Rotational isomerism of vinyl ethers of azines based on the data of IR spectroscopy and quantum-chemical AM1 calculations

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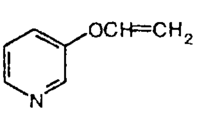
The IR spectra of vinyl ethers of azines have two C=C stretching vibration bands of the vinyl group at 1620 and 1640 cm^{-1}, which correspond to the *s-cis* and nonplanar *s-trans* conformers, respectively. According to the results of AM1 calculations, the hetaryl fragment and the vinyl group in the *s-trans* conformers of all the ethers under study are twisted out of the C—O—C plane by ~30°. In the *s-cis* conformation, the angle of rotation of the heterocycle with respect to the vinyloxy group varies from 45 to 90°. The character of the change in the intensity of the ν(C=C) absorption bands of the doublet under changes of the temperature indicates that the *s-trans* conformer is energetically favorable. The exception is 5-vinyloxyacridine for which the *s-cis* conformation is more favorable.

Key words: hetaryl vinyl ethers, rotational isomerism, IR spectra, semiempirical AM1 method.

The structures of hetaryl vinyl ethers have been studied substantially more poorly than the structures of alkyl vinyl and aryl vinyl ethers. Almost all works[1—5] were devoted to examinations of NMR spectra. The UV and Raman spectra were recorded only for 2-vinyloxypyridine.[6] Owing to low barriers to internal rotation in the case of hetaryl vinyl ethers, the NMR method can provide data on the spatial structure of the predominant conformer but it does not allow one to obtain the spectra of individual rotational isomers.

Previously, criteria were reported which allow one to judge the presence of rotational isomers of aryl vinyl ethers from IR spectra.[7—9] The data on the structures of the conformers obtained by quantum-chemical calculations are also available.[10,11] These results were used for studying the rotational isomerism of related classes of compounds, namely, of vinyl ethers of pyridine and quinoline (**1**—**9**).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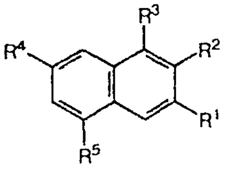
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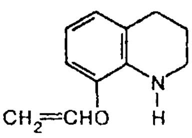
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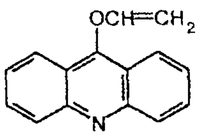
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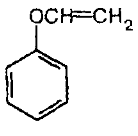
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2: R^1 = R^3 = R^4 = R^5 = H, R^2 = OCH=CH$_2$
3: R^1 = R^2 = R^4 = R^5 = H, R^3 = OCH=CH$_2$
4: R^2 = R^4 = R^5 = H, R^1 = CH$_3$, R^3 = OCH=CH$_2$
5: R^1 = R^2 = R^3 = R^5 = H, R^4 = OCH=CH$_2$
6: R^1 = R^2 = R^3 = R^4 = H, R^5 = OCH=CH$_2$

Experimental

The IR spectra of compounds **1**—**9** in the liquid phase (in a thin film) were recorded on a double-beam Specord IR-75 spectrometer. The resolution in the 100—1700 cm^{-1} region was 2 cm^{-1}.

Temperature studies were carried out in a standard cell (Carl Zeiss Jena) with the use of a calibrated thermocouple. The extreme point of the low-temperature region was obtained under a stream of liquid nitrogen at T = 103 K.

Results and Discussion

Analysis of the IR spectra of aryl vinyl ethers demonstrated that the C=C stretching vibration of the vinyl group is the most reliable spectral characteristic, which allows one to judge the presence of rotational isomers.[7—11] The *s-cis* conformer is characterized by a vibration at 1620 cm^{-1}. For the *s-trans* conformer, a vibration of the C=C bond is observed at 1640 cm^{-1}.[12] The IR spectra of ethers of azines **1**—**8** also have two bands that correspond to this vibration: at 1620—1628 and 1638—1644 cm^{-1} (Table 1). As the temperature of a thin film of compounds **1**—**7** decreases to 103 K, the intensity of the low-frequency band decreases and the

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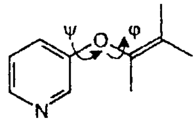
Table 1. Frequencies of the C=C absorption bands (ν(C=C)) of the vinyl group in the IR spectra of hetaryl vinyl ethers

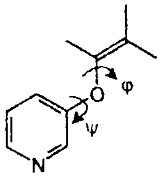
Compound	ν_1	ν_2
	cm^{-1}	
1	1625	1643
2	1627	1644
3	1628	1644
4	1628	1643
5	1620	1643
6	1625	1638
7	1622	1638
8	1622	1643
9	1625	1643

intensity of the high-frequency band increases (Fig. 1). This character of the temperature dependence completely coincides with that observed for phenyl vinyl ether (**9**),[9] which we considered as the "standard" compound. This suggests that the low-frequency band of the ν(C=C) vibration in the spectra of compounds **1**—**7** corresponds to the *s-cis* form and the high-frequency band at 1638—1644 cm^{-1} corresponds to the *s-trans* conformer.

