Dipole moments and molecular conformations of *O*-vinyl- and *O*-ethylacetoximes in solutions

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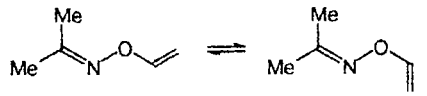
Dipole moments of the molecules of *O*-vinyl- and *O*-ethylacetoximes in octane and THF were measured at different temperatures. In octane, the equilibrium mixture of stable *O*-vinylacetoxime conformers consists of forms with different polarity. Polarity of these conformers, which are due to rotation about the C—O and N—O bonds, is mainly determined by the relative position of the lone electron pairs of nitrogen and oxygen atoms. The fraction of the polar conformer increases as temperature increases, as well as on going from octane to THF. Saturation of the vinyl group in the *O*-vinylacetoxime molecule nearly halves the molecular dipole moment in the nonpolar medium, which radically differentiates this compound from vinyl ethers.

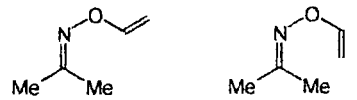
Key words: *O*-vinylacetoxime, *O*-ethylacetoxime, dipole moment, quantum-chemical calculations, conformation.

Poorly studied *O*-vinyloximes,[1—4] the closest analogs of vinyl and divinyl ethers, are new convenient objects for studying hindered internal rotation about the N—O and C—O bonds, which is of interest for theoretical organic chemistry. Recently, conformational isomerism of *O*-vinylacetoxime (**1**) was studied by quantum-chemical methods and IR and NMR spectroscopy.[5] Calculations in the 6-311G(d,p) basis set showed that in the gas phase the molecules of this compound exist as an ensemble of two stable planar conformers, *ap,ap* and *ap,sp* (*ap* means antiperiplanar and *sp* means synperiplanar). Interconversions between these conformers occur due to internal rotation of the vinyl group about the C—O bond.



1 (*ap,ap*) **1** (*ap,sp*)

The energy difference between the lowest energy levels of the conformers is 0.62 kcal mol^{-1} (calculations in the 6-311G(d,p) basis set).[5] At 25 °C, the fractions of the *ap,sp*- and *ap,ap*-forms are 18 and 82%, respectively. The other two planar conformers (*sp,ap* and *sp,sp*) or their possible nonplanar forms (*ac* and *sc*) were not found.



1 (*sp,ap* (*ac*)) **1** (*sp,sp* (*sc*))

The band of C=C bond stretching vibrations, observed in the IR spectra of *O*-vinylacetoxime in the liquid and solid state and in its $CHCl_3$ solution is split into two components. The vibration with the lower frequency was tentatively assigned[5] to the *cis*-rotamer (*ap,sp*). No rotational isomerism is observed in the ^1H and ^{13}C NMR spectra of *O*-vinylacetoxime.[5]

In this work, the dipole moments of *O*-vinylacetoxime (**1**) and *O*-ethylacetoxime (**2**) in octane and THF were studied at different temperatures. The possibility for hindered internal rotation about the N—O bond to occur in molecule **1** was considered.

Calculation procedure and Experimental

Semiempirical quantum-chemical calculations were performed by the CNDO/S and AM1 [6] methods. *Ab initio* calculations were carried out using the GAMESS-95 program package[7] in the 6-31G* and 6-311G(2d,1p) basis sets.

The potential energy surface of internal rotation of the *O*-vinylacetoxime molecule was studied by the AM1 method with an increment of 15°. The search for stable conformers was performed with full geometry optimization.

Dielectric constants (ε) of the solutions were measured on a Sh2-5 instrument (OKBA Joint-Stock Company, Angarsk, Russian Federation) operated at a frequency of 1 MHz. The densities of the solutions were determined pycnometrically and the refractive indices were determined on an IRF-454BM refractometer. The dipole moments (μ) in nonpolar and polar solvents were calculated by the Higasi formula[8] and by the Onsager formula,[9] respectively. The measurement error of μ values was ±0.02 D.

O-Vinyloximes were synthesized following the known procedure.[4] Purity of the compounds (99.5% for **1** and **2**) was monitored by GLC and ^1H NMR and IR spectroscopy.

