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Structural Effects in NMR Spectroscopy of Vinylic Compound 1. Investigation of Intramolecular Specific Interactions C–H···N in Hetaryl Vinyl Ethers by ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR Spectroscopies and Quantum-Chemical Calculations

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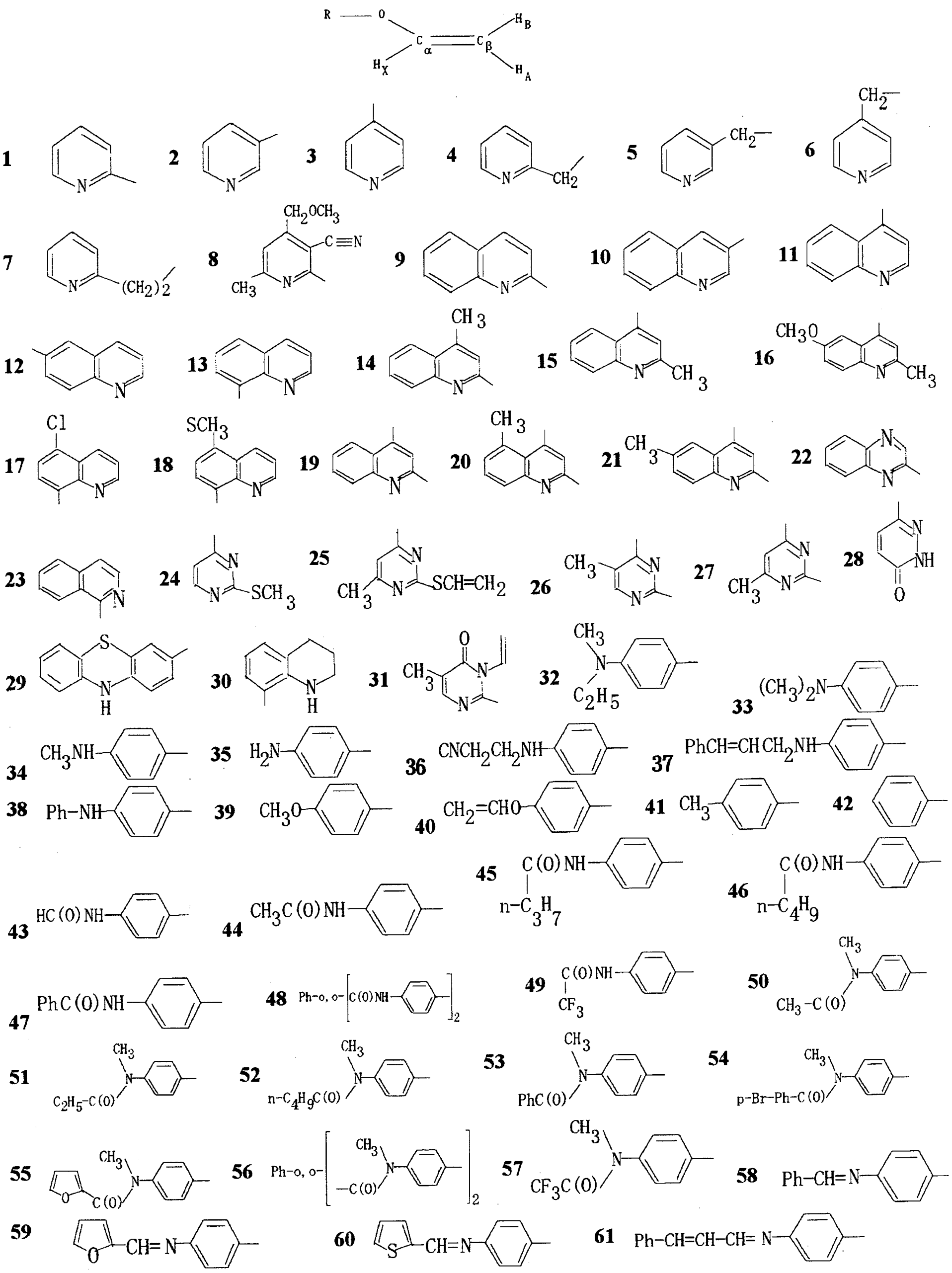
The hydrogen bond-like intramolecular specific interactions between the α-hydrogen of the vinyl group and *endo*-cyclic nitrogen are discovered in the hetaryl vinyl ethers, having the vinyloxyl group neighboring to the endocyclic nitrogen by the ^{1}H and ^{13}C NMR data. It is confirmed by AM1 calculations. The intramolecular specific interaction results to the downfield shift of the α-proton signal by 1 ppm, α-carbon signal by 4—5 ppm, the increase of their one-bond coupling constant by 6—7 Hz, and upfield shift of nitrogen by 17—20 ppm, as it was shown by the regression and dispersion analysis of ^{1}H, ^{13}C, and ^{15}N parameters of wide series of aryl and hetaryl vinyl ethers. The cluster analysis of the spectral data indicates the anomaly of common combination of vinyloxyl group parameters in ethers, possessing the intramolecular specific interaction in comparison with ethers which have no such interaction. The factor analysis of spectral parameters shows that influence of specific interaction on the α-proton and α-carbon chemical shifts as well as their one-bond coupling constant prevails over other structural and electronic effects. In accordance with the AM1 calculation, the hetaryl vinyl ethers possessing the intramolecular specific interaction are more planar that is confirmed by ^{13}C and ^{17}O NMR data.

The intramolecular specific interaction C–H···X (where X-denotes heteroatom) is one of the important factors which determine the stereochemistry of the organic molecules. However, such interaction (which is more often called the C–H···X hydrogen bond) is extremely poorly investigated in comparison with their wide spreading. The small energy of this interaction is probably the objective reason of this situation, although the intermolecular hydrogen bond C–H···X with participation of the polar C–H bond is well known.[1)] The limited amount of the examples can be given for undoubted evidence of intramolecular specific interaction C–H···X. Pinchas, in 1963 year, supposed the existence of the intramolecular hydrogen bond C–H···O in *o*-nitrobenzaldehyde. He based on unusually high frequency shift in IR of formyl-proton bond.[2)] The latter investigations of the molecules, containing the polar C–H bond by Sammes, Harlow, and Li[3—5)] allowed to recognize the following sings of the C–H···X hydrogen bond formation. Firstly, the anomalous lower field (higher frequency) shifts of the corresponding ^{1}H signals were recognized in NMR spectra.[3—5)] Secondly, the increase of infra-red frequency of the relevant C–H bond takes place.[4)] Then, the hydrogen and heteroatom are approached to a distance less than the sum of their van der Waals radii.[3)] The review of the crystallographic data suggests that the hydrogen and heteroatom are approached to the distance less than the sum of van der Waals radii in the case of C–H···X hydrogen bond formation in the solid state.[6,7)] The investigation of 1,2,4-triazole derivatives by Houssin and Henichart exhibited the anomalous downfield shifts of the proton signal involved in the intramolecular specific interaction.[8)]

It was reported, that the signal of α-proton in the vinyl group is anomalously shifted to the lower field in 2-vinyloxypyridine and -quinolines.[9)] These shifts are caused by the intramolecular specific interaction between the mentioned hydrogen and endocyclic nitrogen.[9)] It was interpreted to show the other spectral evidence for C–H···N hydrogen bond formation (which will be called below the intramolecular specific interaction). There are the increase of the corresponding one-bond ^{13}C-^{1}H coupling constant, the additional contributions to the shielding constant of α-carbon atom in the vinyl group and endocyclic nitrogen.[10)] It is in a good agreement with data reported by Satonaka et al.[11)] This paper contains an analysis of ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR parameters in the wide series of various aryl and hetaryl vinyl ethers. The compounds treated in paper are illustrated in Scheme 1. To reach the completeness of the spectral signs of the C–H···N interaction, we analyzed NMR data in combination with data of quantum-chemical calculations.

