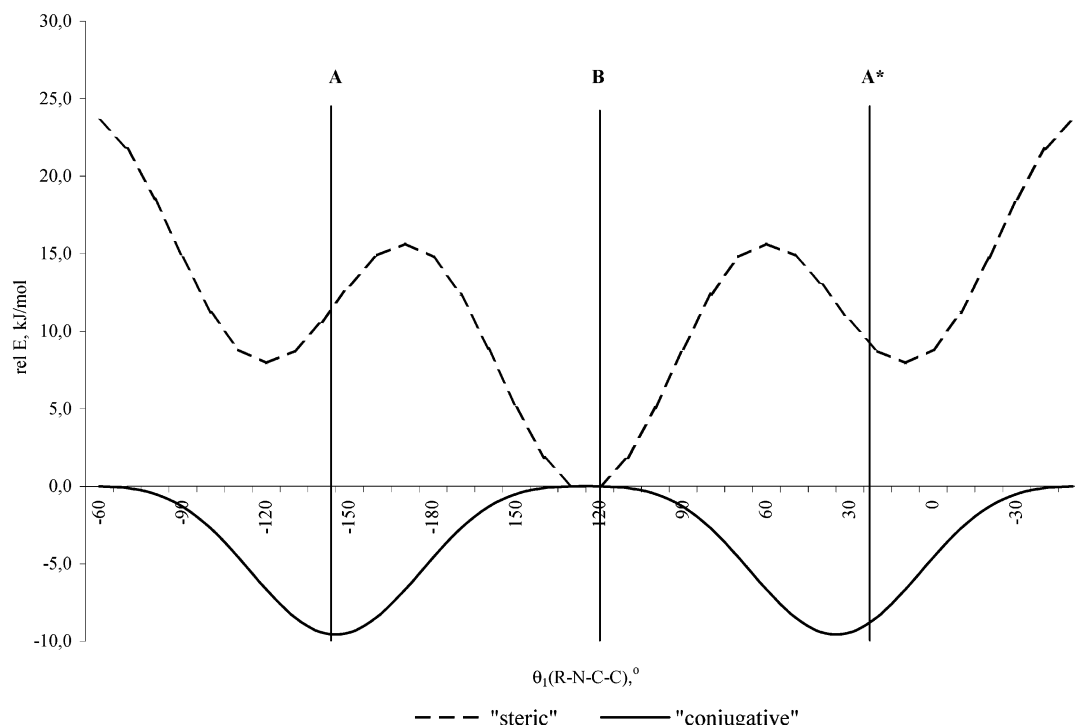


Figure 2. Typical plot of steric and conjugative constituents of the CN rotation potential for *N,N*-bis(silyloxy)enamine **5**.

Table 3. Synthesis of *N,N*-Bis(silyloxy)enamines by Silylation of Aliphatic Nitro Compounds^a

R ¹	R ²	R ³ /X	T, °C/ time, h	BENA	yield, ^b %
H	H	Me/Br	-30 → 20/20	1a	97
H	H	<i>t</i> -Bu/OTf	0/4	1b	92
Me	H	Me/Br	-30/48	1c	89
Me	H	<i>t</i> -Bu/OTf	5/1.5 ^c	1d	90
H	Me	Me/Br	20/40	1e	92
H	Me	<i>t</i> -Bu/OTf	0/3	1f	93
CO ₂ Me	H	Me/OTf	-75/2.5	1g	87
H	CO ₂ Et	<i>t</i> -Bu/OTf	-40/2	1h	55 ^d
CO ₂ Me	Me	<i>t</i> -Bu/OTf	0/3	1i	75
H	CH(OSiMe ₃)Pr- <i>i</i>	Me/Br	20/408	1j	62 ^d
H	CH(OSiMe ₃)Pr- <i>i</i>	<i>t</i> -Bu/OTf	20/144	1k	78 ^d
CH(Me)CO ₂ Et	H	Me/Br	-30/120	1l	79 ^d
CH(Me)CO ₂ Et	H	<i>t</i> -Bu/OTf	0/3	1m	85 ^d
4-NO ₂ C ₆ H ₄	H	Me/OTf	-30/3	1n	23 ^d
				1n'	58 ^d
4-NO ₂ C ₆ H ₄	H	Me/Br	-30/3.5	1n	81 ^d
4-NO ₂ C ₆ H ₄	H	<i>t</i> -Bu/OTf	-30/3	1o	79 ^e

^a See Scheme 1. ^b Yield for the distilled product, unless otherwise indicated. ^c Et₃N instead of CH₂Cl₂ was used as a solvent. ^d The product is a thermally labile oil. The yield was determined for the product with a purity >90% by integration of the ¹H NMR spectra with an internal standard. ^e Yield for the recrystallized product.

group to the nitrogen atom in **8** completely flattens the pyramid of nitrogen (cf. entries 8–11 and 6 and 7, Table 4).

In comparison with enamines, the C,N bond of BENAs is longer and the C,C double bond is shorter (cf. entries 1 and 2 with 6–11, Table 4). This fact testifies to the very inefficient *n*- π -conjugation of the C,C double bond of BENAs with the nitrogen lone pair of high *s*-character.

Thus, X-ray analysis of BENAs proves that the previously observed dynamic NMR process should be N inversion.

Dynamic NMR Studies. Taking into consideration the symmetry relationships of the substituents at the nitrogen atom, one can divide a set of synthesized BENAs into three groups:

Table 4. Structural Parameters of *N,N*-Bis(silyloxy)enamines in Comparison with the Calculated and Literature Data for the Related Derivatives^a

entry	compd	configuration	$\theta_1(\text{C}=\text{C}-\text{N}-\text{R})$, deg (calcd)	$\theta_2(\text{C}=\text{C}-\text{N}-\text{R})$, deg (calcd)	$r(\text{C}-\text{N})$, Å (calcd)	$r(\text{C}=\text{C})$, Å (calcd)	sum of angles at N, deg (calcd)
1	1k	distorted A	3.8	-106.4	1.450	1.313	316.0
2	1o	B	132.8	-119.5	1.439	1.324	312.0
3	1a	A	(21.2)	(134.6)	(1.425)	(1.337)	(321.0)
4	1a	B	(127.2)	(-125.5)	(1.445)	(1.332)	(309.7)
5	7						311.8
6 ^b	6	A	4.2 (4.0)	177.3 (160.9)	1.351 (1.367)	1.348 (1.367)	359.7 (356.1)
7	8	A	4.2	178.6	1.398	1.322	359.9
8	2	A			1.397 ^c		^c
		A	(18.8)	(150.4)	(1.396)	(1.344)	(341.4)
9	3	A	(7.5)	(151.0)	(1.387)	(1.350)	(349.7)
10	9	A	6.9	176.0	1.381	1.366	359.2
11	10	distorted A	7.0	-122.8	1.431	1.353	340.7

^a The geometry optimizations were performed by the DFT PBE/TZP method. ^b The geometrical parameters are represented for the ordered independent molecule. ^c The data of microwave spectroscopy [for the vinylamine **2** angle between the C–N bond extended and the HNH bisector is 34° (that for MeNH₂ is 52°, and that for H₂NCHO is 0°)].²⁹

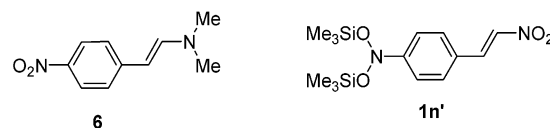


Figure 3.