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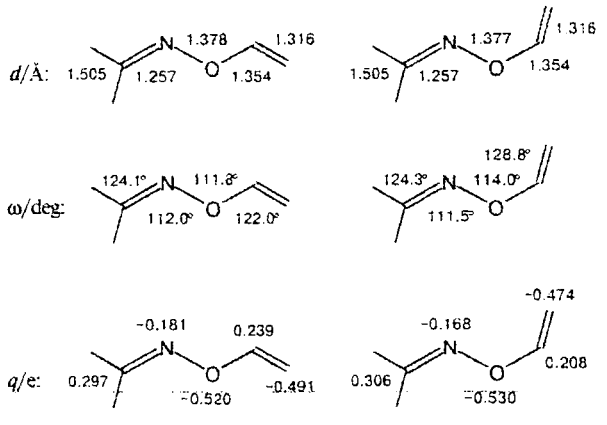
Results and Discussion

Quantum-chemical calculations. Semiempirical AM1 calculations of molecule **1** revealed four minima corresponding to four stable rotamers on the potential energy surface of internal rotation. Two most stable isomers, the *ap,ap*- and *ap,sp*-conformers, are planar (with respect to positions of heavy atoms). The nonplanar *sp,ac*-conformer (the C=N—O—C (θ_1) and N—O—C=C (θ_2) torsion angles are 21° and −143°, respectively) has an "intermediate" stability. The *sc,sp*-conformer is the most energetically unfavorable. *Ab initio* calculations of molecule **1** in the 6-311G(2d,1p) basis set revealed only two stable (*ap,ap* and *ap,sp*) conformers, which is in agreement with the results of calculations[5] in the 6-311G(d,p) basis set. We failed to find minima in the vicinity of the points that, according to AM1 calculations, correspond to *sc,sp*- and *sp,ac*-conformations. The *ap,ap*-conformer appeared to be more stable than the *ap,sp*-form: the energy difference between them is 0.69 kcal mol^{-1} (*cf.* 0.62 kcal mol^{-1} reported in Ref. 5). According to calculations in the 6-311G(2d,1p)//6-31G* basis set, the *ap,ap*-conformer is more energetically preferable by 0.94 kcal mol^{-1}. Since the results of all *ab initio* calculations nearly quantitatively coincide with one another and reproduce well the energetics of internal rotation,[10] it may be concluded that we obtained an additional evidence of preferableness of the *ap,ap*-conformer in the gas phase. The geometric parameters (bond lengths (*d*) and bond angles (ω)) calculated in the 6-31G* basis set and the charges on the atoms (*q*) of stable rotamers of **1** are shown below:



1 (*ap,ap*) **1** (*ap,sp*)

As can be seen, polarity of the bonds in these conformers decreases in the series C—O > C=C ≥ N—O.

Dipole moments. The dipole moment of *O*-vinylacetoxime (**1**) in octane at 25 °C is 1.91 D (Tables 1 and 2). The experimental (μ_{exp}) value is in fairly good agreement with the values calculated for both *ap,ap*- and *ap,sp*-conformers (μ_{calc}, see Table 1). According to the data of the most accurate calculations, the μ values

Table 1. Calculated dipole moments (μ_{calc}) of possible conformers of *O*-vinyl- (**1**) and *O*-ethylacetoximes (**2**) and their analogs, vinyl ethers **3**—**5**