To establish the spatial structures of rotational isomers of vinyl ethers of azines in more detail, possible conformations of 3-vinyloxypyridine (**1**), 3-, 4-, 6-, and 8-vinyloxyquinolines (**2**, **3**, **5**, and **6**, respectively), and 5-vinyloxyacridine (**8**) were calculated by the quantum-chemical AM1 method with full optimization of geometric parameters.[13] For molecules **1**—**3**, **5**, and **6**, three energy minima were found, two of which correspond to the nonplanar *s-trans* conformations with different orientations of the heterocycle with respect to the vinyl group (structures **A** and **B**). The third minimum corresponds to the *s-cis* conformation in which the phenyl ring deviates substantially from the plane of the vinyloxy group (structure **C**).



A



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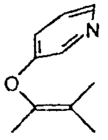

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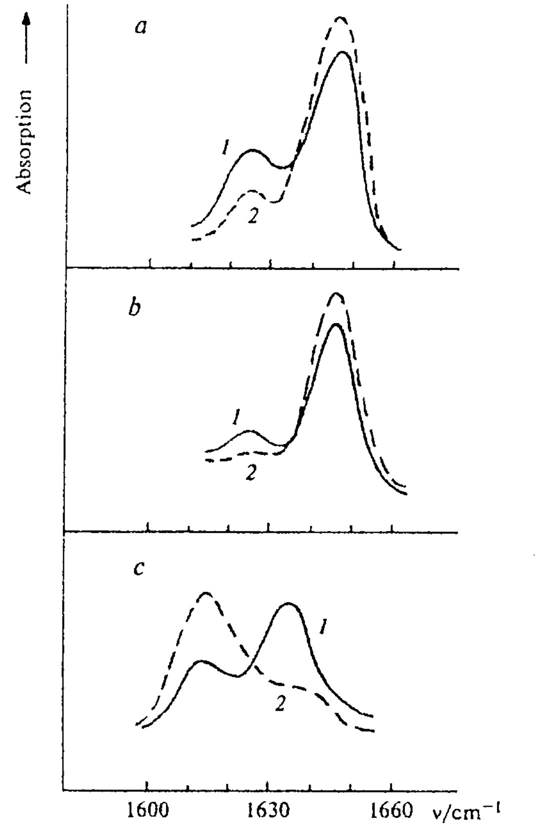


Fig. 1. Temperature dependences of the ν(C=C) doublet in the IR spectra of hetaryl vinyl ethers **1** (*a*), **7** (*b*), and **8** (*c*) in a thin film. T = 293 K (*1*) and 103 K (*2*).

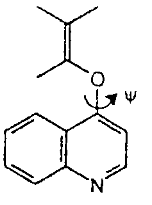
The values of the equilibrium torsion angles ψ (about the O—C$_{\mathrm{Hetar}}$ bond) and φ (about the O—C$_{\mathrm{Vin}}$ bond) and the heats of formation of the conformers are given in Table 2. According to calculations, the nonplanar *s-trans* conformer with ψ = 30±5° and φ = 10—25° is realized in ethers **1**—**3**, **5**, and **6**. In the case of the second nonplanar *s-trans* conformation, similar values of the torsion angles ψ and φ were obtained for 3-vinyl-

Table 2. Heats of formation (E/kcal mol^{-1}) and torsion angles (deg) for the conformers of compounds **1**—**3**, **5**, **6**, **8**, and **9**