(I) BENAs **1a**, **1c**, **1e**, and **1g** that contain OSiMe₃ groups at nitrogen,

(II) BENAs **1j**, **1k**, **1l**, and **1m** that possess a center of chirality at the C,C double bond, and

(III) BENAs **1b**, **1d**, **1f**, **1h**, **1i**, and **1o** that contain OSiMe₂-Bu-*t* groups at nitrogen.

Figure 6 illustrates the situations with the equivalence of substituents that can emerge during the dynamic NMR study

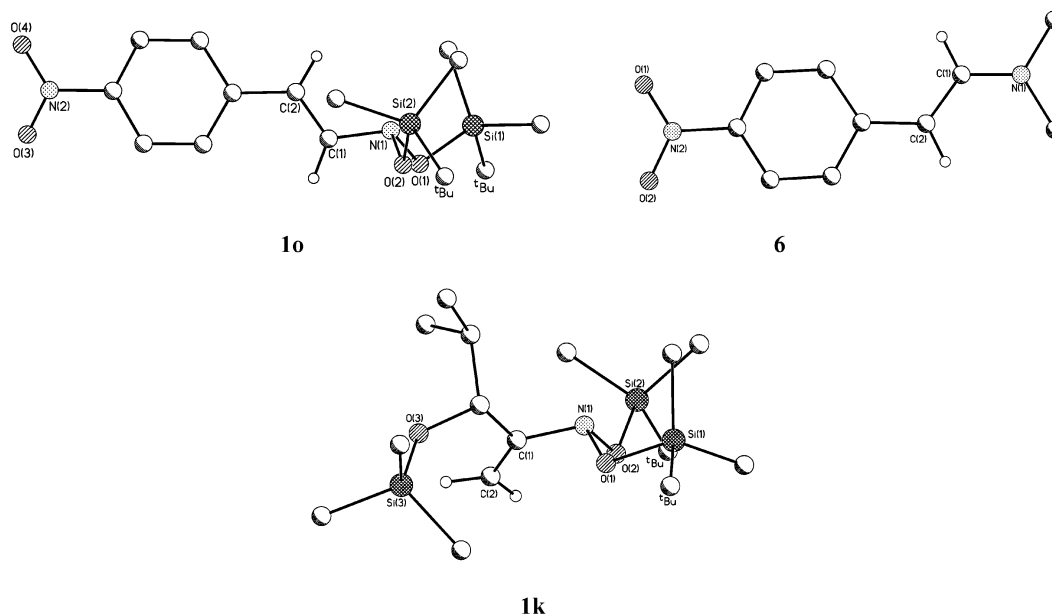


Figure 4. Structures of *N,N*-bis(silyloxy)enamines **1k,o** and enamine **6**. Some hydrogen atoms have been omitted for clarity.

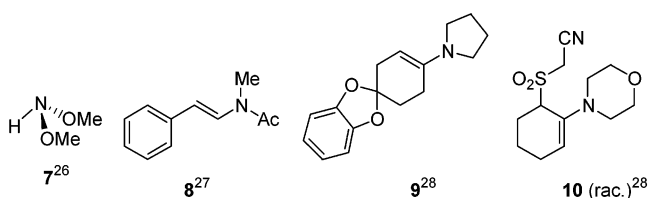


Figure 5. Reference compounds to be compared with *N,N*-bis(silyloxy)-enamines by X-ray analysis.

of BENAs of these three types and enamines on the assumption of the large difference of the rates of N inversion and CN rotation on the NMR time scale.

The presence of two $\text{SiMe}_2\text{Bu-}t$ fragments enables us to see the hindered N inversion in BENAs of group III, since freezing the nitrogen atom in the pyramidal state causes the nonequivalence of the SiMe groups (Figure 6, left). At the same time, Si atoms have to stay equivalent in the ^{29}Si NMR spectra of these BENAs. However, the same behavior of $t\text{-BuMe}_2\text{Si}$ -substituted BENAs will be observed if N inversion is fast and CN rotation by eq 2 is hindered; i.e., conformation type **B** is the most favorable.

The asymmetric center in BENAs of group II makes the substituents at the nitrogen atom nonequivalent if either N inversion or CN rotation is hindered (Figure 6).

The only process that could be observed in Me_3SiO -substituted BENAs of group I is the hindered CN rotation by eq 1. However, we failed to see any exchange processes by dynamic NMR upon their cooling. Thus, it can be concluded that there is no hindered CN rotation by eq 1 for BENAs in the analyzed temperature interval (entries 1, 3, 5, and 8, Table 5). At the same time, this process was observed for enamine **6** possessing an electron-withdrawing substituent in the β -position of the C,C double bond (entry 17, Table 5).

The dynamic NMR study of BENAs with the asymmetric center (group II) and $\text{SiMe}_2\text{Bu-}t$ -substituted BENAs of group III revealed (except for **1i**) some dynamic process that can be referred to either hindered N inversion or CN rotation by eq 2.³⁰ The energies of activation for the observed dynamic processes are presented in Table 5.

However, the obtained data do not allow us to choose whether we deal with the hindered N inversion or with retarded CN rotation by eq 2. Moreover, ΔG^\ddagger for N inversion and CN rotation might be of the same value. Thus, in *N,N*-bis(*tert*-butyldimethylsilyloxy)aniline ΔG^\ddagger_{298} for N inversion is 49 kJ/mol,³¹ while the CN rotation in enamine **6** is hindered with the barrier $\Delta G^\ddagger_{298} = 45$ kJ/mol.