Calculation procedure	μ_{calc}/D			
	ap,ap	*ap,sp*	*sp,ap*	*sp,sp*
O-Vinylacetoxime (**1**) (μ_{exp} = 1.91 D)[a]				
Vector scheme of calculations (μ_O)	1.2	1.2	3.4	3.4
CNDO/S[b]	2.09	2.43	4.61 (*sp,ac*) [21°; −143°][c]	3.57 (*sc,sp*) [63°; 6°][c]
CNDO/S[d]	2.42	2.69		
6-31G*	2.01	2.07		
6-311G(2d,1p)[d]	2.15	2.16		
O-Ethylacetoxime (**2**) (μ_{exp} = 1.04 D)				
Vector scheme of calculations (μ_O)	1.4	1.4	3.2	3.2
CNDO/S[b]	1.28	1.18	4.06	4.13 (*sp,sc*) [28°; 68°][e]
Divinyl ether (**3**) (μ_{exp} = 1.10 D[11])				
Vector scheme of calculations (μ_O)	1.3	1.3		1.3
CNDO/S[b]	2.11	1.18—1.23 [0 to −15°; 180—150°][f]		0.45 [30°; 27°][f]
CNDO/S[g]	2.05	1.24 (*sp,ac*) [−13°; 145°][f]		0.47
Ethyl vinyl ether (**4**) (μ_{exp} = 1.19 D[11])				
Vector scheme of calculations (μ_O)	1.3	1.3	1.3	1.3
CNDO/S[b]	2.23	2.28 (*ap,sc*) [−174°; 72°][h]	1.02	1.03 (*sp,sc*) [0°; 79°][h]
tert-Butyl vinyl ether (**5**) (μ_{exp} = 1.79 D[11])				
Vector scheme of calculations (μ_O)		1.3		1.3
CNDO/S[b]		1.88 (*ac*) [103°][i]		1.05 (*sp*)

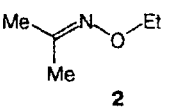
[a] In octane, at 25 °C (see also Table 2).
[b] The geometry was optimized by the AM1 method.
[c] The C=N—O—C and N—O—C=C torsion angles, respectively.
[d] The geometry was obtained by optimization in the 6-31G* basis set.
[e] The C=N—O—C and N—O—C—C torsion angles, respectively.
[f] The C=C—O—C and C—O—C=C torsion angles, respectively (experimental geometry[12]).
[g] The geometry was optimized by the *ab initio* method in the 6-31G basis set.[20]
[h] The C=C—O—C and C—O—C—C torsion angles, respectively.
[i] The (C=C—O—C) torsion angle.

Table 2. Experimental dipole moments (μ_{exp}) of *O*-vinyl- and *O*-ethylacetoximes

Oxime	Solvent	T/°C	μ_{exp}/D
O-Vinylacetoxime (**1**)	Octane	−30	1.85
		25	1.91
		50	1.96
	THF	15	2.21
		25	2.14
O-Ethylacetoxime (**2**)	Octane	5	1.04
		25	1.04
		50	1.04
O-Vinylacetophenoxime (**6**)	THF	25	2.54
	Octane	25	2.10

for these conformers virtually coincide. Hence, it is impossible to distinguish these two rotamers using measurements of the dipole moment of oxime **1** in nonpolar solvents.

The measured dipole moment increases by ~0.1 D (see Table 2) as the temperature of the solution of oxime **1** in octane increases from −30 to 50 °C. The observed changes in the μ values by a factor of 2.5 and more exceed the measurement error and are well reproducible, which makes it possible to consider these results as a functional dependence. Such a $\mu = f(T)$ dependence can be explained by two reasons. The first reason is that the fractions of the conformations are redistributed "in favor" of another form with higher polarity, which is formed upon rotation of molecular fragments about the N—O bond (see Table 1). The second reason is that the population of torsional vibrational levels in one of the conformations changes as temperature increases, which means that the equilibrium state of the vibrating group is disturbed as the molecular configuration approaches *sp,ac*- or *sc,sp*-conformations with higher polarity (in the case of vibration about the N—O bond) or a form characterized by a 90° angle of rotation about the C—O bond. The following explanation makes it possible to rule out the latter case. The orthogonal conformation of *O*-vinylacetoxime **1**, in which no p—π-interaction between the O atom and the C=C bond occurs or, at least, it is much weaker than in the planar conformation, can be simulated taking the molecule of oxime **2** as an example. From the data on the dipole moment of oxime **2** in octane (see Table 2) it follows that the polarity of molecule **1** becomes nearly halved as the vinyl group is replaced by the ethyl group. The dipole moments calculated in the semiempirical CNDO/S approximation also sharply decrease in the series of *ap,ap*- and *ap,sp*-conformers of oximes **1**, **2** (see Table 1), which rules out the above interpretation of the temperature dependence.