Experimental

The ^{1}H and ^{13}C spectra were recorded on the Tesla BS 567A



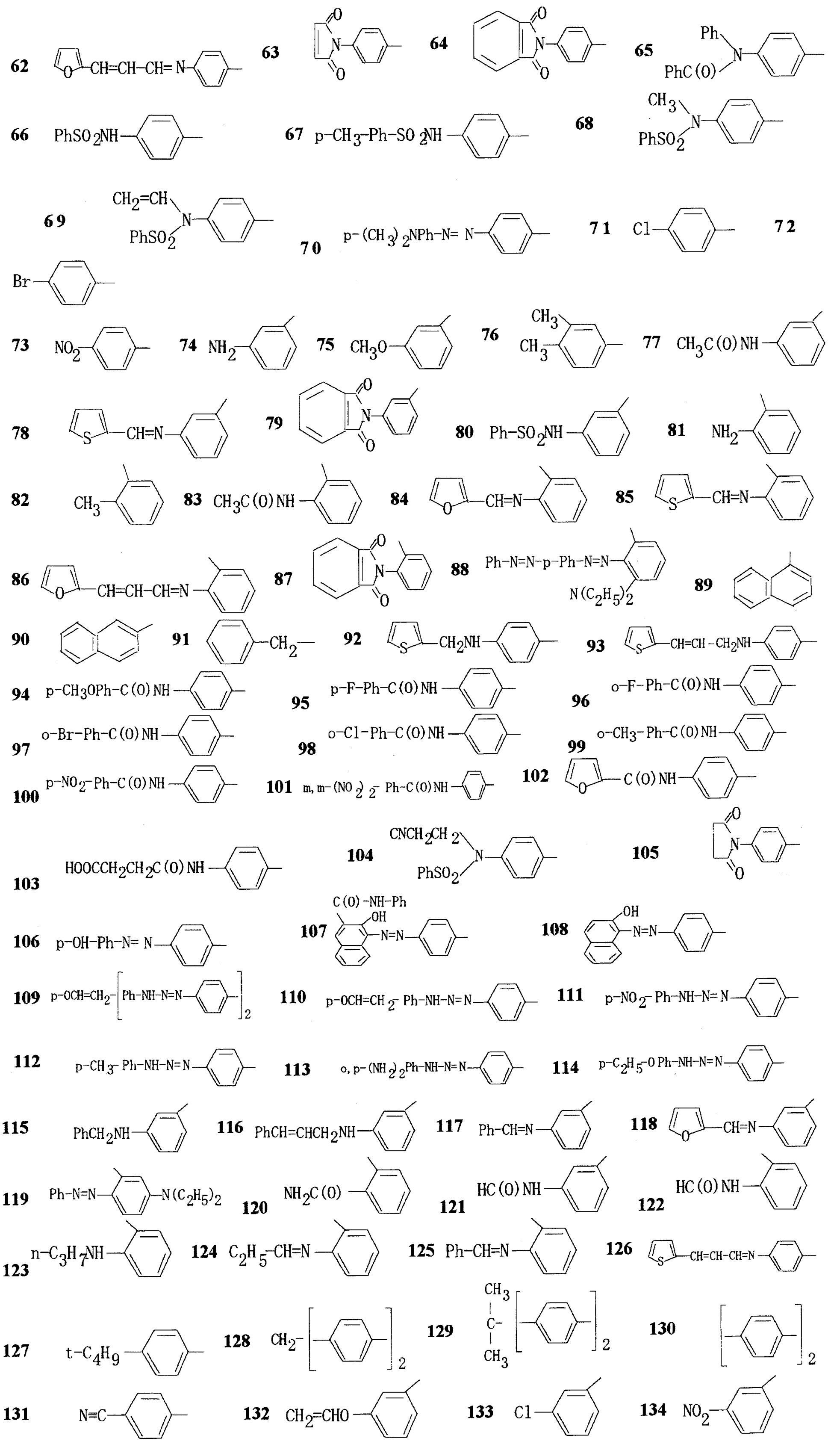
Scheme 1. The referenced vinyloxyl compounds.

spectrometer (100 and 25.1 MHz, respectively). The ^{14}N, ^{15}N, and ^{17}O spectra were obtained on the Bruker CXP 300 (21.68, 30.41, and 40.69 MHz, respectively). At the same conditions all samples were recorded. The solvent was $CDCl_3$, the internal reference was HMDS for ^{1}H and ^{13}C, and the external references were $CH_3{}^{15}NO_2$ and $D_2{}^{17}O$ for ^{15}N and ^{17}O NMR, respectively. The concentration was 5% for ^{1}H, 30% for ^{13}C, 80% for ^{15}N, and ^{17}O NMR experiments. The recording was performed at the ambient temperature (25±2 °C). The proton-coupled spectra were obtained by the gated decoupling techniques.[12] The acquisition parameters were as the following: The spectral width was 760 Hz and the data point was 16 K. The ^{15}N chemical shifts values are given in the NH_3 scale.

The chemical shifts and coupling constants of more than 130 compounds (Tables 1, 2, and 6) were deposited as Supplementary Material (Document No. 69018) at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The Preferable Conformations of the Hetaryl Vinyl Ethers and a Character of p–π Conjugation with Unsaturated Fragments. The ^{1}H and ^{13}C NMR data for wide series of the hetaryl(aryl) vinyl ethers are summarized in the Table 1 (Supplementary). There are two conformationally dependent parameters in vinyl ethers. It is β-protons chemical shifts difference ($\delta\Delta = \delta H_B - \delta H_A$) and geminal coupling constant $^{2}J_{AB}$.[13] Hence, these parameters can be used for the conformational analysis of hetaryl vinyl ethers **1**—**31**. The value of $\Delta\delta$ parameter in compounds **1**—**3** and **8**—**31** is changing from 0.30 to 0.44 ppm. It indicates that *s-trans* conformer is more preferential.[13] The heterocycle and vinyloxyl group are separated by one or two methylene groups



Scheme 1. (Continued.)

in molecules **4**—**7**. Parameter $\Delta\delta$ is reduced to 0.15—0.20 ppm, that indicates preferential *s-cis* conformation.[13] The value $\Delta\delta$ in compounds **1**—**3** and **8**—**31** is close to the same parameter in para- and meta-substituted aryl vinyl ethers **32**—**80** (where $\Delta\delta = 0.29$—0.36 ppm). The same range of changing in $^2J_{AB}$ (-1.5—-2.0 Hz) is also observed in aryl vinyl ethers **32**—**80** and hetaryl vinyl ethers **1**—**3**, and **8**—**31** (Table 1, supplementary). It suggests the conformational homogeneity of the discussed series.

The value of β-carbon chemical shift, in the vinyloxyl group, should be used as a criterion of efficiency in p–π conjugation.[14,15] The $\delta^{13}C_\beta$ values of **1**—**3** and **8**—**31** change from 95.01 to 99.83 ppm. The close range of $\delta^{13}C_\beta$ changing takes place in **32**—**80** (92.53—99.11 ppm). The p–π conjugation in the vinyloxyl group of the aryl vinyl ethers is efficient and depends upon electronic effect of the substituents in a cycle.[10] Similar values of $\delta^{13}C_\beta$ in the series of the hetaryl and aryl vinyl ethers imply the efficiency of p–π conjugation in the vinyloxyl group of the former.

To estimate the efficiency of p–π conjugation with hetaryl cycle, the chemical shifts of carbons in ortho- and para-positions, concerning the vinyloxyl group, should be taken into account.[16] An introduction of vinyloxyl group into one of position in pyridine or quinoline cycle (compounds **1**—**3** and **9**—**13**) results to upfield shift of ^{13}C signals of ortho- and para-carbons in comparison with those in the parent pyridine and quinoline (Table 2, supplementary). The upfield shift of ^{13}C signals of ortho- and para-carbons constitutes 6.4—18.2 and 2.3—5.7 ppm, respectively. The ^{13}C signals of peri-carbon in **11** is also shifted to higher field by 6.3 ppm in respect to that in quinoline. The same upfield shift of the corresponding carbon signals are detected in phenyl vinyl and naphthyl vinyl ethers **42**, **89**, and **90** in the case of vinyloxyl group introduction (Table 2, supplementary). Therefore, the similar conditions of the p–π conjugation with aromatic fragments take place in aryl and hetaryl vinyl ethers, i.e. the p–π conjugation with heterocycle is effective.

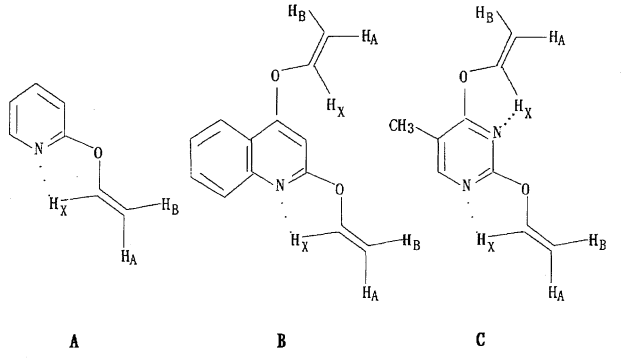
The introduction of the methylene group between the vinyloxyl group and a heterocycle in molecules **4**—**6** leads to the loss of the competitive character of the p–π conjugation. The p–π conjugation in the vinyloxyl group becomes intensive in **4**—**6**, and the upfield shift of $\delta^{13}C_\beta$ is observed by 7—12 ppm relative to other hetaryl vinyl ethers (Table 1, supplementary). The same effect is revealed in the phenyl vinyl ethers **42**—**88**, naphthyl vinyl ethers **89**—**90**, and benzyl vinyl ether **91**.

It has been recognized that the chemical shifts of ^{17}O atom in the α,β-unsaturated ethers have been sensitive to the condition of p–π conjugation.[17] The resemblance of p–π conjugation conditions in the aryl and hetaryl vinyl ethers is also traced from ^{17}O NMR data. The chemical shifts of ^{17}O in the hetaryl vinyl ethers **1**—**3**, **5**, **6**, **9**, **10**, **12**—**15**, **19**, and **30** cover the range from 105 to 142 ppm and in the aryl vinyl ethers **32**, **39**—**42**, **73**, and **82** they are within 114—139 ppm.[17] It suggests the same intensity of p–π conjugation in both series of ether. The upfield shift of ^{17}O signal in the benzyl vinyl ether **91** is related with the loss of the competitive p–π conjugation[17] in respect to that in the phenyl vinyl ether **42**. Analogous upfield shift is observed in the ^{17}O signal of 3- and 4-vinyloxypyridines **2** and **3** and 3- and 4-(vinyloxymethyl)pyridines **5** and **6** (Table 2, supplementary).