Nevertheless, the analysis of the influence of the electron-withdrawing substituents at the C,C double bond on the value of ΔG^\ddagger gives indisputable evidence that the dynamic process in BENAs is N inversion. The value of ΔG^\ddagger significantly decreases if the electron-withdrawing substituent is introduced to the β -position of the C,C double bond in BENAs (cf. entry 16 with entries 2 and 4, Table 5). It is worthy to note that we did not observe any dynamic process upon cooling the highly electron deficient BENA **1i** (group III) to -100 °C (entries 10 and 11, Table 5). Such a tendency may be due to the flattening of the nitrogen pyramid by the involvement of the lone pair in the $n-\pi$ -conjugation.³² At the same time, the introduction of the π -electron-withdrawing substituent to the C,C double bond should slow the rate of CN rotation.³³

The experimental values of ΔG^\ddagger for the dynamic process in BENAs are in agreement with the calculated energies of

- (26) Antipin, M. Yu.; Struchkov, Yu. T.; Shishkov, I. F.; Golubinsky, A. V.; Ef'fimova, T. L.; Vilkov, L. V.; Bredikhin, A. A.; Vereshchagin, A. N.; Ignatov, S. M.; Rudchenko, V. F.; Kostyanovsky, R. G. *Izv. Acad. Nauk. SSSR, Ser. Khim.* **1986**, 2235 (in Russian); *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1986**, 2040 (English translation).
- (27) Song, F.; Snook, J. H.; Foxman, B. M.; Snider, B. B. *Tetrahedron* **1998**, *54*, 13035.
- (28) Brown, K. L.; Damm, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, *61*, 3108.
- (29) Lovas, F. J.; Clark, F. O. *J. Chem. Phys.* **1975**, *62*, 1925.
- (30) The typical dependence of the spectra of BENAs on temperature is presented in the Supporting Information.
- (31) Dilman, A. D.; Lyapkalo, I. M.; Belyakov, P. A.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovskiy, V. A. *Russ. Chem. Bull.* **2000**, 1659 (in Russian); **2000**, 1649 (English translation). The observation of hindered N inversion in $\text{PhN}(\text{OSiMe}_2\text{Bu-}t)_2$ is evidence that the dynamic process in BENAs is also hindered N inversion.
- (32) The introduction of π -electron-withdrawing groups to the nitrogen atom significantly decreases the activation barrier for N inversion in the series of aziridines: Kessler, V. H. *Angew. Chem.* **1970**, 227.
- (33) For example, see ref 7b.

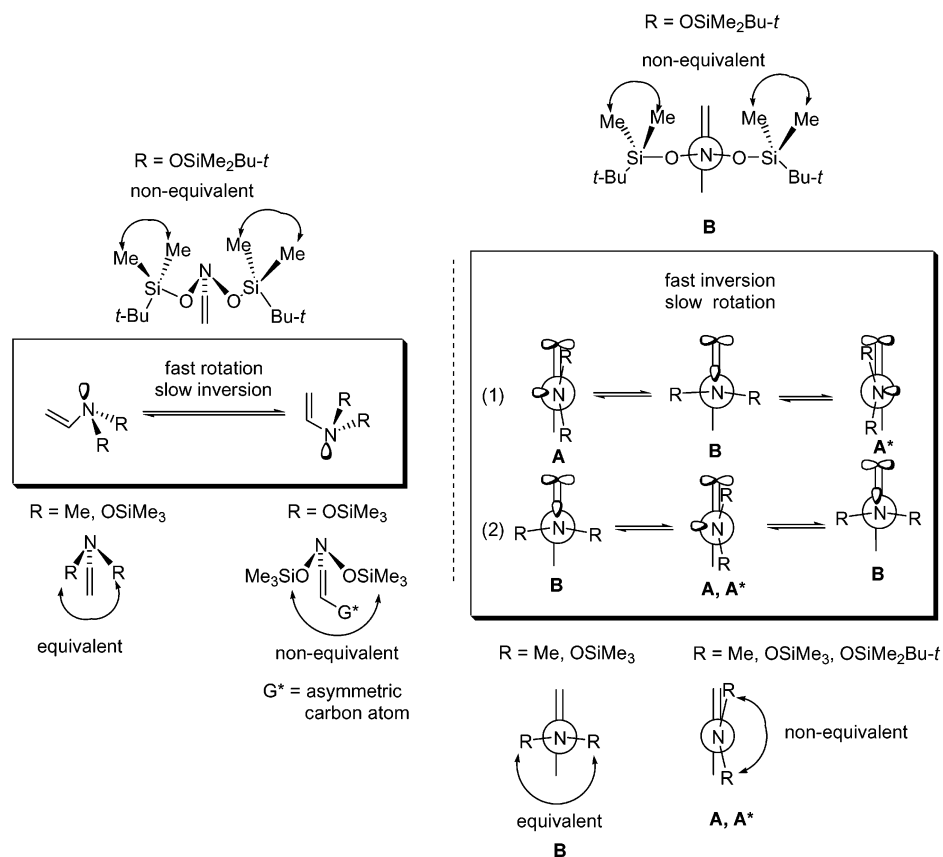


Figure 6. Different situations of the substituents' equivalence upon the hindering of either N inversion or CN rotation in BENAs and enamines.

Table 5. Results of the Study of BENAs by Dynamic NMR

entry	BENA	nuclei obsd by NMR	exchanging groups (the lowest temp (K) at which the exchange was not obsd)	$\Delta G^{\ddagger}_{298}$, kJ/mol
1	1a	²⁹ Si	(210)	
2	1b	¹³ C	OSiMe ₂ Bu- <i>t</i>	49 ± 3
3	1c	²⁹ Si	(180)	
4	1d	¹³ C	OSiMe ₂ Bu- <i>t</i>	63 ± 1
5	1e	²⁹ Si	(200)	
6	1f	¹³ C	OSiMe ₂ Bu- <i>t</i>	56 ± 2
7	1f	²⁹ Si	(210)	
8	1g	²⁹ Si	(210)	
9	1h	¹³ C	OSiMe ₂ Bu- <i>t</i>	58 ± 1
10	1i	²⁹ Si	(170)	
11	1i	¹ H, ¹³ C	(230)	
12	1j	²⁹ Si	OSiMe ₃	59 ± 3
13	1k	²⁹ Si	OSiMe ₂ Bu- <i>t</i>	56 ± 2
14	1l	²⁹ Si	OSiMe ₃	59 ± 1
15	1m	²⁹ Si	OSiMe ₂ Bu- <i>t</i>	52 ± 4
16	1o	¹³ C	OSiMe ₂ Bu- <i>t</i>	37 ± 1
17	6	¹³ C	Me	45 ± 1

transition states of N inversion for **4**, **5**, and **1a** (cf. experimental $\Delta G^{\ddagger} \approx 50$ –60 kJ/mol and calculated $\Delta E \approx 52$ –65 kJ/mol).