2

Let us consider some consequences of the rotation of molecular fragments about the O—N bond. According to calculations using the vector-additive scheme, the *gauche*-conformer of oxime **1**, formed by rotating the azomethine group by 90°, has a dipole moment of 2.2 D, which is intermediate between the μ values for, *e.g.*, *ap,ap*- and *sp,ap*-conformers. In principle, this makes it possible to explain the dependence of μ on T in octane (however, not in THF, see Table 2).

Let us consider in detail a hypothesis according to which relative stability of rotamers of *O*-vinylacetoxime (**1**) is determined by electrostatic and electrodynamic interactions with the medium. Within the framework of such a scheme it is apparent that *ap,ap*- and *ap,sp*-conformers with lower polarity must be more stable in the gas phase. In these conformers the lone electron pairs (LEP) of oxygen and nitrogen atoms are at the longest distance, while corresponding μ_{LEP} are directed oppositely. At the same time, the *sp,ac*- and *sc,sp*-conformers are unstable in the gas phase because of electrostatic repulsion of the LEP of oxygen and nitrogen atoms and have higher polarity owing to their position on one side of the N—O bond. Larger dipole moments of these conformers favor their additional stabilization due to interaction with the medium. A simple theoretical estimate of the polarity of the conformers was made in the vector-additive scheme approximation. The dipole moments of *ap,sp*- and *ap,ap*-conformers were estimated at 1.2 D, while those of *sp,ap*- and *sp,sp*-forms were estimated at 3.4 D (see Table 1), which is in qualitative agreement with the aforesaid. Both *ab initio* and semiempirical calculations show that the μ values of stable *ap,sp*- and *ap,ap*-conformers of oxime **1** are close. According to the data of these calculations, the dipole moments of unstable (in the gas phase) conformers of **1** are larger than those of stable forms (see Table 1).

In principle, the experimental μ value of compound **1** does not contradict the conclusion[5] about thermodynamic equilibrium of the two conformers of the molecule with the same dipole moments. However, as was shown above, it is impossible to explain the dependence of μ on temperature (see Table 2) using this model. Taken together, experimental data can be rationalized by assuming that the third conformer with a larger dipole moment or a mixture of two conformers with different dipole moments are present in solutions. It is likely that the conformer with the larger dipole moment is stabilized in solution due to interaction with the medium. In turn, the efficiency of this interaction must increase as the polarity of the medium increases. In fact, the experimental μ value of oxime **1** in THF increases (see Table 2). Hence, the hypothesis for the presence of the third conformer with higher polarity, whose fraction increases in the polar solvent and as temperature increases in the nonpolar medium, is adequate to the experimental data.

The dipole moment of *O*-ethylacetoxime (**2**) in octane is independent of temperature (see Table 2), though this molecule can also have four conformations. This makes it possible to conclude that only two equilibrium

forms (*ap,sp* and *ap,ap*) with close μ values (see Table 1) are present in octane. Thus, oximes **1** and **2** have identical molecular conformations in octane; however, the energy gap separating stable and unstable rotamers of compound **2** is much larger than in the case of oxime **1**.

The μ values of rotamers of compound **2** (see Table 1) were also estimated in the vector-additive scheme approximation. The two types of conformers of oximes **1** and **2** have almost equal calculated dipole moments. Thus, according to a simple model without considering mutual bond polarization, p—π-interaction, and other factors, the contribution of the vinyl group to the dipole moment of oxime **1** in the nonpolar medium is half the experimental value of the dipole moment, which is a significant result.

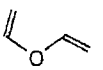
However, the situation becomes quite different on going to THF. In this solvent, the measured dipole moment of *O*-ethylacetoxime (**2**) is larger than that of *O*-vinylacetoxime (**1**) (see Table 2). Hence, the fractions of polar forms of compound **2** in THF are much larger. Currently, it is unclear which type of rotamer and solvation mechanism is responsible for these distinctions.

Data on the dipole moments of conformers of acetoximes are insufficient to reveal the details of internal rotation of their fragments in a nonpolar solvent. To this end, we used the results of experimental and quantum-chemical studies of vinyl ethers **3**—**5**, which are analogs of the oximes considered (see Table 1).