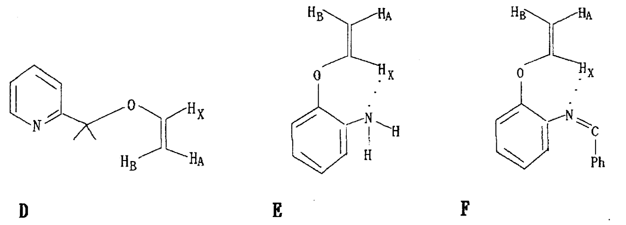
Thus, the analysis of ^1H, ^{13}C, and ^{17}O NMR parameters allows to propose similar spatial and electronic structure of the aryl and hetaryl vinyl ethers, i.e. both series of ethers exist predominantly in s-trans form (except **4**—**7** and **91**). The competitive p–π conjugation is realized in these ethers. Therefore, it is possible to analyze NMR data of both series ethers, in common, in order to reveal the specific features of the hetaryl vinyl ethers.

The Anomalies of ^1H and ^{13}C NMR Parameters in 2-Vinyloxypyridines and 2-Vinyloxyquinolines. The chemical shift of α-proton in the vinyloxyl group (H_X) changes from 6.49 to 6.81 ppm. There are ethers where the vinyloxyl group is neighboring to the endocyclic nitrogen **1**, **8**, **9**, **14**, **19a**, **20a**, **21a**, **22**—**25**, **26a** and **b**, **27a** and **b**, **28**, and **31** (symbol "**a**" through the text denotes the 2-vinyloxyl group of **19**—**21**, **26**, and **27** and symbol "**b**" denotes the 4-vinyloxyl group of these ethers). These ethers will be called the ethers of A-class unlike to others which will be called the ethers of class B. In the A class the signal of H_X is drastically shifted to the lower field (7.20—7.88 ppm) though such shifting of the H_A and H_B protons are not observed. It should be noted, that presence of nitrogen, neighboring to the vinyloxyl group, is decisive factor for the rising of anomalous downfield shift of the H_X signal. Thus, in bis(vinyloxy)quinolines **19**—**21** the H_X signals in 2-vinyloxyl group are anomalously shifted, rather than those of 4-vinyloxyl group (Table 1, supplementary). In bis(vinyloxy)pyrimidines **26** and **27** vinyloxyl groups are neighboring to the endocyclic nitrogen. The H_X signals of both vinyloxyl group are anomalously shifted. The mentioned downfield shift is caused by the intramolecular specific interaction (ISI) between H_X hydrogen and the endocyclic nitrogen.[9,10] The ISI arises if the favorable stereochemical conditions are provided, i.e. when 2-vinyloxypyridine (quinoline) exists in *s-trans* conformation and *syn*-arrangement of nitrogen to vinyloxyl group (**A** in Scheme 2). The ISI C–H···N can be realized in any of these compounds **1**, **8**, **9**, **14**, **19**—**28**, and **31**. Only H_X hydrogen of 2-vinyloxyl group can be involved into C–H···N interaction in divinyloxyquinolines **19**—**21**, but H_X hydrogen of both vinyloxyl groups in **26** and **27** can takes part in this interaction. The sharp upfield shift of H_X proton (ca. 0.9 ppm) is observed in the molecules **2**, **3**, and **42** compared to **1**. There is the disappearance of C–H···N interaction in these compounds. However, there are no significant changes of δH_X on going from 2-(vinyloxymethyl)pyridine **4** to 3- and 4-(vinyloxymethyl)pyridines **5** and **6** or benzyl vinyl ether **91**.

(Vinyloxymethyl)pyridines **4**—**6** in opposition to (vinyloxy)pyridines exist essencially in *s-cis* conformation and *syn*-arrangement of the methylene proton to the double bond (**D** in Scheme 3). An absence of δH_X changing, under the changing of the vinyloxymethyl group position in **4**—**6** is explained by the spatial withdrawing of H_X signal, provoked



Scheme 2.



Scheme 3.

by the endocyclic nitrogen in *s-cis* conformation.[18)]

The successive change of the vinyloxyl group mutual arrangement to nitrogen-containing substituents (NH_2-**35**, **74**, and **81**; NHC(O)H-**43**, **121**, and **122**; $NHC(O)CH_3$-**44**, **77**, and **83**; phthalimido-**64**, **79**, and **87**; Ph-CH=N-**58**, **117**, and **125**; furyl-CH=N-**59**, **84**, and **118** and thienyl-CH=N-**60**, **78**, and **85**) does not result in the significant change of δH_X parameter (Table 1, supplementary). It implies that H_X hydrogen does not take part in ISI with exocyclic nitrogen in the listed compounds, although this interaction could be presents (**E** and **F** in Scheme 3).

The existence of C–H···N interaction in A class of ethers have to influence on another spectral parameters. Thus, the substantial increase of $^2J_{AB}$ takes place in **1** and **9** (0.4—0.7 Hz) in a comparison with an isomeric **2**, **3**, and **10**—**13**. The one-bond ^{13}C-^1H coupling constants ($^1J_{C_\alpha H_X}$), in the vinyloxyl group, are larger in ethers of A class than in B. The varying range of $\Delta\delta$ values is shifted by 0.1 ppm towards larger ones among ethers of class A in according to B (Table 1, supplementary). Moreover, one may mark also some increase of the difference in one-bond ^{13}C-^1H coupling constants ($^1J_{C_\beta H_A}$-$^1J_{C_\beta H_B}$) of β-carbon in vinyloxyl group in A class ethers. However, these distinctions of ^1H and ^{13}C NMR parameters of A and B classes of ethers do not have a regular character at the qualitative analysis of the spectral data. Hence, we used the various statistical methods to process a spectral information.

The Regression and Dispersion Analysis of ^1H and ^{13}C NMR Data of Aryl and Hetaryl Vinyl Ethers. It has been shown[15,19)] that the $\delta^{13}C$ values of phenyl vinyl ethers are determined by the intensity of p–π conjugation in vinyloxyl group, which influences by the electronic effects of substituents on the ring. From this observation, we have selected the $\delta^{13}C_\beta$ as a reference in order to clear up the influence of an electronic effect of aryl of hetaryl ring on another ^1H and ^{13}C NMR parameters of vinyloxyl group.

The chemical shifts of β-protons (H_A and H_B) are satisfactorily correlated with $\delta^{13}C_\beta$ values in B class ethers, except ortho-substituted ones:

$$\delta H_A = 0.073\delta^{13}C_\beta - 2.55;\ r = 0.979, s = 0.026, n = 66 \qquad (1)$$

$$\delta H_B = 0.075\delta^{13}C_\beta - 2.45;\ r = 0.943, s = 0.046, n = 66 \qquad (2)$$

Where r is correlation coefficient, s is standard deviation, and n is number of data. The distinction of both coefficients in Eqs. 1 and 2 are negligible. Therefore, δH_A and δH_B values show the same sensitivity to alteration of the charge on β-carbon, which is the main factor defining the behavior of these parameters. The δH_A and δH_B values of A class ethers exhibit the steady deviation from Eqs. 1 and 2 (Fig. 1). These deviations are in the field from 0.09 to 0.19 ppm for δH_A and from 0.08 to 0.21 ppm for δH_B (molecules **1**, **8**, **9**, **14**, **19a**, **20a**, **22**, and **23**). The deviations of δH_A and δH_B values from Eqs. 1 and 2 are less (0.04—0.11 and 0.02—0.08 ppm, respectively) in vinyloxypyrimidines **24**—**26**, and **28**. Discussed deviations of δH_A and δH_B values exceed to 7 and 5 times, respectively, from the parameter s in Eqs. 1 and 2. Consequently, they can not be caused by the random factors.[20)] These deviations appear as a result of the existence of ISI C–H_X···N in A class ethers, leading to the additional negative contribution into the shielding of the H_A and H_B atoms. The $^1J_{C_\beta H_A}$ and $^1J_{C_\beta H_B}$ values vary within the narrow range, 161.2—162.8 Hz and 157.4—159.3 Hz, respectively. The deviations of $^1J_{C_\beta H_A}$ and $^1J_{C_\beta H_B}$ values in A class ethers from those in B class are not observed.

The $^1J_{C_\alpha H_X}$ coupling constant changes within the wide range 181.7—192.2 Hz (Table 1, supplementary). These values in B class ethers (except ortho-substituted derivatives) show the excellent linear dependence upon the $\delta^{13}C_\beta$:

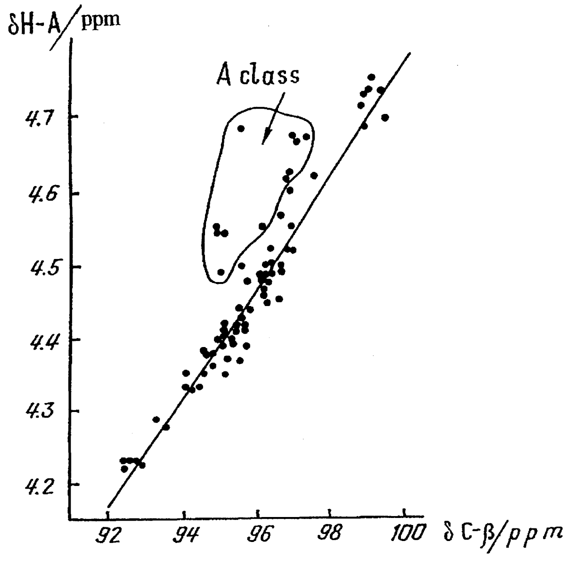


Fig. 1. The dependence of δH_A chemical shifts on the $\delta^{13}C_\beta$ chemical shifts in ethers **2**, **3**, **10**—**13**, **15**—**18**, **19b**, **20b**, **29**, **30**, **32**—**80**, **89**, and **90**.

$$ {}^1J_{C_\alpha H_X} = 0.61\delta^{13}C_\beta + 124.8;\ r = 0.964, s = 0.282, n = 65 \quad (3)$$

The relationship (3) serves as another evidence of the conformational homogeneity of the aryl and hetaryl vinyl ethers. A stereoselective contribution into the ${}^1J_{C_\alpha H_X}$ magnitude from the oxygen lone-pairs is exhibited in the conformationally heterogeneous ethers. It leads to the failure of the linear dependence of ${}^1J_{C_\alpha H_X}$ upon $\delta^{13}C_\beta$.[18] This contribution is invariable in conformationally homogeneous ethers and, therefore, the ${}^1J_{C_\alpha H_X}$ values are determined mainly by the distribution of the charges in vinyloxyl group.

