

^{13}C – ^{13}C Spin–Spin Coupling Constants in Structural Studies: XLII. Stereochemical Study on Functionalized 2,5-Dihydrofuran-2-imines

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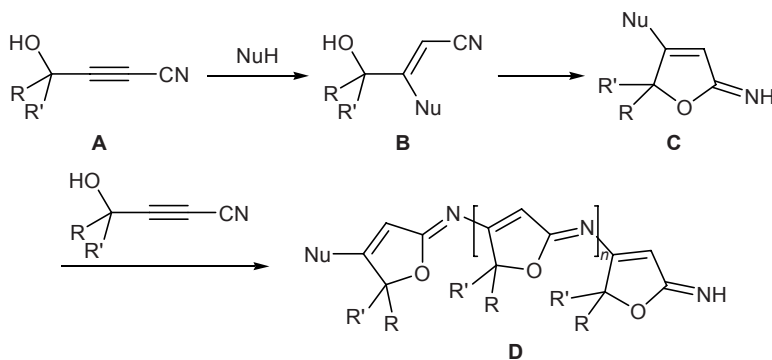
Abstract—The configurations and conformations of twelve 5-imino-2,5-dihydrofuran-3-carboxamides and 5-imino-2,5-dihydrofuran-3-amines were determined by analysis of the experimental ^{13}C – ^{13}C coupling constants and those calculated by nonempirical methods, as well as by quantum-chemical calculations of the total energies and optimization of geometric parameters of preferential conformations at the MP2/6-311G** level. All the examined compounds were found to be formed and to exist in solution as individual *Z* isomers with orthogonal orientation of the amino and dialkylamino groups and *s-trans* orientation of the carbamoyl group in the ring with restricted internal rotation about the C(O)–N bond.

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The chemistry of polyfunctional acetylene compounds is an extensively developing field of fine organic synthesis. α,β -Acetylenic acids and their derivatives are typical representatives of activated acetylenes and synthetic precursors of many biologically important compounds. The reactivity of nitriles **A** derived from α,β -acetylenic γ -hydroxy acids toward nucleophiles was reviewed in [1, 2]. Studies in this line resulted in the development of a general strategy for the synthesis of functionalized nitrogen-, oxygen-, and sulfur-containing trisubstituted electron-deficient

ethenes **B** having *Z* configuration of the double bond. Intramolecular cyclization of compounds like **B** was shown to give 2-imino-2,5-dihydrofurans **C** (Scheme 1) that are structurally related to some vitamins (ascorbic, penicillic, and tetronic acids and their sulfur-containing analogs) [3], as well as to anti-HIV drugs, e.g., d4T, AZT, etc. [4]. Also, a general synthetic approach to sequentially linked iminodihydrofurans **D** having an extended conjugation system and their pyrrole analogs was proposed; structural and electronic lability of such compounds [5] can be reversibly developed by

Scheme 1.

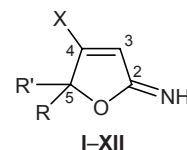


$R = R' = \text{Me}$; $R = \text{Me}$, $R' = \text{Et}$; $RR' = (\text{CH}_2)_5$; $\text{Nu} = \text{NH}_2$, AlkNH , Alk_2N , ArNH , $\text{Ar}(\text{Alk})\text{N}$, N_3 , AlkO , AlkS , ArS , $\text{HO}(\text{CH}_2)_n\text{NH}$, $\text{HO}(\text{CH}_2)_2\text{O}$, azoly1.

the action of physical and chemical factors, which may be used for the design of optoelectronic devices and sensors for biological and chemical species in newest information technologies. Therefore, studies on the relations between the properties and reactivity of the iminodihydrofuran fragment, on the one hand, and its electronic and steric structure, on the other, seem to be exceptionally important.

