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Dedicated to Academician M. G. Voronkov on occasion of his 80th birthday

Molecular and Electronic Structure of Trimethylsilylpropiolamides

G. I. Sarapulova, M. V. Andreev, L. P. Safronova, and A. S. Medvedeva

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia

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Abstract—The specific features of molecular and electronic structure of trimethylsilylpropiolic acid amides were studied by means of IR spectroscopy and quantum chemistry (AM1). The competition between p,π-conjugation in the amide fragment and π,π-conjugation in the ethynylcarbonyl group C≡C–C=O was established. The prevailing conformers were revealed, their geometrical parameters were established, the barriers to internal rotation around the amide C–N bond were calculated for acyclic (13 kcal mol^{-1}) and heterocyclic (8.12 kcal mol^{-1}) amides.

We formerly prepared biologically active α,β-silicoacetylene amides, promising reagents for the fine organic synthesis [1]. By IR spectroscopy was demonstrated the higher basicity of the carbonyl oxygen in these amides as compared with that in acetylene and siliconacetylene ketones [2]. The mass-spectrometric investigation of trimethylsilylpropiolic acid N-arylamides showed that the $Si–C_{sp}$ bond was resistant to the electron impact and that the fragmentation of N-arylamides and the N-unsubstituted amide occurred along different patterns [3]. However the study did not concern the geometrical structure, conformational features, and electronic structure of trimethylsilylpropiolamides that combined several functional groups and conjugation types (between silicon atom and the triple bond, between double C=C bond and C=O group, between the unshared electron pair of nitrogen and C=O group). Taking into account the lability of the amide group properties affected by the surrounding functional groups we might presume that the compounds would have unexpected characteristics and reactivity.

The target of the present study was investigation of the specific features in molecular and electronic structure by comparison of new compounds, *N*,*N*-diethyl-3-trimethylsilyl-2-propiolamide (**I**) and its heterocyclic analog, 1-morpholino-3-trimethylsilyl-2-propyn-1-one (**II**), by means of IR spectroscopy and quantum-chemical calculations [4].

For both compounds the ν(C=O) value is by 25–30 cm^{-1} lower than for *N*,*N*-diethylacetamide (1655 cm^{-1}) and *N*,*N*-dimethylacetamide (1660 cm^{-1}); the absorption is represented by doublet bands [5–7]. At the same time the ν(C=O) for heterocyclic amide **II** is somewhat higher than for acyclic compound **I** (Table 1).

The data on transfer of substituents effect through the multiple bonds C=C and C≡C to the vibration frequency of C=O group was summarized [14, 15] in correlation equations of Hammett’s type with separate accounting for σ and π-effects, field effects, mesomeric effects, and effects of direct polar conjugation. It was shown that introduction of electron-donor substituents, in particular, $SiMe_3$ (σ^* –0.76), in the series of acetylene ketones resulted in reduction of ν(C=O). In the α-acetylene organoelemental compounds also operates the electron-donor effect of σ,π-conjugation that together with the discussed in the literature p_π–d_π effect may be described with a constant σ_R [15]. This effect obviously also contributes to the final value of ν(C=O).

The combined treatment of the mentioned effects by an example of our models provides a quite plausible base for qualitative characteristic of the behavior of carbonyl group frequency in the spectra of compounds **I, II** in comparison with *N*,*N*-dimethylacetamide, namely, explain its reduction. The ν(C=O) values in the spectra of compounds **I** and **II** are sensitive to the polarity of medium and to molecular surroundings.