In all A class ethers the ${}^1J_{C_\alpha H_X}$ values fall outside (Fig. 2). The magnitude of the ${}^1J_{C_\alpha H_X}$ deviation is in the limit 5.2—8.1 Hz and exceeds parameter *s* (Eq. 3) to 20—30 times. It excepts the possibility of a deviation from random cause. The magnitude of the ${}^1J_{C_\alpha H_X}$ deviation may be interpreted as an additional positive contribution to the ${}^1J_{C_\alpha H_X}$ coupling constant of A class ethers, arising from C–H$_X$···N interaction.

It should be noted that the points of the 2-vinyloxyl groups fall out the Eq. 3 only in molecules **19**, and **20**, but the points of the 4-vinyloxyl groups follows this equation (Fig. 2). The points of both vinyloxyl groups fall outside the Eq. 3 in **26** (Fig. 2), since it is possible to form a double ISI in opposition to **19** and **20** (**E** and **F** in Scheme 3). The magnitude of ${}^1J_{C_\alpha H_X}$ deviation for 2-vinyloxyl group in **26** is similar to 4-vinyloxyl group. It means that the electronic effect of the neighboring nitrogen does not influence the ${}^1J_{C_\alpha H_X}$ deviation.

The deviation of ${}^1J_{C_\alpha H_X}$ from dependence (3) also takes place in ortho-substituted aryl vinyl ethers **81**—**88** towards larger values by 1—2 Hz. However, the increase of ${}^1J_{C_\alpha H_X}$ is not accompanied by the downfield shift of the H$_X$ signal in this case. This increase may be ascribed to the enhancement of *s-cis* conformation population owing to steric effect of the ortho-substituents. The additional positive contribution to ${}^1J_{C_\alpha H_X}$ is provided by the spatial approach of the oxygen lone-pairs to C$_\alpha$–H$_X$ bond.[21]

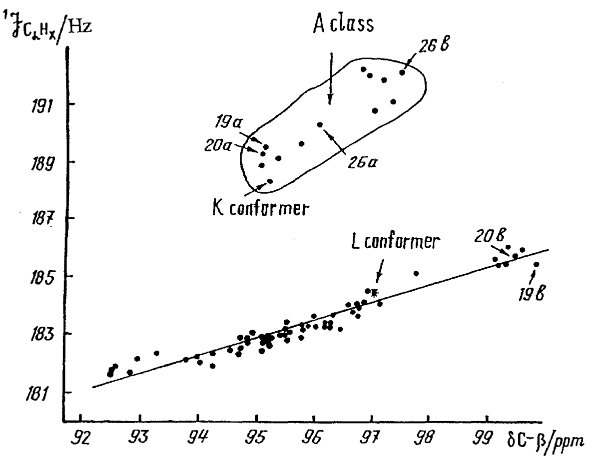


Fig. 2. The dependence of ${}^1J_{C_\alpha H_X}$ coupling constants on the δC_β chemical shifts in ethers **2**, **3**, **10**—**13**, **15**—**18**, **19b**, **20b**, **30**, **32**—**80**, **89**, and **90**. *denotes the calculated values of ${}^1J_{C_\alpha H_X}$ and δC_β for the hypothetical conformer **L** of 2-vinyloxypyridine **1**.

The $\delta^{13}C_\alpha$ and $\delta^{13}C_\beta$ in the B class ethers (besides ortho-substituted derivatives) change in opposite direction:

$$\delta^{13}C_\alpha = -0.654\delta^{13}C_\beta + 210.7;\ r = 0.974, s = 0.246, n = 66 \quad (4)$$

The existence of the relationship (4) implies the redistribution of a charge onto C$_\alpha$ and C$_\beta$ carbons under the influence of an electronic effect of aryl or hetaryl moiety, i.e. the diminution of the charge onto C$_\beta$ atom corresponds to increase of the charge onto C$_\alpha$ atom. The interconnection of the $\delta^{13}C_\alpha$ and $\delta^{13}C_\beta$ has been observed in any aryl vinyl ethers, sulfides, and selenides.[15] The points of A class ethers fall outside again from dependence (4) (Fig. 3), but towards less values. The $\delta^{13}C_\alpha$ deviations are equal to 3.8—5.0 ppm and amout to 15—20 *s*. The ISI C–H$_X$···N may results to delocalization of the nitrogen lone-pairs onto C$_\alpha$H$_X$ bond of A class ethers. It rises the paramagnetic contribution into the shielding constant of C$_\alpha$ atom. However, there is another explanation for $\delta^{13}C_\alpha$ atom anomalous shielding considering torsion angles change.

As in the case of ${}^1J_{C_\alpha H_X}$, the $\delta^{13}C_\alpha$ values of 2-vinyloxyl groups deviate from the dependence (4) in **19** and **20**. The same values of 4-vinyloxyl groups are subordinated to this equation (Fig. 3). The $\delta^{13}C_\alpha$ values of both vinyloxyl groups fall outside the dependence (4) in compound **26** (Fig. 3). Thus, there is obvious anomaly of ${}^1J_{C_\alpha H_X}$ and $\delta^{13}C_\alpha$ values for A class ethers.

The δH_X values are not correlated with $\delta^{13}C_\beta$ even in B class ethers ($r < 0.7$). Consequently, it is not only electronic effect of aryl or hetaryl moiety that influences upon the δH_X. It was detected by interesting regularity of δH_X changes in B class ethers. We divided the total range (6.49—6.71 ppm) of δH_X varying into 8 equal subranges (compounds **2**, **3**, **30**, **32**—**87**, **92**—**118**, and **120**—**133**). Then, we counted the δH_X appearance *h* in each of the subranges (the results are presented in Table 3). The greatest *h* value takes place for a central subrange. The *h* value significantly decreases on the edges (Fig. 4). One may suppose that δH_X parameter in the listed ethers are subordinated to the Gauss law of the distribution. To verify this hypothesis the χ^2 criterion[20] was used. The theoretical values h_t of the δH_X appearance are given

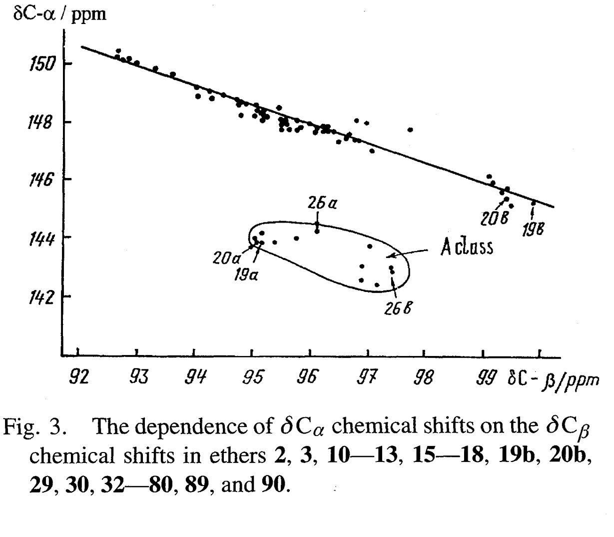


Fig. 3. The dependence of δC_α chemical shifts on the δC_β chemical shifts in ethers **2**, **3**, **10**—**13**, **15**—**18**, **19b**, **20b**, **29**, **30**, **32**—**80**, **89**, and **90**.

Table 3. Theoretical and Experimental Values of H_X Chemical Shifts. Distribution into Subranges

No.	Subrange/ppm	h_t[a]	$h-h_t$	$(h-h_t)^2/h_t$
1.	6.49—6.51	2.76	−0.76	0.29
2.	6.52—6.54	9.84	−0.84	0.08
3.	6.55—6.57	17.92	2.08	0.22
4.	6.58—6.60	24.95	−0.95	0.04
5.	6.61—6.63	23.34	−0.34	0.01
6.	6.64—6.66	14.70	−0.70	0.03
7.	6.67—6.69	6.11	0.89	0.13
8.	6.70—6.72	1.73	0.27	0.04
				$\chi^{2\,\text{b)}}=-0.84$

a) The h_t values are calculated by equation: $h_t=\frac{nd}{\sigma}\phi$ $(\frac{\delta H_X-\overline{\delta H_X}}{\sigma})$, where h_t is number of compounds, d is width of subrange, and ϕ is Gauss function;[21] b) $\chi^2=\sum(h^i-h_t^i)^2/h_t^i$, where sum is from $i=1$ to $i=m$ (m is number of subranges).