In the present work we examined the configuration and performed conformational analysis of 5-imino-2,5-dihydrofuran-3-carboxamides **I–III** and 5-imino-2,5-dihydrofuran-3-amines **IV–XII** possessing a variety of practically useful properties [2]. From the viewpoint of stereochemistry, iminodihydrofuran molecules **I–XII** attract interest in two aspects. The first of these is related to configuration of the exocyclic C=N bond, and the second, to internal rotation of the X substituent about the C–X bond. We tried to elucidate these problems by analysis of the experimental ^{13}C - ^{13}C coupling constants and those calculated by quantum-chemical methods, taking into account that this parameter is very sensitive to orientation of both lone electron pairs (LEP) on the imino and amino nitrogen atoms and amide carbonyl group in the examined series of iminodihydrofurans.

The stereochemistry of 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-carboxamide (**I**) and 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-amide (**IV**) that are parent structures of the two examined series, **I–III** and **IV–XII**, was studied in most detail. Analysis of the ^1H and ^{13}C NMR spectra showed that iminodihydrofurans **I–**



I–III, X = NH_2CO ; **IV–VI**, X = H_2N ; **VII**, X = MeNH ; **VIII**, X = PrNH ; **IX**, X = $t\text{-BuNH}$; **X**, X = $\text{MeCH}(\text{OH})\text{CH}_2\text{NH}$; **XI**, X = $\text{C}_{18}\text{H}_{37}\text{NH}$; **XII**, X = Me_2N ; **I**, **IV**, **VIII–XII**, R = $\text{R}' = \text{Me}$; **II**, **V**, R = Me , $\text{R}' = \text{Et}$; **III**, **VI**, **VII**, $\text{RR}' = (\text{CH}_2)_5$.

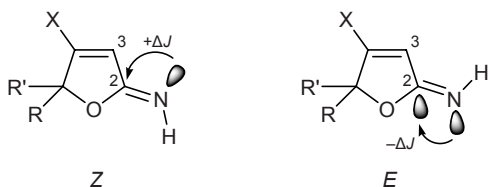
XII in solution exist exclusively as single isomers. Their structure was determined, and signals in their ^1H and ^{13}C NMR spectra were assigned, using two-dimensional homo- and heteronuclear correlation techniques (NOESY, HSQC, HMBC, INADEQUATE). In addition, high-level theoretical calculations of the corresponding ^{13}C - ^{13}C coupling constants was performed, and the calculated values were compared with the experimental coupling constants (Table 1).

As stated above, the direct ^{13}C - ^{13}C coupling constants are strongly sensitive to orientation of the LEP on the nitrogen atom in Schiff bases [6], as we showed for the first time using oximes as examples [7]. Sharp difference in the direct ^{13}C - ^{13}C coupling constants for the C=N carbon atom in configurational isomers of Schiff bases results from the through-space interaction between the nitrogen LEP and the neighboring *cis* bond, which gives rise to an additional channel for coupling transmission and positive contributions to the total coupling constant between the carbon atoms at the bond oriented *cis* with respect to the LEP. On the other hand, electron density transfer from the nitrogen LEP

Table 1. ^{13}C chemical shifts and ^{13}C - ^{13}C and ^{13}C - ^1H coupling constants of iminodihydrofurans **I–XII**

Compound no.	Chemical shifts δ_{C} , ppm				Coupling constants J , Hz			
	C^2	C^3	C^4	C^5	$\text{C}^2\text{--}\text{C}^3$	$\text{C}^3\text{--}\text{C}^4$	$\text{C}^4\text{--}\text{C}^5$	$\text{C}^3\text{--}\text{H}$
I	163.4	123.5	156.8	89.1	65.5	65.1	41.7	179.0
II	163.3	124.2	155.7	91.4	65.5	64.7	39.8	179.1
III	161.1	123.9	179.7	93.7	65.4	65.2	40.8	179.0
IV	175.3	85.4	171.1	81.8	72.6	73.5	42.4	174.4
V	177.2	89.1	170.4	84.6	71.2	73.3	42.8	173.8
VI	176.7	88.1	172.4	83.2	71.2	72.1	42.7	174.2
VII	176.3	87.7	172.6	80.2	71.6	73.6	42.2	173.9
VIII	176.3	86.4	171.8	80.1	72.2	73.8	41.9	174.6
IX	175.9	87.2	167.8	82.9	71.6	72.8	42.0	173.9
X	176.0	86.2	171.8	81.1	70.1	73.5	42.7	174.6
XI	176.2	86.9	172.4	79.8	72.0	74.0	42.0	174.3
XII	176.0	89.4	172.0	84.1	71.2	73.9	42.2	175.3