The conclusion about the negligible role of n - π -conjugation in BENAs can be confirmed by the observed strong hypsochromic shift of the UV absorption band of the 4-NO₂C₆H₄-CH=CHN fragment, when the methyl groups at nitrogen are substituted by SiO groups (for **6** $\lambda_{\max} = 404$ nm [log $\epsilon = 4.0$]; for **1o** $\lambda_{\max} = 324$ nm [log $\epsilon = 4.1$]). Changing the substituents at silicon does not affect the position of the absorption maximum (for **1n** $\lambda_{\max} = 327$ nm [log $\epsilon = 4.0$]).³⁴

The introduction of a *t*-Bu group to the silicon atom slightly decreases ΔG^{\ddagger} for N inversion in BENAs (cf. entries 12 and 14 with entries 13 and 15, Table 5), which is consistent with the tendency for activation barriers in the series of *N*-alkylaziridines to decrease slightly upon the introduction of bulky substituents to the nitrogen atom.³⁵

Conclusion

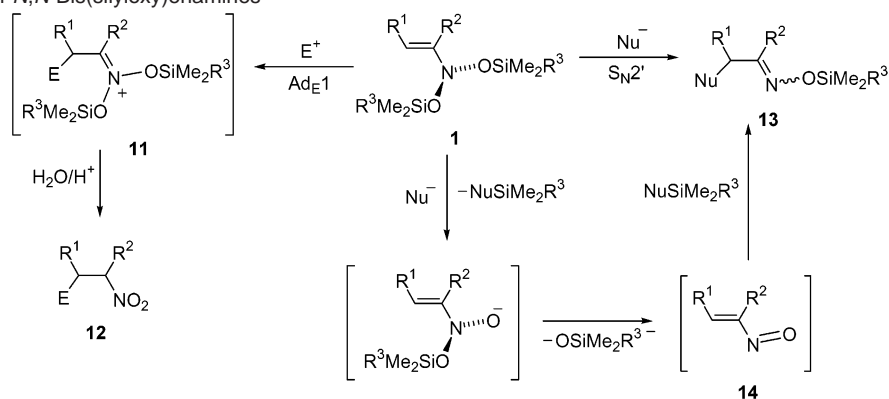
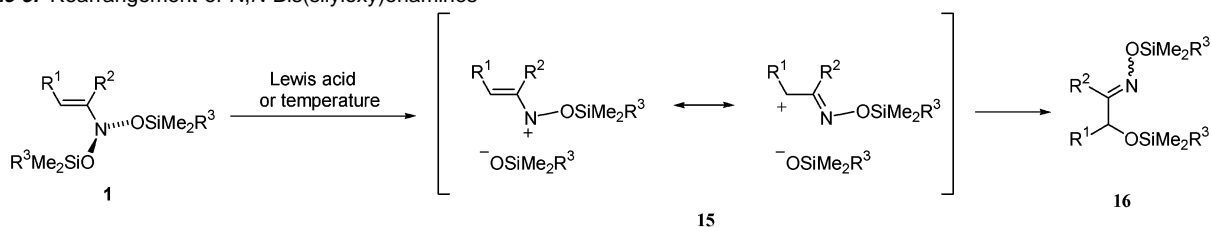
The simulated structure and dynamic behavior of BENAs have been corroborated with the results of X-ray analysis and dynamic NMR studies. The results taken together with the data of UV spectroscopy revealed that the role of the n - π -conjugation is negligible in the structure of BENAs, the nitrogen atom is highly pyramidal, the barrier for rotation around the C,N bond is low, and the barrier for inversion of the nitrogen atom is high.

Despite the evidently low efficiency of the n - π -conjugation in BENAs, they act as nucleophiles in reactions with strong electrophiles. Apparently, the electron-donating effect of the N(OSi)₂ group can stabilize the α -carbocations **11**, which emerge after the attack of electrophiles on the C,C double bond of BENAs (Scheme 2, left, reaction **1** → **11** → **12**).¹⁷

The existence of the stable conformation of type **B**, where the σ^*_{N-O} orbital is close to coplanar with the π -orbital, may govern the reactivity of BENAs. However, it is still unclear whether the formerly suggested S_N2' mechanism is operative

(34) The discussed UV spectra contain additional bands that refer to the CH=CHN fragment absorption: **1n**, $\lambda_{\max} = 233$ nm [log $\epsilon = 3.9$]; **1o**, $\lambda_{\max} = 232$ nm [log $\epsilon = 4.0$]; **6**, $\lambda_{\max} = 256$ nm [log $\epsilon = 3.8$].

(35) Kessler, V. H. *Angew. Chem.* **1970**, 227.

Scheme 2. Reactivity of *N,N*-Bis(silyloxy)enamines**Scheme 3.** Rearrangement of *N,N*-Bis(silyloxy)enamines

in any reaction of BENAs with nucleophiles (Scheme 2, right, reaction $1 \rightarrow 13$).³⁶ Now we have solid evidence that such reactions proceed via the initial attack of the nucleophile on the silicon atom to give highly electrophilic nitrosoalkenes **14** after the elimination of the SiO^- anion (Scheme 2, right, reaction $1 \rightarrow 14 \rightarrow 13$).³⁷

At the same time, the π -double bond could participate in the cleavage of the weak N,O single bond ($\sigma^*_{\text{N-O}}-\pi$ -interaction) in the course of the rearrangement of BENAs (Scheme 3).

In accord with this suggestion, the introduction of π -donors to the β -carbon atom of the C,C double bond considerably increases the propensity of BENAs **1** for rearrangement into α -silyloxy oximes **16**.³⁸ However, this trend may be explained considering only the stability of the intermediate cation **15**. The elucidation of the role of the $\sigma^*_{\text{N-O}}-\pi$ -interaction in this rearrangement will be the subject of our further studies.