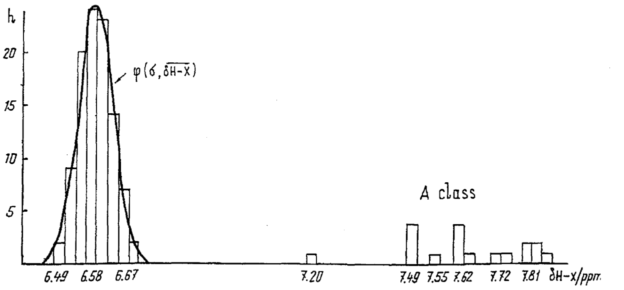
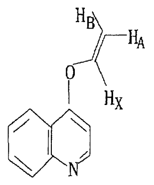


Fig. 4. The distribution of δH_X chemical shifts in ethers **2**, **3**, **30**, **32—87**, **92—118**, and **120—133** in subranges; Φ $(\sigma, \overline{\delta H_X})$ is the Gauss function.

in Table 3. The χ^2 parameter for **2**, **3**, **30**, **32—87**, **92—118**, and **120—133** is equal to 0.84 only. This is much less than a 99% confidence level.[20] Consequently, the distribution of the experimental δH_X values well corresponds to the Gauss law. A middle value of the δH_X ($\overline{\delta H_X}$) is 6.60 ppm and a dispersion (σ) is 0.0474 ppm. It allows to suppose that the superposition of the same random effects result to the Gauss distribution of δH_X values in the series of aryl and hetaryl vinyl ethers. They present: the local conformational heterogeneity; the electronic and steric effects of substituents; and the heterogeneous gradient of intramolecular electric field.[22] The probability of appearance of δH_X value is determined by the Eq. 5:

$$p(\delta H_X)=\frac{1}{\sigma\sqrt{\pi}}\exp\left(-\left(\delta H_X-\overline{\delta H_X}\right)^2/2\sigma\right) \tag{5}$$

where $p(\delta H_X)$ is the probability of appearance δH_X value. The deviation of δH_X suggests a predominance of the specific factor. In some ethers, it exceeds 3 times parameter s. For example, the δH_X values are 6.74—6.79 ppm in compounds with a fused benzene ring **11**, **13**, **15—18**, **19b**, and **89**. This deviation of δH_X from $\overline{\delta H_X}$ (0.15—0.20 ppm) (Fig. 4) may be refereed as an influence of fused cycle anisotropy (**G** in Scheme 4). The δH_X values fall outside from distribution (5) in A class ethers (Fig. 4). The deviation, in this case, is equal to 0.60—1.28 ppm or 15—25σ. The



G

Scheme 4.

ISI C–H_X···N is a factor causing this dramatic deviation.

Thus, the deviations of δH_A, δH_B, ${}^1J_{C_\alpha H_X}$, $\delta^{13}C_\alpha$, and δH_X values from Eqs. 1, 2, 3, 4, and 5 in A class ethers are interconnected and are due to the same reason, which is C–H_X···N interaction between α-hydrogen of the vinyl group and endocyclic nitrogen. The magnitude deviations of listed parameters from Eqs. 1, 2, 3, 4, and 5 can serve as an empirical estimation of the additional contributions into the corresponding shielding and coupling constants arising from the ISI C–H_X···N. They are equal to 0.10—0.15 ppm for δH_A and δH_B, 6—7 Hz for ${}^1J_{C_\alpha H_X}$, 4—5 ppm for $\delta^{13}C_\alpha$, and ca. 1 ppm for δH_X (Figs. 1, 2, 3, and 4).

These estimations have an essential shortcoming. They do not take into account the possibility of the additional contribution into the referenced $\delta^{13}C_\beta$ value. Moreover, it is difficult to estimate how the ISI C–H_X···N influences the ${}^2J_{AB}$ and other parameters. To recognize an anomaly of the parameters combination for A class ethers the multidimentional statistical analysis should be used.

The Cluster Analysis of ^{1}H and ^{13}C NMR Data for Aryl and Hetaryl Vinyl Ethers. The distinction of parameters combination in A and B classes ethers can be provided by the cluster analysis.[23] In terms of this method, the parameters combination of the vinyloxyl group of each i and j-compounds is represented by $\overline{X}_i$ $\overline{X}_j$ vectors in n-dimentional Euclid metric space. The chemical shifts and coupling constants are the components of these vectors. The dimension n is defined by the number of components (in our case $n=11$). The square of distance d_{ij}^2 between $\overline{X}_i$ and $\overline{X}_j$ vectors in Euclid metric space is calculated by Eq. 6:[23]

$$d_{ij}^2=\left(\overline{X}_i-\overline{X}_j\right)^t\left(\overline{X}_i-\overline{X}_j\right), \tag{6}$$

where t is transposition symbol. The ethers **1**, **8**, **9**, **14**, **19a**, **20a**, **24—26a,b**, **2**, **10—13**, **15—17**, **19b**, **20b**, **30**, **32—35**, **38—42**, **56**, **58—60**, **63**, **65**, **68—76**, **81**, **82**, **84**, **88**, and **89** were selected to perform the cluster analysis. The clusterization procedure consists in the subsequent unification of the most similar objects in the n-dimentional Euclid space.[23] This process is represented by a dendogram (Fig. 5). The points a, b, c, d, e, and f designate the junction in which the unification of objects into the cluster takes place. It was supposed, the d_{ij}^2 value to be equal 1 for the most distant clusters. The unification of the most distant clusters occurs in the last junction a. The one of them consists of A class ethers and another contains B class ethers. This implies that the vinyloxyl group parameters of A class ethers are anomalous in comparison with B class. It is caused in C–H···N interaction.

The vinyloxyl groups of **19** and **20** belong to the different clusters, but the vinyloxyl groups of **26** are involved into the same cluster (Fig. 5). The molecules **2**, **10**, **11**, **15**—**17**, **19b**, **20b**, **69**, and **73** are untied with other B class ethers in *b* junction. These ethers are separated on the two clusters up to *e* junction. The *d* junction unites two clusters of A class ethers. The composition of these clusters **1**, **9**, **14**, **19a**, **20a**, **26a** and **8**, **24**, **25**, **26b** differs by $\delta^{13}C_{\beta}$ ranges (95.01—96.12 and 96.94—97.46 ppm, respectively) and, therefore, by intensity of p–π conjugation in vinyloxyl group. The *f* junction unites **32**—**35**, **39**, **41**, and **82** with more electron-donating substituents ($\delta^{13}C_{\beta}$=92.53—94.27 ppm). Also, in *f* junction are included ethers **12**, **13**, **38**, **40**, **42**, **56**, **58**—**60**, **63**, **65**, **68**, **71**, **72**, **74**—**76**, **81**, and **89** with substituents having weak electronic effect ($\delta^{13}C_{\beta}$ differs less than 1.7 ppm from that in phenyl vinyl ether **42**) (Fig. 5).

Using previous consideration, one can distinguish two factors determining the ^{1}H and ^{13}C NMR parameters of vinyloxyl groups under discussion. At first, there is an electronic effect of the substituents. Then, there is intramolecular specific interaction $C–H_X\cdots N$. The influence of this factor (if it takes place) is more essential than the first one. The most unambiguous interpretation of the factors affecting on ^{1}H and ^{13}C NMR parameters may be made on the base of the factor analysis.

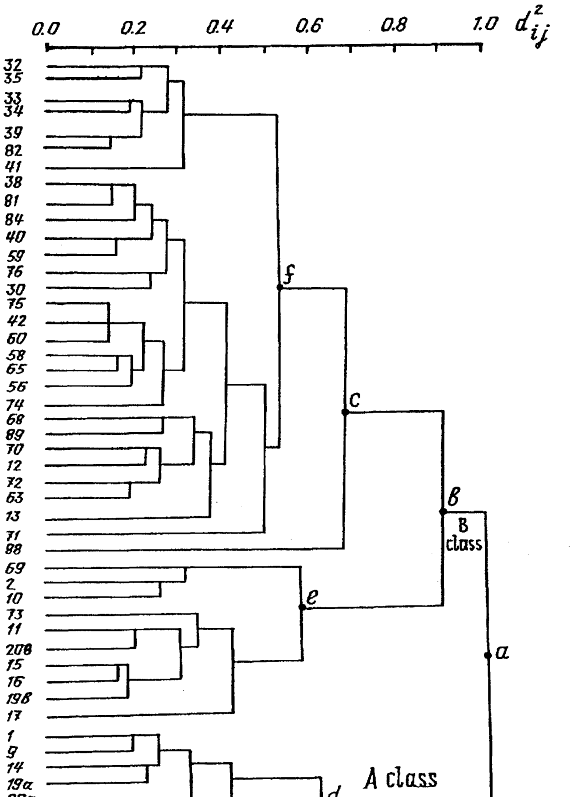


Fig. 5. The dendogramme of clusterization procedure of ethers **1**, **2**, **8**—**17**, **19**, **20**, **24**—**26**, **30**, **32**—**35**, **38**—**42**, **56**, **58**—**60**, **63**, **65**, **68**—**76**, **81**, **82**, **84**, **88**, and **89**.

The Factor Analysis of ^{1}H and ^{13}C NMR Data for Aryl and Hetaryl Vinyl Ethers. The factor analysis allows to separate the various factors which influence on the spectral parameters. Moreover, it is possible to do quantitative analysis of contributors.[24] The matrix of spectral data P_{ij} (where *i* row corresponds to *i* compound and *j* column corresponds to *j* parameter) presents as a multiplication of the matrix F_{ik} and A_{kj}:[25]

$$P_{ij} = F_{ik} \cdot A_{kj} + P_{ij}^{\circ} \tag{7}$$

where P_{ij}° is the residual members matrix. The percent contribution from *k* factor to the total dispersion D_k of spectral parameters was calculated by Eq. 8:[25]

$$D_k = (\lambda_k / Sp\{S\}) \cdot 100, \tag{8}$$

where λ_k is *k* eigenvalue of the *S* covariance matrix, $Sp\{S\}$ being a trace of matrix *S*,

$$S = P_{ij} P_{ij}^{t} (1/(N-1)), \tag{9}$$

where *N* is number of compounds.