to the antibonding orbital of the C–C bond located *trans* with respect to the LEP ($n_{\sigma}-\sigma^*$ interaction) makes that bond longer, the spin–spin coupling weakens, and the coupling constant decreases, providing a negative contribution to the coupling constant between the carbon atoms at the bond in the *trans* position with respect to the LEP. The nature of this effect was studied in detail by theoretical methods [8], and it was widely used to determine configuration of various Schiff bases [6].



Iminodihydrofurans **I–XII** might be expected to display a strong difference in the direct coupling constants $J(C^2, C^3)$ due to positive contribution of the nitrogen LEP ($+\Delta J$) for the *Z* isomer and negative contribution ($-\Delta J$) for the *E* isomer. In fact, the difference in the calculated $J(C^2, C^3)$ values for the *E* and *Z* isomers of compounds **I** and **IV** exceeds 10 Hz (Table 2), which is more than sufficient for unambiguous assignment of their configuration. The calculated coupling constants $J(C^3, C^4)$ and $J(C^4, C^5)$ for the *Z* isomers of **I** and **IV** coincide with the corresponding experimental values with very high (at the present level of nonempirical theory) accuracy ($\Delta J = 0.1\text{--}0.6$ Hz; Table 2). This coincidence may be regarded as an additional

support for the above assignment; it also demonstrates appropriateness of the theoretical method employed.

The total values of $^{13}\text{C}\text{--}^{13}\text{C}$ coupling constants were calculated at a high level of theory using the second-order polarization propagator approximation (SOPPA) [9] (which is regarded as one of the most accurate non-empirical methods for calculating coupling constants) in terms of the fundamental Ramsey theory with account taken of four contributions: Fermi-contact (J_{FC}), spin–dipole (J_{SD}), diamagnetic spin–orbital (J_{DSO}), and paramagnetic spin–orbital (J_{PSO}); special Dunning's correlation-consistent basis sets [10] supplemented with internal correlation functions and optimized for calculation of $^{13}\text{C}\text{--}^{13}\text{C}$ coupling constants were involved [11]. The calculations were performed using equilibrium geometric parameters of the most favorable conformers of the *E* and *Z* isomers of **I** and **IV**, which were optimized by the MP2/6-311G** method (Fig. 1).

The data in Table 2 show that the experimental coupling constants $J(C^2, C^3)$ coincide with an accuracy of ~ 0.5 Hz with the corresponding values calculated for the *Z* isomers of **I** and **IV** and differ by more than 10 Hz from the theoretical $J(C^2, C^3)$ values for the *E* isomers. These data unambiguously indicate *Z* configuration of both compounds. On the other hand, the experimental coupling constants $J(C^2, C^3)$ of the examined iminodihydrofurans (Table 1) suggest that all compounds **I–XII** also have *Z* configuration at the exocyclic C=N bond, in keeping with the calculated

Table 2. Calculated^a (SOPPA) and experimental $^{13}\text{C}\text{--}^{13}\text{C}$ coupling constants J (Hz) for compounds **I** and **IV**