Materials and Methods

DFT PBE Calculations. Density functional method PBE calculations were carried out using the quantum chemical program PRIRODA kindly provided by Dr. D. N. Laikov (Moscow State University). All calculations employed the triple- ζ basis plus d-function basis: H (5s2p) \rightarrow [3s2p], C and O (11s6p2d) \rightarrow [6s3p2d], Si (15s11p2d) \rightarrow [10s6p2d]. Expansion of the electron density in the auxiliary basis set was used.³⁹ Stationary points which correspond to conformational minima and saddle points (TS) were obtained by full geometry optimization followed by vibrational frequency calculations. Energies obtained in this way also include corrections to zero-point vibrational energies (ZPVEs). The potential energy curves for *N,N*-bis(oxy)enamines **4** and **5** have been calculated by geometry optimization using fixed values of the torsion angle $\theta(\text{C}-\text{C}-\text{N}-\text{O})$, which were varied in steps of 10° .

General Information. NMR spectra for preparative purposes were recorded on a Bruker AM-300 instrument. Chemical shifts were measured relative to the solvent residual peak, internal reference (SiMe_4 , 0 ppm, for ^{29}Si), and external reference (MeNO_2 , 0 ppm, for ^{14}N). The INEPT pulse sequence was used for ^{29}Si signal observation. All reactions were performed in a dry argon atmosphere using methylene chloride freshly distilled from CaH_2 . Dry benzene was obtained by distillation over sodium wire. Petroleum ether refers to the fraction having bp 60–70 $^\circ\text{C}$. DBU and Et_3N were distilled over CaH_2 . TBSOTf and TMSOTf were simply distilled in a vacuum; TMSBr was distilled over Cu shavings. All other reagents were used as purchased from either Aldrich or Merck. All distillations were performed in a short-path apparatus, and boiling points refer to a bath temperature.

Synthesis of Materials. Nitroethane, 1-nitropropane, 2-nitropropane, 3-nitropropionic acid, and 4-nitrotoluene were purchased from Aldrich. Ethyl 2-nitropropionate,⁴⁰ methyl 3-nitropropionate,⁴¹ methyl 3-nitrobutyrate,⁴² ethyl 4-nitro-2-methylbutyrate,⁴³ 2-nitro-3-trimethylsilyloxy-4-methylpentane,^{1b} 1-(4-nitrophenyl)-2-nitroethane,⁴⁴ BENAs **1a**, **1c**, **1e**, and **1j**,^{1b} **1b**,**1d**, and **1f**,^{1a} and **1g** and **1i**,^{1c} and enamine **6**⁴⁵ were prepared by known procedures.

Ethyl 2-*N,N*-Bis(*tert*-butyldimethylsilyloxy)aminoacrylate (1h). To a stirred solution of ethyl 2-nitropropionate (147 mg, 1 mmol) in CH_2Cl_2 (2 mL) at -40°C were added successively Et_3N (0.32 mL, 2.3 mmol) and TBSOTf (0.49 mL, 2.1 mmol). The reaction mixture was stirred for 2 h at -40°C , and a separately prepared mixture of citric acid (133 mg, 0.7 mmol), Et_3N (0.56 mL, 4 mmol), and CH_2Cl_2 (1.3 mL) was added simultaneously. The resulting mixture was stirred for 5 min, petroleum ether (10 mL) was added, and the cold resulting emulsion was poured into H_2O (10 mL). The organic layer was washed with saturated aqueous NaHCO_3 (5 mL), H_2O (10 mL), a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (580 mg, 4.2 mmol) in H_2O (50 mL), H_2O (20 mL), and brine (10 mL) and dried over Na_2SO_4 . The solvents were removed in

(36) The $\text{S}_{\text{N}}2'$ -type mechanism has been formerly postulated for the reaction of BENAs with amines (ref 1a).

(37) For the results of the investigations into the mechanism of the reaction of BENAs with N-centered nucleophiles, see: Lesiv, A. V.; Ioffe, S. L.; Strelenko, Y. A.; Tartakovsky, V. A. *Helv. Chim. Acta*, in press.

(38) BENAs with strong π -donating substituents in the β -position of the C,C double bond have never been isolated due to their fast rearrangement in the reaction media (e.g., $\text{R}^1 = 4\text{-MeOC}_6\text{H}_4$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$, Scheme 3).

(39) Laikov, D. N. *Chem. Phys. Lett.* **1997**, *281*, 151.

(40) Kornblum, N.; Blackwood, R. K.; Powers, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 2507.

(41) Rodriguez, A.; Nomen, M.; Spur, B. W. *Tetrahedron Lett.* **1998**, *39*, 8563.

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(44) Zalukajevs, L.; Vanags, E. *J. Gen. Chem. USSR* **1956**, *26*, 3115 (in Russian); **1956**, *26*, 3469 (English translation); *Chem. Abstr.* **1957**, *51*, 8668b.

(45) Vetelino, M. G.; Coe, J. W. *Tetrahedron Lett.* **1994**, 219.

a vacuum to give 207 mg (55%) of pure **1h** as a colorless oil. The purity is >95% according to ^1H NMR with a quantitative standard ($\text{CH}_2\text{-Cl}_2$).

^1H NMR (CDCl_3): $\delta = 0.22$ (s, 12 H, SiMe_2), 0.90 (s, 18 H, *t*-Bu), 1.31 (t, $J = 7.1$ Hz, 3 H, MeCH_2), 4.22 (q, $J = 7.2$ Hz, 2 H, MeCH_2), 5.76 (s, 1 H, $\text{CH}_2=\text{C}$), 5.79 (s, 1 H, $\text{CH}_2=\text{C}$). ^{13}C NMR (CDCl_3): $\delta = -4.1$ (br, SiMe_2), 14.2 (MeCH_2), 17.9 (CMe_3), 25.9 (CMe_3), 60.9 (MeCH_2), 111.5 ($\text{CH}_2=\text{C}$), 151.7 ($\text{CH}_2=\text{C}$), 163.1 ($\text{C}=\text{O}$). ^{29}Si NMR (CDCl_3): $\delta = 26.74$ ($\text{OSiMe}_2\text{Bu-}t$).