The factor analysis of eleven parameters (the five chemical shifts and six coupling constants) results to selection of two factors, describing the 87% of total dispersion. First factor F_e corresponds to the eigenvalue of *S* matrix (λ_1=6.12) and describes 56% of total parameters dispersion. Second factor F_{SI} corresponds to the eigenvalue of *S* matrix (λ_2=3.40) and describes 31% of total parameters dispersion. The next factor contributes less than 6% of total dispersion. Thus, the contribution of the third factor is negligible (Table 4). Hence, the analysis were performed in approximation of the two factors.

Table 4. The Values of F_e and F_{SI} Factors

Compound	F_e	F_{SI}	Compound	F_e	F_{SI}
1	6.84	7.67	**38**	1.66	−0.97
2	10.42	−0.82	**39**	−1.29	0.59
8	14.66	9.49	**40**	2.11	−0.35
9	8.05	8.86	**41**	0.19	1.08
10	11.01	−0.84	**42**	2.75	0.17
11	17.02	1.59	**56**	4.45	−0.45
12	8.37	0.30	**58**	3.58	−0.46
13	8.97	1.02	**59**	3.91	0.31
14	6.23	9.82	**60**	3.48	−0.03
15	16.43	0.32	**63**	6.01	0.12
16	16.75	−0.33	**65**	4.84	−0.71
17	12.80	−0.60	**68**	5.69	1.48
19a	6.58	9.26	**69**	9.71	0.19
19b	17.73	−0.40	**70**	6.38	0.43
20a	8.65	9.77	**71**	7.20	−2.06
20b	16.98	0.50	**72**	7.07	−0.85
24	13.74	8.71	**73**	17.92	−1.32
25	13.93	8.61	**74**	2.35	0.61
26a	10.69	7.45	**75**	3.85	0.59
26b	15.35	7.23	**76**	1.05	0.37
30	2.16	−0.22	**81**	1.34	−0.60
32	−2.74	−1.11	**82**	1.07	0.32
33	−3.01	−0.27	**84**	3.12	−0.86
34	−2.30	−0.63	**88**	1.70	4.35
35	−1.65	−0.21	**89**	4.72	1.06

The distribution of the ethers in a factor space is depicted on Fig. 6. To minimize the sum of F_{SI} factors for B class ethers, the rotation of the factor space was carried out by 166°. The electron-withdrawing property of aryl or hetaryl part is intensified and the increase of F_e factor is observed. The F_e values are found into the range from −3.01 to 1.07 for **32**—**39**, **41**, **76**, and **82**. In these compounds the substituents reveal electron-donating properties. The F_e values change from 1.34 to 4.84 for **40**, **56**, **58**—**60**, **75**, and **84** with moderate electron effect ($\delta\,^{13}C_\beta$=94.51—95.78 ppm). When the F_e values are shifted up to 5.69—17.92 in molecules **63** and **68**—**73**, the substituents are an electron-acceptor ($\delta\,^{13}C_\beta$=95.82—99.11). Therefore, the F_e factor is responsible for the spectral parameters dispersion, provided by the electronic effect of aromatic part. Such interpretation of F_e factor is confirmed by the linear dependence between F_e and Taft constants[26] (σ_R) in molecules **33**, **35**, **39**, **41**, and **71**—**73**.

$$F_e = 21.07\sigma_R + 1.68; \quad r = 0.995, s = 0.757, n = 7 \qquad (10)$$

The F_{SI} values are randomly changed in B class ethers (from −2.06 to 1.59) (Fig. 7). There is drastic increase of F_{SI} factors up to 7.23—9.28 for A class ethers. Therefore, the F_e factor appears to reflect mainly the influence of intramolecular specific interaction on the parameters of vinyloxyl groups.

In **19** and **20** the sharp increase of F_{SI} value occurs for 2-vinyloxyl groups only (Fig. 6). The F_{SI} values of 4-vinyloxyl groups in **19** and **20** get into the range of random changes (Fig. 6). In **26** the F_{SI} factor dramatically increases for both vinyloxyl groups (Fig. 6). The F_{SI} of both vinyloxyl groups is negligibly different in **26** (7.45 and 7.23), though the 2-vinyloxyl group is found between two nitrogens. It demonstrates F_{SI} insensitivity to electronic effect of *endo*-cyclic nitrogen. The electronic effect of nitrogen is displayed in increasing F_e factor for 4-vinyloxyl group, i.e., 4.66 (Table 4). The F_{SI} of ortho-phenylazo-substituted ether **88** takes intermediate position between A and B classes of ethers. Furthermore, the **88** forms an individual cluster (Fig. 5), which is united with other ethers in junction *c* only. Moreover, the ${}^1J_{C_\alpha H_X}$ in **88** takes value 3.2 Hz (11*s*). It is more than calculated from Eq. 3. The parameter δH_X is deviated by 0.21 ppm (>4σ) from the center of distribution (5). These facts suggest the ISI C–$H_X\cdots$N, which is formed by β-nitrogen of azo group **88** (**H** in Scheme 5). The ISI with α-nitrogen of azo group is absent because this interaction would be revealed in *o*-(vinyloxy)phenyliminomethyl compound **84**.

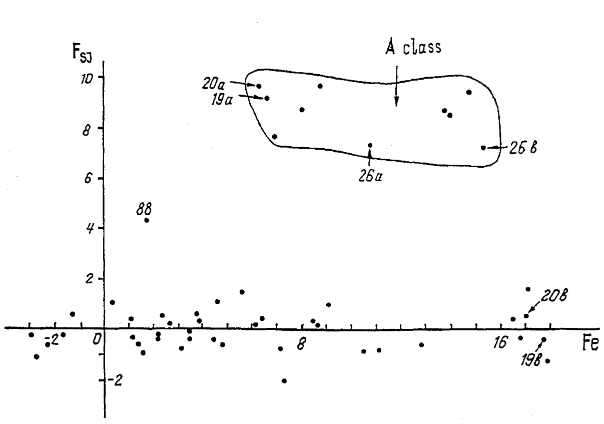


Fig. 6. The distribution of ethers **1**, **2**, **8**—**17**, **19**, **20**, **24**—**26**, **30**, **32**—**35**, **38**—**42**, **56**, **58**—**60**, **63**, **65**, **68**—**76**, **81**, **82**, **84**, **88**, and **89** in the factor space.

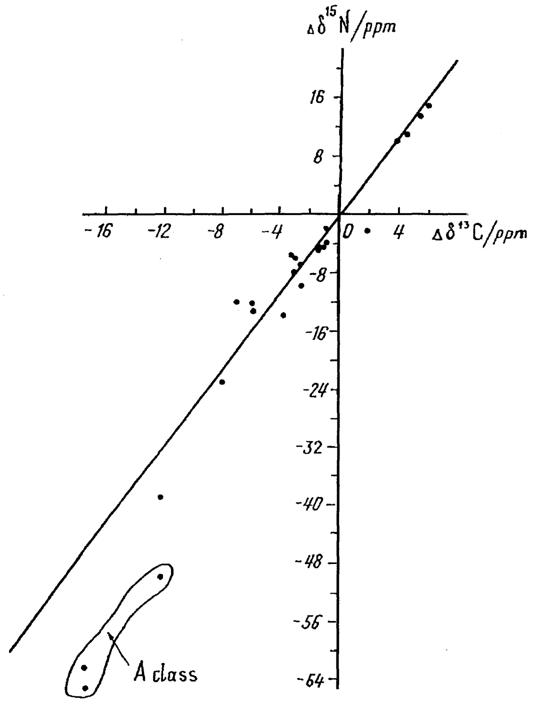
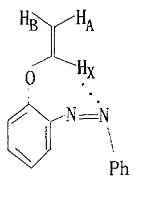


Fig. 7. The dependence of $\Delta\delta\,^{15}N$ chemical shifts increments in pyridines and quinolines on the $\Delta\delta\,^{13}C$ chemical shifts increments in benzenes and naphthalenes.

All eleven parameters of vinyloxyl group under consideration were expanded by F_e and F_{SI} factors. The parameters of this expansion are given in Table 5. The expansion of ${}^2J_{AB}$, ${}^3J_{AX}$, ${}^3J_{BX}$, and ${}^1J_{C_\beta H_A}$ have poor correlation (0.8<r<0.9). It may be explained by the shortage of two factors for description of the mentioned parameters as well as by their small dispersion.

The electronic effect of substituent and ISI are the main factors for remaining parameters. Proceeding from the factor (A_{SI}/A_e) one can estimate the relative significance of F_e and F_{SI} factors for δH_A, δH_B, $\delta\,^{13}C_\beta$, ${}^1J_{C_\beta H_B}$, and ${}^1J_{C_\alpha H_X}$ parameters (Table 5). The contribution of F_e is more significant for δH_A, δH_B, and $\delta\,^{13}C_\beta$ (A_{SI}/A_e=0.20—0.36), i.e. these parameters are relatively insensitive to ISI. The δH_X shows



H

Scheme 5.

Table 5. The Parameters of Chemical Shifts and Coupling Constants Expansion Factors (Eq. 7).