Compound no.	Isomer	Coupling	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	J_{exp}
I	<i>E</i>	$C^2\text{--}C^3$	0.34	−1.85	0.99	55.94	55.42	
		$C^3\text{--}C^4$	0.32	−8.86	3.24	73.51	68.21	
		$C^4\text{--}C^5$	0.39	−1.37	0.70	38.54	38.26	
	<i>Z</i>	$C^2\text{--}C^3$	0.34	−2.01	0.90	66.90	66.13	65.5
		$C^3\text{--}C^4$	0.32	−8.78	3.22	69.79	64.55	65.1
		$C^4\text{--}C^5$	0.39	−1.47	0.74	41.95	41.61	41.7
IV	<i>E</i>	$C^2\text{--}C^3$	0.34	−2.16	0.67	62.33	61.18	
		$C^3\text{--}C^4$	0.32	−7.27	2.16	78.02	73.23	
		$C^4\text{--}C^5$	0.39	−1.32	0.84	40.99	40.90	
	<i>Z</i>	$C^2\text{--}C^3$	0.34	−2.26	0.66	73.4	72.14	72.6
		$C^3\text{--}C^4$	0.32	−7.35	2.27	78.06	73.3	73.5
		$C^4\text{--}C^5$	0.39	−1.29	0.85	41.86	41.81	42.4

^a The calculations were performed for the most favorable conformations (Fig. 1).