4-Methyl-2-*N,N*-bis(*tert*-butyldimethylsilyloxy)amino-3-trimethylsilyloxy-1-ene (1k**).** To a stirred solution of 2-nitro-3-trimethylsilyloxy-4-methylpentane (219 mg, 1 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added DBU (0.18 mL, 1.2 mmol), and the mixture was stirred for 30 min at ambient temperature. Then a solution of TBSCl (181 mg, 1.2 mmol) in CH_2Cl_2 (1 mL) was added, and after 2 h of stirring at ambient temperature the solvents were removed in a vacuum. The residue was diluted with dry C_6H_6 (15 mL), and a white precipitate was filtered off in an Ar atmosphere. The mother liquor was evaporated to give the crude silyl nitronate as a colorless oil. (*Caution! Silyl nitronates are very sensitive to air and they should be submitted to further transformations immediately after the preparation!*)

To the solution of crude silyl nitronate in CH_2Cl_2 (1.7 mL) at 0 °C were added successively Et_3N (0.21 mL, 1.51 mmol) and TBSOTf (0.28 mL, 1.22 mmol). The reaction mixture was stirred for 144 h at ambient temperature, and a separately prepared mixture of citric acid (133 mg, 0.69 mmol), Et_3N (0.56 mL, 4.02 mmol), and CH_2Cl_2 (1.3 mL) was added simultaneously. The resulting mixture was stirred for 5 min, petroleum ether (20 mL) was added, and the resulting emulsion was poured into H_2O (10 mL). The organic layer was washed with saturated aqueous NaHCO_3 (10 mL), H_2O (20 mL), a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (621 mg, 4.5 mmol) in H_2O (60 mL), H_2O (20 mL), and brine (10 mL) and dried over Na_2SO_4 . The solvents and volatile impurities were removed in a vacuum at 40 °C/0.05 mmHg to give 370 mg (78%) of pure **1k** as a colorless oil, which was solidified in a refrigerator at -20 °C to give a colorless solid, mp 27–30 °C.

^1H NMR (CDCl_3): $\delta = 0.11$ (s, 9 H, COSiMe_3), 0.24 (s, 6 H, $\text{NOSiMe}_2\text{Bu-}t$), 0.76 (d, 3 H, CHMe_2 , $^3J = 6.7$ Hz), 0.95 (CMe_3), 0.96 (d, 3 H, CHMe_2 , $^3J = 6.7$ Hz), 2.02 (m, 1 H, CHMe_2), 4.29 (br s, 1 H, CHOSiMe_3), 4.85 (s, 1 H, $\text{C}=\text{CH}_2$), 5.20 (s, 1 H, $\text{C}=\text{CH}_2$). ^{13}C NMR (CDCl_3): $\delta = -3.7$ ($\text{NOSiMe}_2\text{Bu-}t$), 0.5 (COSiMe_3), 14.4 and 20.9 (CHMe_2), 18.2 (CMe_3), 26.3 (CMe_3), 31.1 (CHMe_2), 74.7 (CHOSiMe_3), 99.9 ($\text{CH}_2=\text{CN}$), 161.2 ($\text{CH}_2=\text{CN}$). ^{29}Si NMR (CDCl_3): $\delta = 16.76$ (COSiMe_3), 24.83 (br, $\text{N}(\text{OSiMe}_2\text{Bu-}t)_2$). Anal. Calcd for $\text{C}_{21}\text{H}_{49}\text{NO}_3\text{-Si}_3$: C, 56.32; H, 11.03; Si, 18.81; N, 3.13. Found: C, 56.80; H, 11.40; Si, 18.76; N, 2.95.

Ethyl 4-*N,N*-bis(trimethylsilyloxy)amino-2-methyl-3-butenate (1l**).** To a stirred solution of ethyl 4-nitro-2-methyl-3-butenate (175 mg, 1 mmol) in CH_2Cl_2 (2 mL) at -40 °C were added successively Et_3N (0.35 mL, 2.5 mmol) and TMSBr (0.29 mL, 2.2 mmol). The reaction mixture was stirred for 120 h at -30 °C, and petroleum ether (20 mL) was added dropwise at the same temperature. The cold resulting suspension was poured into H_2O (20 mL), and the organic layer was washed with a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (70 mg, 0.5 mmol) in H_2O (30 mL), H_2O (20 mL), and brine (10 mL) and dried over Na_2SO_4 . The solvents were removed in a vacuum to give 253 mg (79%) of **1l** as yellow oil. The purity is >95% according to ^1H NMR.

^1H NMR (CDCl_3): $\delta = 0.20$ (s, 18 H, SiMe_3), 1.25 (t, $J = 7.2$ Hz, 3 H, MeCH_2), 1.28 (d, $J = 6.7$ Hz, 3 H, MeCH), 3.11 (m, 1 H, MeCH), 4.13 (q, $J = 7.2$ Hz, 2 H, MeCH_2), 5.59 (dd, $J = 8.7$, 13.4 Hz, 1 H, $\text{CH}=\text{CHN}$), 6.06 (d, $J = 13.4$ Hz, 1 H, $\text{CH}=\text{CHN}$). ^{13}C NMR (CDCl_3): $\delta = 0.1$ (SiMe_3), 14.0 (MeCH_2), 17.0 (MeCH), 39.7 (MeCH), 60.5 (MeCH_2), 120.4 ($\text{CH}=\text{CHN}$), 143.3 ($\text{CH}=\text{CHN}$), 173.8 ($\text{C}=\text{O}$). ^{29}Si NMR (CDCl_3): $\delta = 24.10$ (OSiMe_3).

Ethyl 4-*N,N*-bis(*tert*-butyldimethylsilyloxy)amino-2-methyl-3-butenate (1m**).** To a stirred solution of ethyl 4-nitro-2-methyl-3-butenate (175 mg, 1 mmol) in CH_2Cl_2 (2 mL) at 0 °C were added

successively Et_3N (0.32 mL, 2.3 mmol) and TBSOTf (0.49 mL, 2.1 mmol). The reaction mixture was stirred for 3 h at 0 °C, and a separately prepared mixture of citric acid (133 mg, 0.7 mmol), Et_3N (0.56 mL, 4 mmol), and CH_2Cl_2 (1.3 mL) was added simultaneously. The resulting mixture was stirred for 5 min, petroleum ether (10 mL) was added, and the cold resulting emulsion was poured into H_2O (10 mL). The organic layer was washed with saturated aqueous NaHCO_3 (5 mL), H_2O (10 mL), a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (580 mg, 4.2 mmol) in H_2O (50 mL), H_2O (20 mL), and brine (10 mL) and dried over Na_2SO_4 . The solvents were removed in a vacuum to give 343 mg (85%) of pure **1m** as a colorless oil. The purity is >95% according to ^1H NMR with a quantitative standard (CH_2Cl_2).