P	P_0	$A_e\cdot10^2$	$A_{SI}\cdot10^2$	$\lvert A_{SI}/A_e\rvert$	r[a)]
δH-a	4.30	2.33	0.46	0.20	0.977
δH-b	4.63	2.41	0.94	0.39	0.950
δH-x	6.57	0.98	11.40	11.63	0.977
δC-β	93.8	32.1	−11.5	0.36	0.979
δC-α	149	−22.2	−37.8	1.70	0.961
$^2J_{AB}$	1.58	2.05	−3.75	1.83	0.886
$^3J_{AX}$	6.15	−1.1	−2.0	1.82	0.864
$^3J_{BX}$	13.8	−1.25	2.83	2.26	0.810
$^1J_{C_\beta H_A}$	162	5.41	1.30	0.24	0.876
$^1J_{C_\beta H_B}$	158	8.73	−1.91	0.22	0.953
$^1J_{C_\alpha H_X}$	182	21.9	64.6	2.95	0.969

a) The coefficients of correlation.

the highest sensitivity to ISI in comparison with the electronic effect of the substituent (A_{SI}/A_e=11.63). The $\delta^{13}C_\alpha$ and $^1J_{C_\alpha H_X}$ possess the less sensitivity to ISI (A_{SI}/A_e=1.70 and 1.95, respectively). Thus, the existence of ISI C–H···N in A class ethers is mainly reflected by δH_X, $\delta^{13}C_\alpha$, and $^1J_{C_\alpha H_X}$ values. The $\delta^{13}C_\beta$ value is almost insensitive to the discussed interaction. It allows to believe, that the quantitative estimation of the additional contribution into the shielding constants of $^{13}C_\alpha$ and $^1J_{C_\alpha H_X}$ coupling constants from Eqs. 3 and 4 are reliable.

The Anomalous of ^{15}N NMR Parameters of 2-Vinyloxypyridine and 2-Vinyloxyquinoline. It has been recognized that the chemical shifts of ^{15}N are sensitive to the state of lone-pair electrons.[27)] Therefore, the ISI should affects on δ^{15}N values in A class ethers. To estimate an additional contribution to ^{15}N shielding constants, the dependence of δ^{15}N increments in pyridines and quinolines ($\Delta\delta^{15}$N) has been built, resulting from electronic effect of para- and peri-substituents upon those for δ^{13}C ($\Delta\delta^{13}$C) in benzenes and naphthalenes (Table 6, suppl.):

$$\Delta\delta^{15}N = 2.707\Delta\delta^{13}C - 0.527;\quad r = 0.960, s = 3.36, n = 22 \tag{11}$$

Let us choose the pairs of the isostructural derivatives of pyridine and benzene. The increments of δ^{15}N and δ^{13}C would be subordinated by dependence (11), if they are influenced by the same factors. For example, the increments $\Delta\delta^{15}$N and $\Delta\delta^{13}$C of 2-fluorine atom in 2-fluoropyridine and fluorobenzene are interconnected by relation (11) (Fig. 7). The fluorine atom has the electronic effect similar to vinyloxyl group. It follows from the comparison of fluorine increments and CH_2=CHO group in benzene ring (Δ*C-o* are −12.9 and −11.5; Δ*C-m* are +1.4 and +1.0; Δ*C-p* are −4.5 and −5.6 ppm). However, the $\Delta\delta^{15}$N of 2-vinyloxyl group in **1**, **9**, and **19** fall outside the Eq. 11 (Fig. 7). The deviations are equal to 17—20 ppm towards less values. The magnitude serves as the empirical estimation of the additional positive contribution into the shielding constant of nitrogen, arising from the ISI C–H_X···N. It should be stressed that the additional positive contribution into shielding constant is observed in the case of usual bonding of hydrogen with nitrogen, and the magnitude is 140 ppm.[28)]

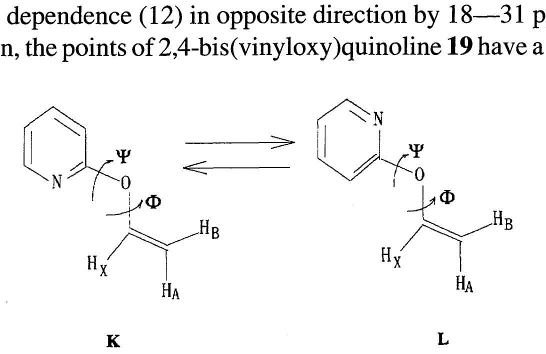
The Quantum-Chemical Calculations of Aryl and Hetaryl Ethers. The spectral data do not allow the structural anomaly of A class ethers in a comparison with B class ethers. We provided the quantum-chemical calculation of **1**, **2**, **35**, **39**—**43**, **71**—**73**, and **131** by AM1 method.[29)] The structure of ethers can be characterized by two torsion angles: around O–C_α bond (Φ) and around O–$C_{\text{hetaryl(aryl)}}$ (Ψ) (**K** in Scheme 6). The surface of internal rotation energy for **1** was calculated. The results are presented on Fig. 8. This surface has two minima in the field of *s-trans* conformation, corresponding to non-planar *syn* (**K**) and *anti* (**L**) conformers (Scheme 6). First minimum (Fig. 8) is by 4.48 kcal mol^{-1} lower than the second one, i.e. the **L** conformer is poor populated at the room temperature. The energetic preference of the *syn*-arrangement of pyridine cycle in comparison with *anti*-arrangement may be attributed for stabilization of **K** conformer by the C–H···N interaction. The intramolecular specific interaction results to enhancement of *s-trans* conformation population in A class ethers, that is indicated in increasing of $\Delta\delta$ parameter in a comparison with B class ethers.

The equilibrium values of Ψ and Φ for **K** conformer are equal to 31° and 11° (compound **1**). In B class ethers the Ψ and Φ values vary within 18—50° and 5—41° range (Table 7). At the same time, the sum of $\Psi+\Phi$ is almost invariable (52—59°) in these ethers. This sum is reduced to 42° in **1**. Thus, the molecule **1** is more planar than aryl and hetaryl vinyl ethers **2**, **35**, **39**—**43**, **71**—**73**, and **131**. This also may be the reflection of attractive ISI C–H···N.

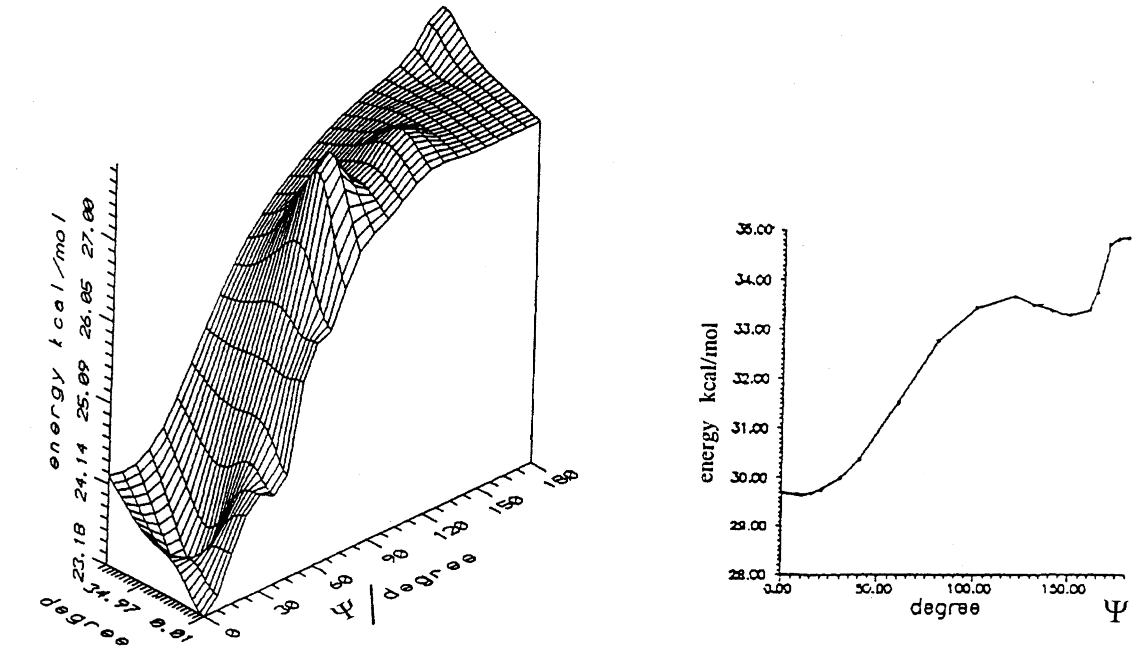
There are an experimental data which are in favor of decrease in torsion angle in A class ethers. There is correlation between the chemical shifts of ^{17}O and $^{13}C_\beta$ in vinyl ethers. This correlation is presented by Eq. 12 for molecules **32**, **39**—**42**, **73**, and **82**.

$$\delta^{17}O = 3.69\delta^{13}C_\beta - 227;\quad r = 0.958, s = 2.34, n = 7 \tag{12}$$

The Eq. 12 reflects the community of substituents electronic effect on the ^{17}O and $\delta^{13}C_\beta$ shielding. The δ^{17}O values in **2**, **3**, **12**, **13**, **19b**, and **30** are systematically deviated from the Eq. 12 towards the less magnitudes by 11—17 ppm (Fig. 9). Probably, these deviations are caused by the various experimental conditions in literature[17)] and the present work. The δ^{17}O values in **1**, **9**, **14**, and **19a** display steady deviation from dependence (12) in opposite direction by 18—31 ppm. Again, the points of 2,4-bis(vinyloxy)quinoline **19** have a gap



Scheme 6.