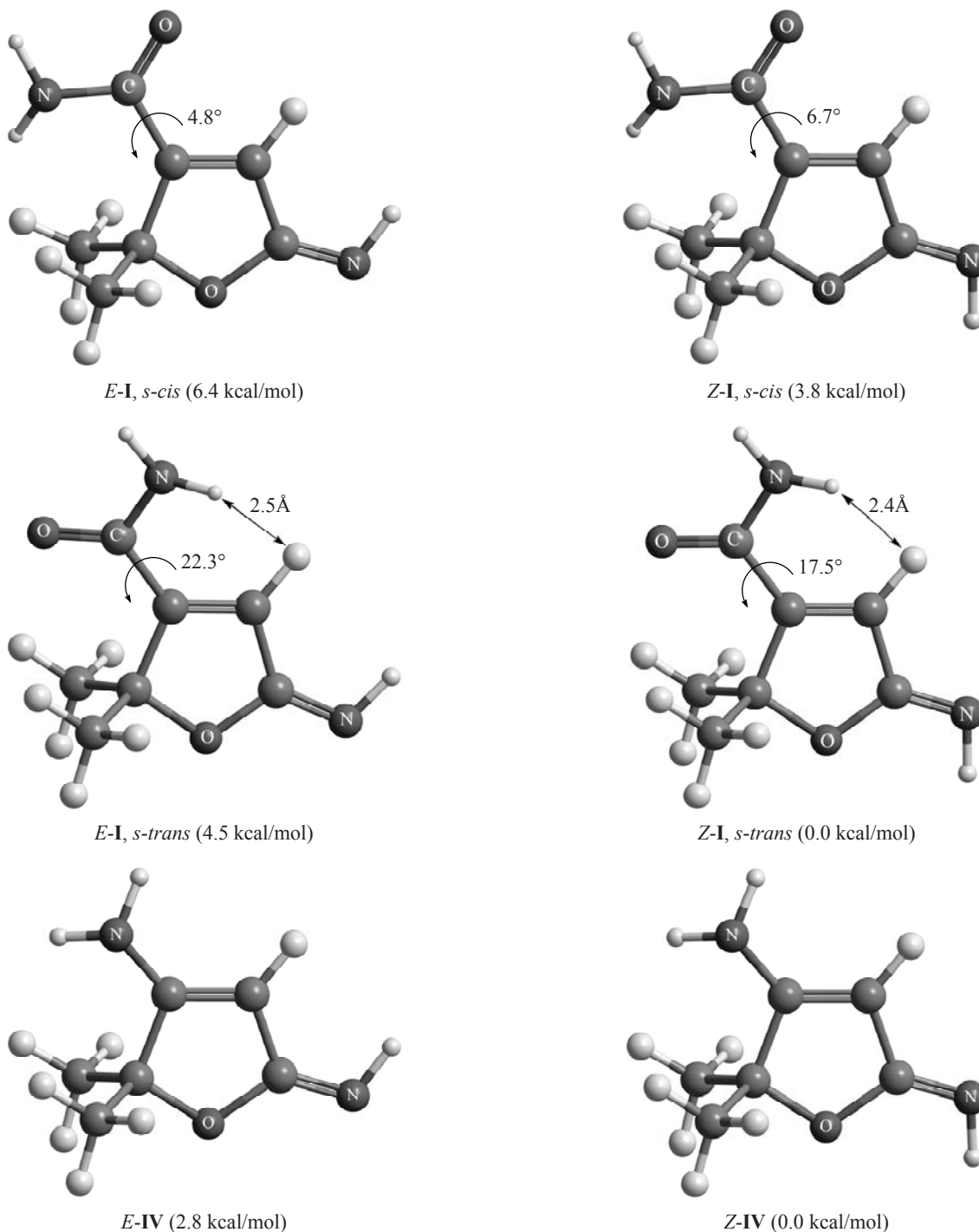


Fig. 1. Equilibrium structures of the *E* and *Z* isomers of compounds **I** and **IV**, optimized by the MP2/6-311G** method. The relative energies are given in parentheses. Deviations of substituents from the plane of the iminodihydrofuran fragment are shown with arrows. Interatomic distances are also given.

relative thermodynamic stabilities of their *Z* and *E* isomers. In fact, the preferential conformers of the *Z* isomers of compounds **I** and **IV** (Fig. 1) are more stable than the corresponding *E* isomers by 4.5 and 2.8 kcal/mol, respectively.

The second equally interesting aspect of the stereochemistry of iminodihydrofurans **I–XII** is their conformation related to internal rotation of the X substituent on C^4 about the $\text{C}^4\text{–X}$ bond (Fig. 2). The potential energy curve for internal rotation in molecule **I** con-

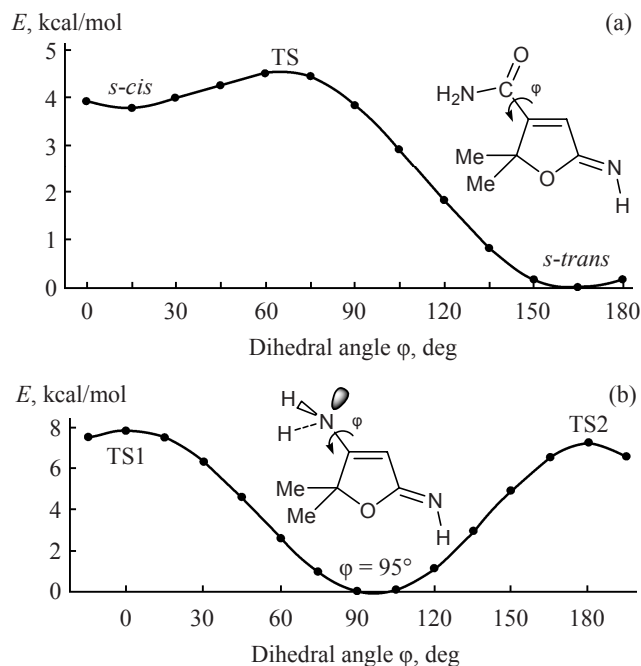


Fig. 2. Potential energy curves for internal rotation in the molecules of (a) 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-carboxamide (**I**) and (b) 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-amine (**IV**) according to the MP2/6-311G* calculations with optimization of geometric parameters at each rotational point.

tains two energy minima corresponding to $\varphi \approx 15$ and 165° (*s-cis* and *s-trans* conformers) and one maximum at $\varphi \approx 70^\circ$ (transition state TS for internal rotation of the amide fragment relative to the C^4 -X bond; Fig. 2a). The *s-trans* conformer is more favorable than the *s-cis* conformer by 3.8 kcal/mol, while the energy difference between the second high-energy *s-cis* conformer and transition state TS is less than 1 kcal/mol. Refined search for stationary points in the regions of $\varphi \approx 15$ and 165° by the MP2/6-311G** method allowed us to localize two conformers, *s-cis* ($\varphi = 6.7^\circ$) and *s-trans* ($\varphi = 162.5^\circ$), whose optimized structures are shown in Fig. 1.