^1H NMR (CDCl_3): $\delta = 0.17$ (s, 12 H, SiMe_2), 0.91 (s, 18 H, *t*-Bu), 1.25 (t, $J = 7.1$ Hz, 3 H, MeCH_2), 1.27 (d, $J = 7.3$ Hz, 3 H, MeCH), 3.03–3.20 (m, 1 H, MeCH), 4.12 (q, $J = 7.1$ Hz, 2 H, MeCH_2), 5.61 (dd, $J = 8.7$, 13.5 Hz, 1 H, $\text{CH}=\text{CHN}$), 6.08 (d, $J = 13.5$ Hz, 1 H, $\text{CH}=\text{CHN}$). ^{13}C NMR (CDCl_3): $\delta = -4.2$ (SiMe_2), 14.3 (MeCH_2), 17.1 (MeCH), 17.9 (CMe_3), 25.9 (CMe_3), 39.8 (MeCH), 60.6 (MeCH_2), 120.1 ($\text{CH}=\text{CHN}$), 143.3 ($\text{CH}=\text{CHN}$), 173.8 ($\text{C}=\text{O}$). ^{29}Si NMR (CDCl_3): $\delta = 25.77$ ($\text{OSiMe}_2\text{Bu-}t$).

β -*N,N*-[bis(trimethylsilyloxy)amino]-4-nitrostyrene (1n**).** To a stirred solution of 1-(4-nitrophenyl)-2-nitroethane (40 mg, 0.2 mmol) in CH_2Cl_2 (0.4 mL) at -40 °C were added successively Et_3N (0.084 mL, 0.6 mmol) and TMSBr (0.066 mL, 0.5 mmol). The reaction mixture was stirred for 3.5 h at -30 °C, and petroleum ether (10 mL) was added dropwise. The cold resulting suspension was poured into H_2O (10 mL), and the organic layer was washed with a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (30 mg, 0.22 mmol) in H_2O (10 mL), H_2O (10 mL), and brine (5 mL) and dried over Na_2SO_4 . The solvents were removed in a vacuum to give 55 mg (81%) of **1n** as a yellow oil. The purity is >95% according to ^1H NMR.

^1H NMR (CDCl_3): $\delta = 0.27$ (s, 18 H, OSiMe_3), 6.37 (d, $J = 13.9$ Hz, 1 H, $\text{CH}=\text{CHN}$), 6.81 (d, $J = 13.9$ Hz, 1 H, $\text{CH}=\text{CHN}$), 7.44 (d, $J = 8.8$ Hz, 2 H, 4- $\text{NO}_2\text{C}_6\text{H}_4$), 8.16 (d, $J = 8.8$ Hz, 2 H, 4- $\text{NO}_2\text{C}_6\text{H}_4$). ^{13}C NMR (CDCl_3): $\delta = 0.3$ ($\text{N}(\text{OSiMe}_3)_2$), 116.2 ($\text{CH}=\text{CHN}$), 124.2 and 127.1 (2 CH_{Ar}), 142.2 and 146.8 (2 C_{Ar}), 145.5 ($\text{CH}=\text{CHN}$). ^{14}N NMR (CDCl_3): $\delta = -12.1$ (NO_2 , $\Delta\nu_{1/2} \approx 320$ Hz). ^{29}Si NMR (CDCl_3): $\delta = 26.0$ ($\text{N}(\text{OSiMe}_3)_2$).

Mixture of β -Nitro-4-*N,N*-[bis(trimethylsilyloxy)amino]styrene (1n'**) and **1n**.** To a stirred solution of 1-(4-nitrophenyl)-2-nitroethane (40 mg, 0.2 mmol) in CH_2Cl_2 (0.4 mL) at -40 °C were added successively Et_3N (0.072 mL, 0.52 mmol) and TMSOTf (0.085 mL, 0.45 mmol). The reaction mixture was stirred for 3 h at -30 °C, petroleum ether (10 mL) was added dropwise, and the excess of the silylating agent was quenched by addition of MeOH (0.02 mL, 0.49 mmol) with vigorous stirring. The cold resulting emulsion was poured into H_2O (10 mL), and the organic layer was washed with a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (30 mg, 0.22 mmol) in H_2O (10 mL), H_2O (10 mL), and brine (5 mL) and dried over Na_2SO_4 . The solvents were removed in a vacuum to give 55 mg of a mixture of **1n'** and **1n** in a ratio of 2.7:1 as a yellow oil. The purity is >95% in both cases according to ^1H NMR.

(**1n'**) ^1H NMR (CDCl_3): $\delta = 0.21$ (s, 18 H, OSiMe_3), 7.39 (d, $J = 8.8$ Hz, 2 H, 4-($\text{Me}_3\text{SiO})_2\text{NC}_6\text{H}_4$), 7.52 (d, $J = 8.8$ Hz, 2 H, 4-($\text{Me}_3\text{SiO})_2\text{NC}_6\text{H}_4$), 7.56 (d, $J = 13.8$ Hz, 1 H, $\text{CH}=\text{CHNO}_2$), 7.98 (d, $J = 13.8$ Hz, 1 H, $\text{CH}=\text{CHNO}_2$). The irradiation of the protons of the ($\text{Me}_3\text{SiO})_2\text{N}$ group (0.21 ppm) leads to the enhancement of the signals of the aryl protons at 7.39 ppm. ^{13}C NMR (CDCl_3): $\delta = 0.4$ (OSiMe_3), 120.9 and 129.8 (2 CH_{Ar}), 136.7 ($\text{CH}=\text{CHNO}_2$), 138.5 ($\text{CH}=\text{CHNO}_2$), 127.8 and 158.5 (2 C_{Ar}). ^{14}N NMR (CDCl_3): $\delta = -11.1$ (NO_2 , $\Delta\nu_{1/2} \approx 520$ Hz, for both **1n'** and **1n**). ^{29}Si NMR (CDCl_3): $\delta = 26.24$ (OSiMe_3).

β -*N,N*-[bis(*tert*-butyldimethylsilyloxy)amino]-4-nitrostyrene (1o**).** To a stirred solution of 1-(4-nitrophenyl)-2-nitroethane (40 mg, 0.2 mmol) in CH_2Cl_2 (0.4 mL) at -40 °C were added successively Et_3N (0.084 mL, 0.6 mmol) and TBSOTf (0.1 mL, 0.44 mmol). The reaction