CH_2=CHOCH=CH_2 CH_2=CHOEt CH_2=CHOBu^t

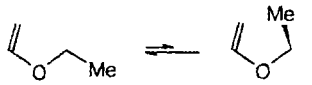
3 **4** **5**

Like compound **2**, divinyl ether (**3**) is also characterized by the absence of the dependence of μ on temperature in a nonpolar solvent.[11] Moreover, the values of the dipole moments of compounds **2** and **3** appeared to be close (1.04 and 1.10 D, respectively, see Table 1) and are ~0.8 D smaller than the μ value for oxime **1**. In studies by microwave spectroscopy, gas-phase electron diffraction,[12] and using theoretical calculations,[13] it was established that free molecules of **3** exist in the gas phase at room temperature as a mixture of nonplanar *sp,ac*-form (80%) (the angles of rotation about C—O bonds are −13° and 145°) and planar *ap,ap*-form (20%). The calculated μ values of individual conformers of molecule **3** and the absence of a temperature dependence indicate that only one conformer, either the nonplanar *sp,ac*- or planar *sp,ap*-form with a statistical weight of 2 due to structural symmetry, is present in solution (see Table 1).



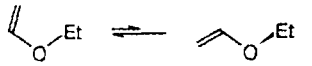
3 (*sp,ap*)

Saturation of one double bond in the molecule of divinyl ether (**3**) has no effect on the dipole moment of the molecule in a nonpolar medium. For instance, compound **3** and ethyl vinyl ether (**4**) have dipole moments of 1.10 D and 1.19 D, respectively, which radically differentiates these ethers from oxime **1**. The experimental value of the dipole moment of compound **4** corresponds to those calculated for the planar *sp,ap*-form and nonplanar *sp,sc*-form (see Table 1). It cannot also be ruled out that these forms exist as an equilibrium mixture, since the dipole moment is independent of the angle of rotation about the O—C(sp^3) bond. However, it should be taken into account that the *sp,sc*-conformer is thermodynamically unfavorable in this case and that its fraction in solution should be small.



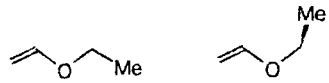
4 (*sp,ap*) **4** (*sp,sc*)

The conclusion that the *sp,ap*-form of **4** is predominant is in agreement with the results of previous studies.[14—16] For instance, according to the published data,[14] the *sp,ap*-form is the most stable for ether **4**. In a nonpolar solvent,[15,16] the synperiplanar (with respect to the O—C(sp^3) bond) *s-cis*-conformer is predominant, while the *ac*(*gauche*)-conformer has a somewhat lower stability.



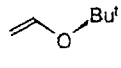
4 (*sp*) **4** (*ac*)

No stable *ac*(*gauche*)-form of compound **4** was revealed by semiempirical AM1 calculations. According to the data of calculations, the *gauche*-conformer suggested previously[15,16] corresponds to its limiting structure, *i.e.*, to the *ap,sc*- or *ap,ap*-form (see Table 1).



4 (*ap,ap*) **4** (*ap,sc*)

In this connection mention should be made that our data on *tert*-butyl vinyl ether (**5**), for which the *ac* → *ap* interconversion is unlikely (see Table 1), completely coincide with the reported data.[15,16]

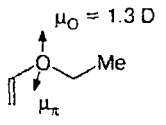


5 (*ac*)

Thus, the equilibrium conformations of the molecules of divinyl (**3**) and ethyl vinyl (**4**) ethers in solutions are identical and the *sp,ap*-conformer is predominant in both cases. What is the reason for retaining the polarity of the molecule on saturation of one of the double bonds of compound **3**? In fact, in the series of analogous acetoximes having the same structure of rotamers their polarity changes drastically. Two reasons can be considered. Phase transition has no effect on the conformation of divinyl ether (**3**), so it remains nonplanar (*sp,ac*) in solution. Then, it can be suggested that a weak interaction occurs between the LEP of the O atom and one double bond and the latter has little effect on the dipole moment. However, calculations of

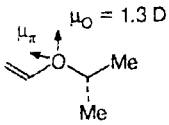
the *sp,ac*- and *sp,ap*-forms showed that their dipole moments have close values (see Table 1). In this case, one can assume that, for any conformation, the dipole moment of the molecule of ether **3** is to a greater extent determined by the interaction between the LEP of the oxygen atom and one of the double bonds.