At replacement of a solvent the intensity of components of the C=O absorption band undergo redistribution (in going from KBr/microfilm to

Table 1. Analyzed frequencies of absorption bands in the IR spectra of *N*,*N*-diethyl-3-trimethylsilyl-2-propiolamide (**I**) and *N*-morpholino-3-trimethylsilyl-2-propiolamide (**II**)[a]

Compd. no.	$\nu(C=O)$, cm^{-1}				$\nu(C=N)$, cm^{-1}			
	film/KBr	CCl_4	CH_3CN	decene	film/KBr	CCl_4	CH_3CN	decene
I	1630	1635	1626 br	1636	1312	1315	1302 br	1317
	1640 sh	1645 sh		1645	1306 sh	1307 sh		1306
II	1632	1638	1630 br	1642	1300 br	1308	1302 br	1308
	1646 sh	1648		1654		1298		1298

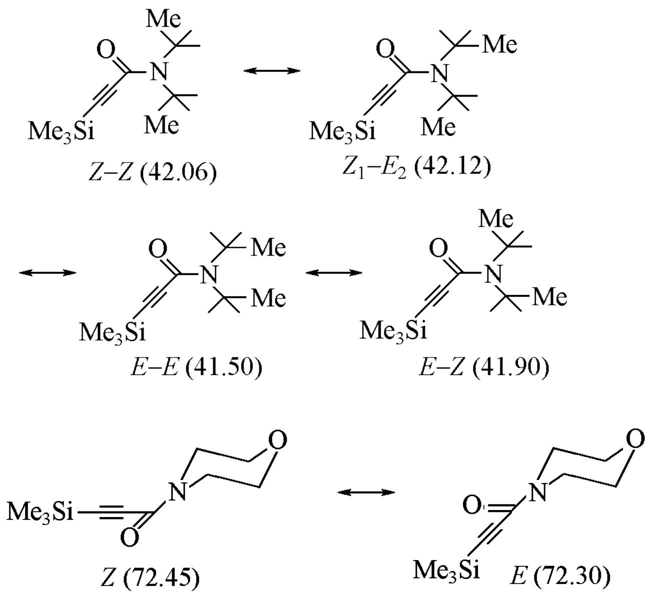
[a] The bands in IR spectra of compounds **I, II** are assigned to vibration types taking into account the data from [8–13].

decene). The stretching vibration bands of amide C–N bond also appear as doublets. In order to elucidate the cause of this structure in these C–N bands the temperature dependence of the IR spectra was measured in the range from –90 (in CH_2Cl_2) to 150°C (in decene). The observed changes we interpreted as conformational transformations basing on the common spectroscopic criteria [16]: the heating of solutions causes the intensity increase in the high-frequency part of the $\nu(C=O)$ doublet and in the low-frequency part of the $\nu(C–N)$ doublet. At –90°C in dichloromethane was also registered the "freezing off" of the high-frequency component in the $\nu(C=O)$ doublet due to prevailing formation of the most stable conformation of the labile amide **I, II** molecules. (The variable-temperature measurements were always performed in both directions). From the temperature dependence of the optical density in the doublet bands $\nu(C=O)$ was experimentally determined (along van't Hoff formula) the energy difference of the existing conformers in compounds **I, II** $\Delta\Delta H$ that did not exceed 0.5 kcal mol^{-1}.

In order to elucidate the molecular and electronic structure of the most abundant conformers under the experimental conditions and to assign properly the observed IR absorption bands to definite forms we performed quantum-chemical calculations along AM1 procedure. We calculated the structures that were to the highest degree responsible for the change in the energy of the internal rotation in the molecules. For compound **I** four structures were considered taking into account the rotation around three bonds C–N, N–C^1, N–C^2 (Schemes 1 and 2).

The values in parentheses correspond to formation enthalpy $-\Delta 1H_f$ (kcal mol^{-1}).

Scheme 1.

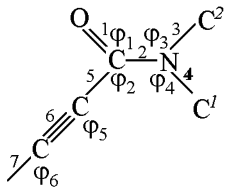


Z–Z (42.06) *Z_1–E_2* (42.12)

E–E (41.50) *E–Z* (41.90)

Z (72.45) *E* (72.30)

Scheme 2.