Compound	*s-trans* Conformers						*s-cis* Conformers		
	E_1	Torsion angles		E_2	Torsion angles		E_3	Torsion angles	
		ψ_1	φ_1		ψ_2	φ_2		ψ_3	φ_3
1	23.1[a]	31.3	24.0	23.1	29.2	20.5	22.6	46.1	11.6
2	43.6[a]	35.7	23.3	43.1	24.8	26.4	42.9	84.6	0.3
3	44.3[b]	31.3	14.0	44.8	55.0	8.2	44.4	54.9	2.9
5	42.9[c]	37.1	11.9	43.0	33.7	20.2	42.4	52.7	9.4
6	45.5[d]	35.7	23.1	47.5	50.1	10.1	44.1	60.3	16.0
8	70.3	60.1	6.7				69.8	88.4	0.7
9	12.5	33.2	22.0				12.0	57.7	8.3

[a—d] Correspond to the *s-cis*(C$_2$), *s-cis*(C$_3$), *s-cis*(C$_5$), and *s-cis*(C$_7$) orientations of the vinyl group, respectively.

oxypyridine (**1**) and 3- and 6-vinyloxyquinolines (**2** and **5**), in which steric interactions between the aromatic fragment and the vinyloxy group are absent. The conformer with the *syn* arrangement of the vinyloxy group and the aromatic fragment (4- and 6-vinyloxyquinolines (**3** and **6**)) is characterized by an additional steric strain, which leads to an increase in the torsion angle ψ to 50—55° (structure **D**).



D

The values of the torsion angles in the *s-cis* conformers of compounds **1**—**3**, **5**, and **6** are as follows: ψ = 45—90° and φ = 0—15°. Unlike the *s-trans* conformers, an essential spread in the calculated values of the torsion angle ψ is observed in the *s-cis* conformers of these compounds. Thus, the hetaryl fragment in 3-vinyloxyquinoline (**2**) is virtually orthogonal to the vinyloxy group, while the pyridine ring in 3-vinyloxypyridine (**1**) is twisted out of the plane of the vinyloxy group by only 46° (see Table 2). However, a change in the torsion angle ψ in compound **1** from 40 to 90° (the remaining geometric parameters of the conformation are fixed) leads to an insignificant change in its energy (~0.2 kcal mol^{-1}). The dependence of the heat formation of 3-vinyloxypyridine (**1**) on the torsion angle ψ in the *s-cis* conformation is given below.

ψ/deg	40	50	60	70	80	90
E/kcal mol^{-1}	22.7	22.6	22.6	22.7	22.7	22.8

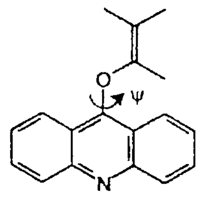
Consequently, the energy plateau exists for the *s-cis* orientations of the vinyloxy group and the heterocycle in ethers **1**—**3**, **5**, and **6**. This plateau corresponds to large-amplitude vibrations of the hetaryl substituent relative to the plane orthogonal to the vinyloxy group.

Therefore, according to the results of AM1 calculations and to the IR spectral data, the rotational isomerism is realized for vinyl ethers of pyridines and quinolines. According to calculations, the *s-cis* conformer is energetically favorable. For compound **3**, the energies of the *s-cis* and nonplanar *s-trans* conformers are virtually identical (see Table 2).

The AM1 calculations of vinyl ether (**9**) revealed two energy minima corresponding to the *s-cis* and *s-trans* conformers, which have torsion angles ψ and φ similar to those found in hetaryl vinyl ethers **1**—**3**, **5**, and **6**. The AM1 method predicted that the *s-cis* conformation is energetically more favorable (by ~0.4 kcal mol^{-1}; see Table 2). This is inconsistent with the results of *ab initio* calculations with the D95++(d,p) basis set, which demonstrate that the *s-trans* conformer is ~0.7 kcal mol^{-1} energetically more favorable (the calculations were carried out by A. V. Vashchenko at the Osaka University (Japan) with the use of the GAUSSIAN-94 program). The existence of hetaryl vinyl ethers **1**—**3**, **5**, and **6** predominantly in the nonplanar *s-trans* conformation is confirmed by the abundant data of NMR spectroscopy.[1—5] In the IR spectra, the low intensity component of the doublet of the C=C absortion band of the vinyl group corresponds to the *s-cis* conformer. The above-mentioned facts suggest that the relative energies of the *s-cis* and *s-trans* conformers of compounds **1**—**3**, **5**, and **6** are inadequately estimated by the AM1 method.