Table 6. Crystal Data and Structure Refinements of **1k**, **1o**, and **6**

ID code	1k	1o	6
empirical formula	C ₂₁ H ₄₉ NO ₃ Si ₃	C ₂₀ H ₃₆ N ₂ O ₄ Si ₂	C ₁₂ H ₁₀ N ₂ O ₂
diffractometer	Smart CCD	Syntex P2 ₁	Smart CCD
fw	447.88	424.69	214.22
temp, K	110	190	110
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triglinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
unit cell dimens			
<i>a</i> , Å	11.961(3)	12.149(4)	9.234(2)
<i>b</i> , Å	10.926(3)	14.155(4)	9.254(2)
<i>c</i> , Å	22.229(6)	14.586(5)	12.706(3)
α, deg			73.199(4)
β, deg	102.837(7)	100.34(3)	76.044(5)
γ, deg			70.494(4)
vol, Å ³	2832.4(13)	2467.6(14)	967.1(4)
Z	4	4	4
density(calcd), g/cm ³	1.050	1.143	1.320
abs coeff, mm ⁻¹	0.186	0.169	0.094
<i>F</i> (000)	992	920	408
cryst size, mm ³	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.2
scan type	ω-scan with 0.3° step in ω and 10 s of exposure per frame	θ/2θ	ω-scan with 0.3° step in ω and 10 s of exposure per frame
2θ _{max} , deg	55	55	50
total no. of reflns	19878	5934	7865
no. of unique reflns	6510 [R(int) = 0.0387]	5674 [R(int) = 0.0555]	3334 [R(int) = 0.0404]
no. of reflns with <i>I</i> > 2σ(<i>I</i>)	4501	3434	2766
completeness, %	99.5	99.4	98.2
no. of params	450	397	362
final <i>R</i> (<i>F</i> _{hkl}): <i>R</i> 1	0.0528	0.0463	0.0758
wR2	0.1457	0.1117	0.1986
GOF	0.984	0.852	1.105
largest diff peak and hole, e/Å ³	0.880 and 0.260	0.574 and 0.323	0.540 and 0.431

mixture was stirred for 3 h at -30 °C, and a separately prepared mixture of citric acid (27 mg, 14 mmol), Et₃N (0.12 mL, 0.86 mmol), and CH₂Cl₂ (0.3 mL) was added simultaneously. The resulting mixture was stirred for 5 min, petroleum ether (10 mL) was added, and the cold resulting emulsion was poured into H₂O (10 mL). The organic layer was washed with saturated aqueous NaHCO₃ (5 mL), H₂O (10 mL), a solution of NaHSO₄·H₂O (30 mg, 0.22 mmol) in H₂O (10 mL), H₂O (10 mL), and brine (5 mL) and dried over Na₂SO₄. The solvents were removed in a vacuum, and the residue was recrystallized from petroleum ether to give 67 mg (79%) of analytically pure **1o** as yellow prisms, mp 95–99 °C.

¹H NMR (CDCl₃): δ = 0.23 (s, 12 H, OSiMe₂), 0.95 (s, 18 H, *Bu*-*t*), 6.41 (d, *J* = 13.9 Hz, 1 H, CH=CHN), 6.84 (d, *J* = 13.9 Hz, 1 H, CH=CHN), 7.42 (d, ³*J* = 8.8 Hz, 2 H, 4-NO₂C₆H₄), 8.16 (d, ³*J* = 8.8 Hz, 2 H, 4-NO₂C₆H₄). ¹³C NMR (CDCl₃): δ = -3.9 (SiMe₂), 18.2 (CMe₃), 26.1 (CMe₃), 115.9 (CH=CHN), 124.2 and 126.9 (2 CH_{Ar}), 142.3 and 146.8 (2 C_{Ar}), 145.5 (CH=CHN). ¹⁴N NMR (CDCl₃): δ = -11.2 (NO₂, Δ*ν*_{1/2} ≈ 510 Hz). ²⁹Si NMR (CDCl₃): δ = 27.44 (OSiMe₂-*Bu*-*t*). Anal. Calcd for C₂₀H₃₆N₂O₄Si₂: C, 56.56; H, 8.54; Si, 13.23; N, 6.60. Found: C, 56.92; H, 8.54; Si, 13.05; N, 6.55.

Crystal Structure Data for 1k, 1o, and 6. The crystals of **1o** and **6** were crystallized from hexane and MeOH, respectively, while for **1k** the crystal has been taken from the sample solidified in the freezer. The crystallographic data for **1k**, **1o**, and **6** are represented in Table 6. Structures were solved by direct methods and refined by full-matrix least-squares against *F*² in the anisotropic (H atoms isotropic) approximation using the SHELXTL-97 package. The analysis of the Fourier electron density synthesis has revealed that in **6** one of the independent molecules is disordered (superposition with occupancies 0.33 and 0.66). The positions of the hydrogen atoms in **1k**, **1o**, and **6** were calculated from the geometrical point of view and refined in the riding approximation.

Dynamic NMR Measurements. The dynamic NMR measurements have been performed on Bruker AM-300 and Bruker DRX-500

instruments. The values of the activation parameters have been obtained by acquiring ¹³C{¹H} or ²⁹Si (INEPT) spectra at different temperatures followed by complete line shape analysis of each spectrum by the Bloch equation modified for the chemical exchange (cross-relaxation times have been measured for each spectrum and used as the constants; resonance frequencies, intensities, and rate constants have been iterated).⁴⁶ Then the least-squares linear fit in coordinates 1/*RT* and ln(*k*/*T*) for the function *Y* = *aX* + *b* have been performed to give the values of the activation parameters and Δ*G*[‡] = Δ*H*[‡] - *T*Δ*S*[‡].

UV Spectral Measurements. UV spectra were recorded on a Specord UV-vis instrument using hexane solutions of **1n**, **1o**, and **6**. The absorption band parameters (λ_{max} and log ε) were calculated taking the average value of three measurements.

Acknowledgment. This work has been supported by the Russian Basic Research Foundation (Grant Nos. 99-03-32015 and 01-03-06027) and Federal Program Integration (Project Nos. A0082 and B0062). This paper is dedicated to Prof. V. A. Tartakovsky on the occasion of his 70th birthday.

Supporting Information Available: Complete data of DFT PBE/TZP calculations of **1a** and **2–6**, characterization of BENAs **1a–1g**, **1i**, and **1j** and enamine **6**, CIF files and complete crystal structure data for **1k**, **1o**, and **6**, general procedure for the measurement of Δ*G*[‡] by dynamic NMR, rate constants of the dynamic process at different temperatures for **1b**, **1d**, **1f**, **1h**, **1j**, **1k**, **1l**, **1m**, **1o**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA026548I

(46) The DYNMNR program has been used for iteration: Shastin, A. V.; Godovikova, T. I.; Golova, S. P.; Povorin, M. V.; Dmitriev, D. E.; Dekaprilevich, M. O.; Strelenko, Yu. A.; Struchkov, Yu. T.; Khmelnytsky, L. I.; Korsunsky, B. L. *Khim. Geter. Soed.* **1995**, *5*, 679 (in Russian); *Chem. Abstr.* **1996**, *124*, 145027c.