The dipole moments of alkyl vinyl ethers calculated using the vector-additive scheme (μ_O) are directed approximately along the bisectrix of the C—O—C angle.[17] They have no components due to p—π-interaction of the LEP of the oxygen atom with the C=C double bond (the π-moment). At the same time, the necessity of considering the π-moment (μ_π) of the vinyloxy group has been shown taking alkyl vinyl ethers as examples. The μ_π amounts to 0.7 D and is directed from the O atom to the β-C atom of the double bond.[17] Taking into account this information and the μ values calculated in the vector-additive approximation[18,19] and by the CNDO/S method (see Table 1), the formation scheme of the dipole moments for the conformers of ethyl vinyl ether (**4**) studied in the gas phase[20] and in solution can be represented as follows:



$\mu_{CNDO/S}$ = 1 D

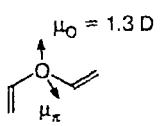
4 (*sp,ap*)



$\mu_{CNDO/S}$ = 2 D

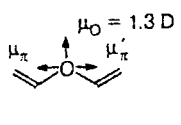
4 (*ap,ap* or *ap,sc*)

In this case, the estimate of the μ value obtained using a simple procedure is in qualitative agreement with the results of quantum-chemical calculations. If a rather strong interaction between the LEP of the O atom and the π-electrons of both double bonds occurs in the molecule of divinyl ether (**3**), the above scheme gives a μ value which is in agreement with the data of semiempirical calculations of its nonplanar *sp,ac*-conformer. However, for the planar *ap,ap*-conformation of the divinyl ether molecule, which is analogous to one of the stable conformations of *O*-vinylacetoxime (**1**), composition of the moments in the case $|\mu_\pi| = |\mu_\pi'|$ leads to a value which differs from the calculated one since the π-components of the dipole moment are cancelled.



$\mu_{CNDO/S}$ = 1 D

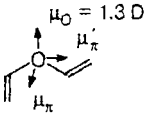
3 (*sp,ac*)



$\mu_{CNDO/S}$ = 2 D

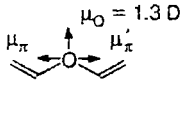
3 (*ap,ap*)

The assumption that $|\mu_\pi| > |\mu_\pi'|$ for these conformations of the divinyl ether molecule makes it possible to obtain satisfactory results.



$\mu_{CNDO/S}$ = 1 D

3 (*sp,ac*)

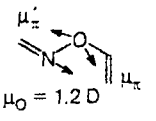


$\mu_{CNDO/S}$ = 2 D

3 (*ap,ap*)

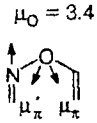
In this case the scheme of composing the dipole moments is the same as for alkyl vinyl ethers.

The fact that experimental data for vinyl ethers are adequately described by this approximate scheme serves as a basis for its application to the molecules of the oximes studied.



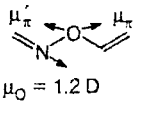
$\mu_{CNDO/S}$ = 2.4—2.7 D

1 (*ap,sp*)



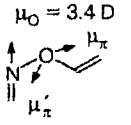
$\mu_{CNDO/S}$ = 3.6 D

1 (*sc,sp*)



$\mu_{CNDO/S}$ = 2.1—2.4 D

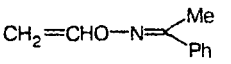
1 (*ap,ap*)



$\mu_{CNDO/S}$ = 4.6 D

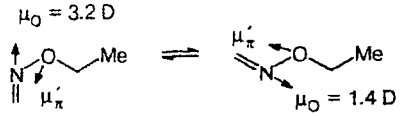
1 (*sp,ac*)

In this case, the agreement between the results of semiempirical calculations and experimental data is achieved only by assuming that μ_π' is appreciably smaller in absolute value than μ_π (*i.e.*, where the LEP of the oxygen atom interacts mainly with the vinyl group). This is confirmed by the fact that the values of the dipole moments of *O*-vinylacetophenonoxime (**6**) and *O*-vinylacetoxime (**1**) are close (see Table 2). Would the dipole moment of molecule **1** be determined by the interaction of the LEP of the oxygen atom with π-electrons of the azomethine group, appreciable change in the μ value of the molecule on replacement of the methyl group by phenyl group should be expected.