For compound **I** energetically preferred forms are Z_1–Z_2 and Z_1–E_2. Similar small difference in conformations energy was previously observed in the study of conformational isomerism in amides [17, 18]. This is manifested in virtually equal abundance of the conformers at room temperature and consequently in similar intensity of the doublet components. (At large difference in free energies of conformers one of the conformations prevails [19]). At "freezing off" in the IR spectrum of compound **I** in dichloromethane remains the low-frequency component of the doublet $\nu(C=O)$ at 1639 cm^{-1} that

Table 2. Comparative values of geometrical and spectral parameters of trimethylsilylpropiolamides **I** and **II** and *N,N*-diethylacetamide (**III**)[a]

Compd. no.	Bond length C–N, Å	Bond order C–N	Bond length C–C,[a] Å	ν(C–N) cm^{-1}
I	1.380	1.08	1.44	1317, 1306
II	1.392	1.06	1.44	1308, 1292
III	1.340	1.25	1.54	1330, 1315

[a] The C–C bond length corresponds to l_5 according to Scheme 1.

Table 3. Geometrical parameters of two prevailing conformers of compounds **I** and **II** according to Aμ1 calculations[a]

Parameter	**I**		**II**	
	1	2	1a	2a
Bond length, Å				
l_1	1.25	1.25	1.25	1.25
l_2	1.39	1.39	1.39	1.39
l_5	1.44	1.44	1.44	1.44
l_6	1.20	1.20	1.20	1.20
l_7	1.74	1.74	1.80	1.80
Bond order				
b_1	1.74	1.74	1.75	1.75
b_2	1.08	1.08	1.06	1.06
b_6	2.86	2.86	2.86	2.86
b_7	0.78	0.77	0.8	0.8
Bond angle, deg				
η_1	121	121	121	121
η_2	118	118	120	120
η_3	120	120	122	120
η_4	122	122	121	123
η_5	177	177	177	177
η_6	179	179	180	180
Torsion angle, deg				
θ_{1-3}	0.1	6	170	–12
θ_{1-4}	–177	174	–1	–174
θ_{5-7}	–32	72	–42	–35
θ_{2-6}	178	–170	52	–178
θ_{1-6}	–4	12	–128	1

[a] Notation of parameters as in Scheme 2.

should be assigned to the Z_1–E_2 form as possessing the least energy and therefore the most stable.

In the case of the *N*-heterocyclic amide **II**, a model of *Z,E* isomerism at the amide bond, the ring conversion and the related process of the nitrogen inversion should be taken into consideration. There are known numerous data on configurational stability of the nitrogen atom in heterocycles, and it was also established that the ring occurred in the *chair* conformation with the equatorial orientation of the substituent attached to the nitrogen. This conformation is retained both in solid state and in solutions, and the thermodynamically stable *chair* form arises due to fast inversion at the pyramidal nitrogen atom [20, 21].

The calculation of model structures morpholine and *N*-acetylmorpholine demonstrated the energetical feasibility of the equatorial orientation of the functional groups N–H and H–C=O, the *chair* form of the ring, and significant thermodynamic disadvantage of the hypothetical axial orientation of the acetyl group. Therefore we subjected to analysis only the structures with an equatorial orientation of the $SiMe_3C{\equiv}C{-}C{=}O$ fragment in compound **II** along Scheme 1. The enhanced value of the vibrational frequency of the C–N bond in compound **II** (to 1317 cm^{-1}) confirms the sp^2-hybridization of the valence orbitals of nitrogen [12].

The difference between formation energy of the two forms of compound **II** is also negligible (about 0.15 kcal mol^{-1}). Similarly to compound **I** the structure *Z* with the minimal formation energy should be assigned to the more stable form of compound **II** molecule; the carbonyl absorption band of this form is that remaining on “freezing off” in dichloromethane, 1645 cm^{-1}.

The behavior of doublet components of the ν(C–N) band at variable temperature of solutions also suggests conformational transitions in amides **I** and **II**. However the temperature dependence of intensity of the doublet components for C–N bond vibrations is reverse to that of C=O bond: at decreasing temperature dominates the high-frequency component.

The barriers to conformational isomerization Δ*G* in trimetylsilylpropiolamides were calculated from the angle dependence (with respect to the central C–N bond) of the formation enthalpy of the molecules. The barriers in both cases were considerably lower than for common amides with no specific groups as substituents: 13.2 (**I**), 8.12 (**II**) kcal mol^{-1}. It is known [22] that with substituents favoring electrons delocalization the barrier of rotation around the amide bond notably decreases: for $HC(O)NMe_2$ 18.3, for $ÞhC(O)NMe_2$ 7.7, for $CH_2{=}CHC(O)NMe_2$ 6.8 kcal mol^{-1}. In our case the considerable lowering of the barrier should be ascribed to the effect of the trimethylsilylethynyl substituent and the associated therewith delocalization of the electron density in the amide fragment.