For 5-vinyloxypyridine (**8**), the ratio of the intensities of the components of the doublet in the ν(C=C) region (see Fig. 1) differs from that observed in compounds **1**—**7** and **9**. As the temperature of a thin layer decreases, the intensity of the band at 1622 cm^{-1} increases and the intensity of the band at 1643 cm^{-1} decreases, *i.e.*, the temperature dependences of the intensities of the low-frequency and high-frequency C=C stretching vibration bands of the vinyl group in the case of 5-vinyloxyacridine (**8**) are in direct opposition to those observed for the other ethers under study (**1**—**7** and **9**). This indicates that the *s-cis* form is energetically favorable for molecule **8**.

5-Vinyloxyacridine (**8**) is characterized by the presence of additional steric hindrances that occur in the case of the *s-trans* conformation (structure **E**). As a consequence, the AM1 method detects an increase in the torsion angle ψ from 30—35° to 60° in going from hetaryl vinyl ethers **1**—**3**, **5**, and **6** to vinyloxyacridine **8**. The *s-trans* conformation of molecule **8** is energetically less favorable due to the disruption of the p—π conjugation caused by an increase in the torsion angle ψ. At the same time, the p—π conjugation with the heterocycle in the *s-cis* conformation of all the above-mentioned ethers is disrupted similarly. Therefore, the stability of the *s-trans* structure of 5-vinyloxyacridine (**8**) relative to its *s-cis* conformer should decrease due to which a predominance of the *s-cis* form of the ether under consideration is quite possible. It should be noted that the decrease in the relative stability of the *s-trans* conformer of compound **8** is not reproduced by the AM1 method (see Table 2).



E

Therefore, studies of the IR spectra of aryl vinyl and hetaryl vinyl ethers, the quantum-chemical calculations, and the available data on the spatial structures of alkyl vinyl ethers and vinyl ethers containing the second unsaturated substituent[12,14] indicate that the rotational isomerism is typical of all vinyl ethers of the type R—O—CH=CH$_2$ regardless of the nature of the substituent R. The specificity of the substituent determines the quantitative ratio of the conformers and their individual structures.

References

1. A. V. Afonin, V. K. Voronov, M. A. Andriyankov, and D. K. Danovich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 317 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 279 (Engl. Transl.)].

2. A. V. Afonin and M. A. Andriyankov, *Zh. Org. Khim.*, 1988, **24**, 1034 [*J. Org. Chem. USSR*, 1988, **24** (Engl. Transl.)].
3. A. V. Afonin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1344 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1185 (Engl. Transl.)].
4. A. V. Afonin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2289 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2003 (Engl. Transl.)].
5. A. V. Afonin, A. V. Vashchenco, and H. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 933.
6. Yu. L. Frolov, V. K. Voronov, N. M. Deriglazov, L. V. Belousova, N. M. Vitkovskaya, S. M. Tyrina, and G. G. Skvortsova, *Khim. Geterotsikl. Soedin.*, 1972, 95 [*Chem. Heterocycl. Compd.*, 1972 (Engl. Transl.)].
7. Yu. L. Frolov, A. Kh. Filippova, A. V. Kalabina, L. K. Pogodaeva, and N. A. Tyukavkina, *Zh. Strukt. Khim.*, 1962, **3**, 676 [*J. Struct. Chem.*, 1962, **3** (Engl. Transl.)].
8. Yu. L. Frolov, Ph.D. Thesis, 1965 (in Russian).
9. T. I. Rozova, G. V. Ratovskii, D. D. Chuvashev, and G. A. Kalabin, *Zh. Obshch. Khim.*, 1982, **52**, 1520 [*J. Gen. Chem. USSR*, 1982, **52** (Engl. Transl.)].
10. D. D. Chuvashev, G. V. Ratovskii, T. I. Rozova, and O. A. Shivernovskaya, *Zh. Obshch. Khim.*, 1989, **59**, 657 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
11. G. V. Ratovskii, O. A. Shivernovskaya, O. V. Burlakova, D. D. Chuvashev, and N. G. Glukhikh, *Zh. Obshch. Khim.*, 1989, **59**, 670 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
12. B. A. Trofimov, *Geteroatomnye proizvodnye atsetilena* [*Heteroatomic Derivatives of Acetylene*], Nauka, Moscow, 1981, 319 pp. (in Russian).
13. M. I. S. Dewar, E. G. Zoebisch, and E. P. Healy, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
14. L. M. Sinegovskaya, V. V. Keiko, and B. A. Trofimov, *Sulfur Reports*, 1987, **7**, 337.

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