6

As was mentioned above, in contrast to vinyl ethers, saturation of the C=C bond in the *O*-vinylacetoxime molecule nearly halves its dipole moment. The components of the dipole moment of ethylacetoxime (**2**) are composed as follows:



$\mu_{CNDO/S}$ = 4 D

2 (*sp,ap*)

$\mu_{CNDO/S}$ = 1 D

2 (*ap,ap*)

The best agreement between the moment obtained using this scheme and that calculated by the CNDO/S method is also achieved by assuming that the μ_π' value is small.

Thus, changes in the dipole moment of molecule **1** on conformational interconversions due to both raising the temperature in the nonpolar medium and going to a solvent with higher polarity can be represented by the following scheme:

1 (*ap,ap*; *ap,sp*) **1** (*sp,ac*; *sc,sp*)

In contrast to rotation about the O—C(sp^2) bond, the dipole moment of molecule **1** substantially changes if rotation about the N—O bond occurs. In this case, the mutual position of the LEP of the O and N atoms is the determining factor.

References

1. B. A. Trofimov, A. I. Mikhaleva, A. N. Vasil'ev, and M. V. Sigalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 695 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28** (Engl. Transl.)].
2. B. A. Trofimov and A. I. Mikhaleva, *N-Vinilpirroly* [*N-Vinylpyrroles*], Nauka, Sib. Division, Novosibirsk, 1984, 262 pp. (in Russian).
3. B. A. Trofimov, *Adv. Heterocycl. Chem.*, 1990, **51**, 253.
4. O. A. Tarasova, S. E. Korostova, A. I. Mikhaleva, L. N. Sobenina, R. N. Nesterenko, S. G. Shevchenko, and B. A. Trofimov, *Zh. Org. Khim.*, 1994, **30**, 810 [*Russ. J. Org. Chem.*, 1994, **30** (Engl. Transl.)].
5. R. Sohlberg, S. P. Leary, N. L. Owen, and B. A. Trofimov, *Vibrational Spectr.*, 1997, **13**, 227.
6. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
7. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, L. Windus, M. Dupuise, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
8. K. Higasi, *Phys. Chem. Res.*, 1943, **22**, 805.
9. E. Grunwald and A. Effio, *J. Solut. Chem.*, 1973, **2**, 373.
10. T. Oie, I. A. Topol, and S. K. Burt, *J. Phys. Chem.*, 1995, **99**, 905.
11. B. A. Trofimov, V. B. Modonov, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1973, **211**, 608 [*Dokl. Chem.*, 1973 (Engl. Transl.)].
12. W. Pychout, C. van Alsenoy, H. J. Geise, B. van der Veken, and G. Pieters, *J. Mol. Struct.*, 1985, **130**, 335.
13. K. Sohlberg, B. L. Baker, S. P. Leeary, N. L. Owen, J. Facelli, and B. A. Trofimov, *J. Mol. Struct.*, 1995, **354**, 55.
14. N. L. Owen and G. O. Sorensen, *J. Mol. Struct.*, 1979, **83**, 1483.
15. O. N. Vylegjanin, V. B. Modonov, and B. A. Trofimov, *Tetrahedron Lett.*, 1972, 2243.
16. B. A. Trofimov, V. B. Modonov, T. N. Bazhenova, N. A. Nedolya, and V. V. Keiko, *Reakts. sposobn. organ. soed.* [*Reactivity of Organic Compounds*], 1975, Issue 3(41), 745 (in Russian).
17. Yu. L. Frolov, V. B. Modonov, N. I. Golovanova, and A. N. Volkov, *Zh. Strukt. Khim.*, 1972, **13**, 538 [*J. Struct. Chem. (USSR)*, 1972, **13** (Engl. Transl.)].
18. L. M. Sinegovskaya, V. V. Keiko, and B. A. Trofimov, *Sulfur Repts.*, 1987, **7**, 337.
19. B. A. Trofimov, *Geteroatomnye proizvodnye atsetilena* [*Heteroatomic Derivatives of Acetylene*], Nauka, Moscow, 1981, 319 pp. (in Russian).
20. I. G. John and L. Radom, *J. Mol. Struct.*, 1977, **36**, 133.

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