(A)

(B)

Fig. 8. The function of potential energy of internal rotation in 2-vinyloxypyridine **1**. (A) 3-Dimentional graphic of internal rotations around C2–O bond (*Ψ*) and O–C$_\alpha$ bond (*Φ*); (B) 2-Dimentional graphic of internal rotation around C2–O bond (*Ψ*).

Table 7. The Calculated Parameters of Aryl and Hetaryl Vinyl Ethers

Compound		Torsion angles/grad			*s*-Bond orders × 10^2			Charge × 10^2/e^-
		Ψ	*Φ*	*Ψ*+*Φ*	$P^2_{S_{C\text{-}\beta}S_{H\text{-a}}}$	$P^2_{S_{C\text{-}\beta}S_{H\text{-b}}}$	$P^2_{S_{C\text{-}\alpha}S_{H\text{-x}}}$	$q_{C\text{-}\beta}$
1	K	11	31	42	30.519	29.685	34.956	−25.756
	L	27	34	61	30.441	29.789	34.512	−24.301
2		31	24	55	30.586	29.752	34.412	−24.957
35		40	16	56	30.607	29.804	34.249	−26.792
39		50	5	55	—	—	—	—
41		32	27	59	—	—	—	—
42		36	19	55	30.491	30.056	34.244	−26.313
43	*syn*	42	12	54	30.638	29.824	34.149	−26.846
	anti	45	8	53	30.631	29.831	34.186	−26.556
71		28	28	56	30.529	29.784	34.358	−25.123
72		30	27	57	30.550	29.784	34.377	−25.093
73		18	41	59	30.432	29.738	34.652	−22.569
131		28	25	53	—	—	—	—

in the scale $\delta^{17}O/\delta^{13}C_\beta$ (Fig. 9). Therefore, the oxygen in A class ethers is deshielded relative to those in B class ethers. It may be connected with intensification of p–π conjugation, if *Ψ* and *Φ* values decrease in A class ethers. The intensification of p–π conjugation in A class ethers is confirmed by substantial upfield shift of $^{13}C_\beta$ signal in respect to other hetaryl vinyl ethers (Table 1, supplementary), although the 2-position of pyridine or quinoline is electron-withdrawing. The total increase of the charge transference onto vinyl group from oxygen due to the decrease of *Ψ* and *Φ* values may also leads to the failure of dependence (4) for A class ethers.

The changes of Δ*J* parameter in vinyl ethers account for the changes of torsion angle *Φ*.[30] The Δ*J* parameter in **1** is 0.2 and 0.6 Hz, more than those in isomeric **2** and **3**, respectively. The Δ*J* parameter in **9** is 0.3, 0.7, 0.2 and 0.9 Hz, more than in isomeric **10**, **11**, **12**, and **13**. At last, the Δ*J* parameter in 2-vinyloxyl group of **19** and **20** is 0.8—1.0 Hz, more than in 4-vinyloxyl group (Table 1, supplementary). It also suggests that the torsion angle *Φ* is decreased[30] in A class ethers, and it is caused by ISI C–H···N.

In according with AM1 calculation, the distance between H$_X$ hydrogen and nitrogen in **1** is less (2.57 Å) than the sum of van der Waals radii of these atoms (2.75 Å). This fact is in according with the supposition of ISI C–H···N in **1**.

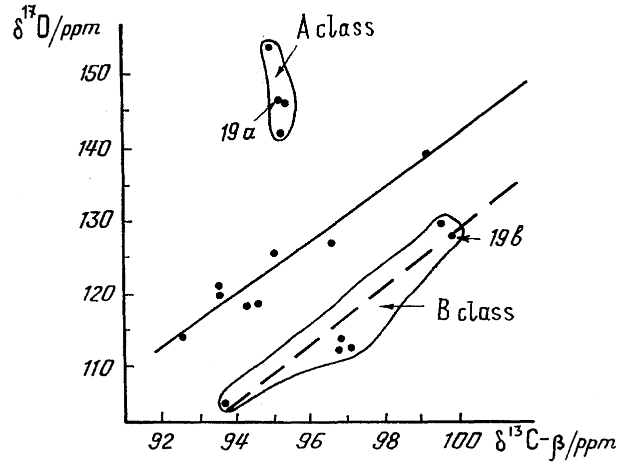


Fig. 9. The dependence of ^{17}O NMR chemical shifts on the δC_β chemical shifts in ethers **32**, **39**—**42**, **73**, and **82**.

The equilibrium distance C–H···X in **2** increases to 3.86 Å. Hence, any spectral signs of ISI C–H···N are absent in **2**.

The overlapping integral of H_X hydrogen *s*-orbital and nitrogen *s*-, p_x-, and p_y-orbitals, forming its lone-pair, is none zero for **1** ($\int N_\sigma H_X = 0.034$) in opposition to **2** ($\int N_\sigma H_X = 0.003$). The perturbation of hydrogen *s*-electron clouds and nitrogen lone-pair, causing by their overlapping, results to the observed anomaly of δH_X, $\delta^{13}C_\alpha$, $^1J_{C_\alpha H_X}$, and $\delta^{15}N$ parameters.

The one-bond ^{13}C-^1H coupling constants depend upon the square of C–H *s*-bond order. The values of C–H *s*-bond orders ($P^2_{S_H S_C}$) in vinyl group of **1**, **2**, **35**, **42**, **43**, and **71**—**73** are give in the Table 7. The changes of $P^2_{S_{C_\beta} S_{H_A}}$ and $P^2_{S_{C_\beta} S_{H_B}}$ are negligible, that relates to a small range of $^1J_{C_\beta H_A}$ and $^1J_{C_\beta H_B}$ changes. The most appreciable changes are observed for $P^2_{S_{C_\alpha} S_{H_X}}$ values. They correlate with $^1J_{C_\alpha H_X}$ coupling constants:

$$^1J_{C_\alpha H_X} = 710\, P^2_{S_{C_\alpha} S_{H_X}} - 60.5;\ r = 0.950, s = 0.548, n = 9 \quad (13)$$

In this case $^1J_{C_\alpha H_X}$ value of **1** does not deviate from Eq. 13 (Fig. 10). Therefore, the additional positive contribution into $^1J_{C_\alpha H_X}$ magnitude arises from ISI C–H···N. It is connected with the increase of $C_\alpha H_X$ *s*-bond order in A class ethers. The $P^2_{S_{C_\alpha} S_{H_X}}$ value substantially decreases in **L** conformer of molecule **1**. An experimental detection of $^1J_{C_\alpha H_X}$, in **L** conformer, is impossible due to the low barrier of the internal rotation (ca. 4.5 kcal mol^{-1} in according with AM1 calculation). This value can be predicted by the Eq. 13. The substitution of $P^2_{S_{C_\alpha} S_{H_X}}$ value, for hypothetical conformer **L**, in Eq. 13 gives $^1J_{C_\alpha H_X} = 184.5$ Hz. The $\delta^{13}C_\beta$ can be also predicted. The correlation between the calculated total charge (Table 7) on C_β atom and $\delta^{13}C_\beta$ values is discovered in **1**, **2**, **3**, **5**, **42**, and **71**—**73**.

$$\delta^{13}C_\beta = 131.8 q_{C-\beta} + 129;\ r = 0.964, s = 0.492, n = 7 \quad (14)$$

The substitution of $q_{C-\beta}$ value in Eq. 14 gives $\delta^{13}C_\beta = 97.02$ ppm for **L** conformer. The following substitution of this magnitude in Eq. 3 gives $^1J_{C_\alpha H_X} = 184.2$ Hz. This estimation is in an excellent accordance with previous one.

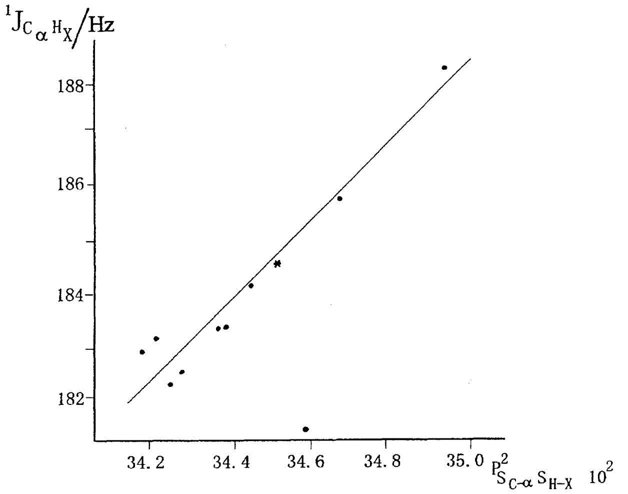


Fig. 10. The dependence of $^1J_{C_\alpha H_X}$ coupling constants on the *s*-bond order squares $P^2_{S_{C_\alpha} S_{H_X}}$ in ethers **1**, **2**, **35**, **42**, **43**, and **71**—**73**; ∗denotes the calculated value $P^2_{S_{C_\alpha} S_{H_X}}$ of **L** conformer 2-vinyloxypyridine **1**.

Thus, the $^1J_{C_\alpha H_X}$ value of **L** is "usual", i.e. as in B class ethers (Fig. 2). The distance H_X···N in **L** of **1** is near to that in **2** (3.71 Å). Consequently, the ISI in **L** is impossible. Hence, the $^1J_{C_\alpha H_X}$ values in **L** of **1** and **2** are negligibly different. The increase of $\Phi + \Psi$ sum to the "usual" magnitude in **L** (Table 7) also accounts for the absence of intramolecular specific interaction in this conformer.

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