Note the considerable shortening of the C–C bond (l_5), the elongation of the C–N bond (l_2) and decreased order of this bond (b_1) in amides **I** and **II** as compared to *N,N*-diethylacetamide (**III**) [12] (Table 2). Besides for such combination of bonds were determined the following lengths: C–C=C 1.5, C–C≡C 1.46, C–C=O 1.5, aryl-C=O 1.49 Å respectively [23]. The comparative analysis of these data evidences the reduced amide *p*,π-conjugation in compounds **I** and **II** under study as a result of competing π,π-conjugation. The degree of violation of conjugation in the amide moiety is greater in the heterocyclic than in the acyclic compound.

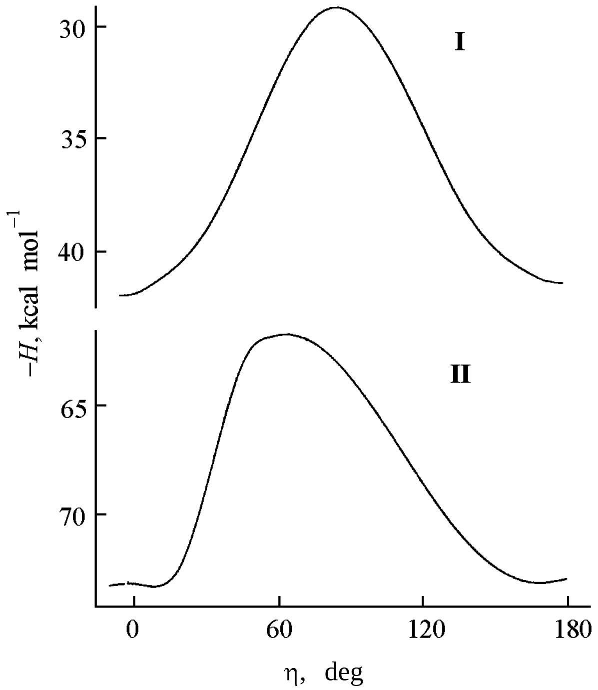
The torsion angles in the amide fragment of acyclic amide **I** do not exceed 2–6 deg (Table 3). However these angles in heterocyclic amide **II** are significantly larger and attain 12 deg evidencing its worse coplanarity. It is just the cause of higher value of ν(C=O) in the IR spectra of amide **II** than in those of amide **I**. To this also corresponds the larger bond order (b_1) of the carbonyl group in the heterocyclic amide.

The curve of potential function for internal rotation around the central C–N bond (see figure) for the ground state of acyclic amide **I** is relatively even and symmetrical indicating the predominant contribution of a single effect.

At the same time the potential energy surface for heterocyclic amide **II** is asymmetrical and covered with hills and hollows that at sections with the coordinate planes will appear as wells and barriers separating them. This form of potential curve is due to complicated interactions in the molecule and to contribution of several effects: concerted process of ring conversion, sufficiently fast inversion of the nitrogen atom, and the rotation around the amide bond.

EXPERIMENTAL

IR spectra of compounds **I** and **II** were obtained on spectrometer Specord 75IR from thin films (**I**), KBr pellets (**II**), and also from solutions in CCl_4, CH_3CN, and decene in the concentration range 0.4–0.001 mol l^{-1}. The variable-temperature measurements were carried out in a cell from Karl Zeiss Company equipped with a graduated thermocouple. The measurement scale in the range of ν(C=O) and ν(C–N) 200/100 cm^{-1}, time of measurement 22 min, resolution 1 cm^{-1}. Compounds **I** and **II** were obtained by procedure [1].



Potential function for internal rotation around C–N bond in trimethylsilylpropiolamides **I** and **II**.

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