Both conformers of **I** are characterized by essentially nonplanar structure: the amide group deviates from the plane of the iminodihydrofuran fragment by 6.7° in the *s-cis* conformer and 17.5° in the *s-trans* conformer. The larger deviation in the *s-trans* conformer is likely to result from steric interactions involving hydrogen atoms on the amide nitrogen and C^3 -H, the distance between these atoms is as short as 2.4 Å; analogous pattern is observed for the *s-cis* and *s-trans* conformers of **E-I** (Fig. 1).

On the other hand, the potential energy curve for internal rotation in amine **IV** displays only one energy

minimum at $\varphi \approx 95^\circ$, which corresponds to the orthogonal conformer (orthogonal orientation of the nitrogen LEP and iminodihydrofuran ring plane), and two maxima at $\varphi \approx 0$ and 180° corresponding to two transition states TS1 and TS2 for internal rotation of the amino group about the C^4 -X bond (Fig. 2b). The orthogonal conformer is characterized by the most efficient conjugation between the nitrogen LEP and π -system of the iminodihydrofuran fragment, while both transition states TS1 and TS2 lack such conjugation, for the LEP on the nitrogen atom is completely forced out from the conjugation plane. As a result, the energy difference between the orthogonal conformer and transition states is as large as ~ 8 kcal/mol. Refined search for stationary point in the region of $\varphi = 95^\circ$ revealed one orthogonal conformer, whose optimized structure is shown in Fig. 1.

The nature of all conformers of compounds **I** and **IV** and the corresponding transition states was determined by analysis of the normal harmonic vibrational spectrum. The results showed that all vibrational frequencies of all conformers are real numbers and that the vibrational spectra of all localized transition states contain one imaginary frequency.

Unique information on internal rotation of the amide fragment in molecule **I** and of the amino group in **IV** can be drawn from the coupling constants $J(C^3, C^4)$ and $J(C^4, C^5)$ which should depend on mutual orientation of the corresponding carbon-carbon bonds and amide C=O bond in **I** or LEP on the amino nitrogen atom in **IV**. In fact, the calculated dependences of $J(C^3, C^4)$ and $J(C^4, C^5)$ on the dihedral angles for compounds **I** and **IV** revealed pronounced stereospecificity for internal rotation about the C^4 -X bond (X = CONH₂, NH₂) in both compounds (Fig. 3).

The nature of the dependences of $J(C^3, C^4)$ and $J(C^4, C^5)$ upon the dihedral angle characterizing rotation of the amino group about the C^4 -N bond in **IV** (Fig. 3b) is the most obvious. Decrease in $J(C^3, C^4)$ and increase in $J(C^4, C^5)$ upon rotation of the amino group by 0 to 90° should be attributed to reduction of the positive contribution of the nitrogen LEP to $J(C^3, C^4)$ and reduction of its negative contribution to $J(C^4, C^5)$. Further decrease in $J(C^3, C^4)$ and increase in $J(C^4, C^5)$ upon variation of the dihedral angle from 90 to 180° results from increase in the negative contribution of the nitrogen LEP to $J(C^3, C^4)$ and increase of its positive contribution to $J(C^4, C^5)$.

Analysis of the experimental values of $J(C^3, C^4)$ and $J(C^4, C^5)$ in the series of amines **IV-XII** (Table 1)

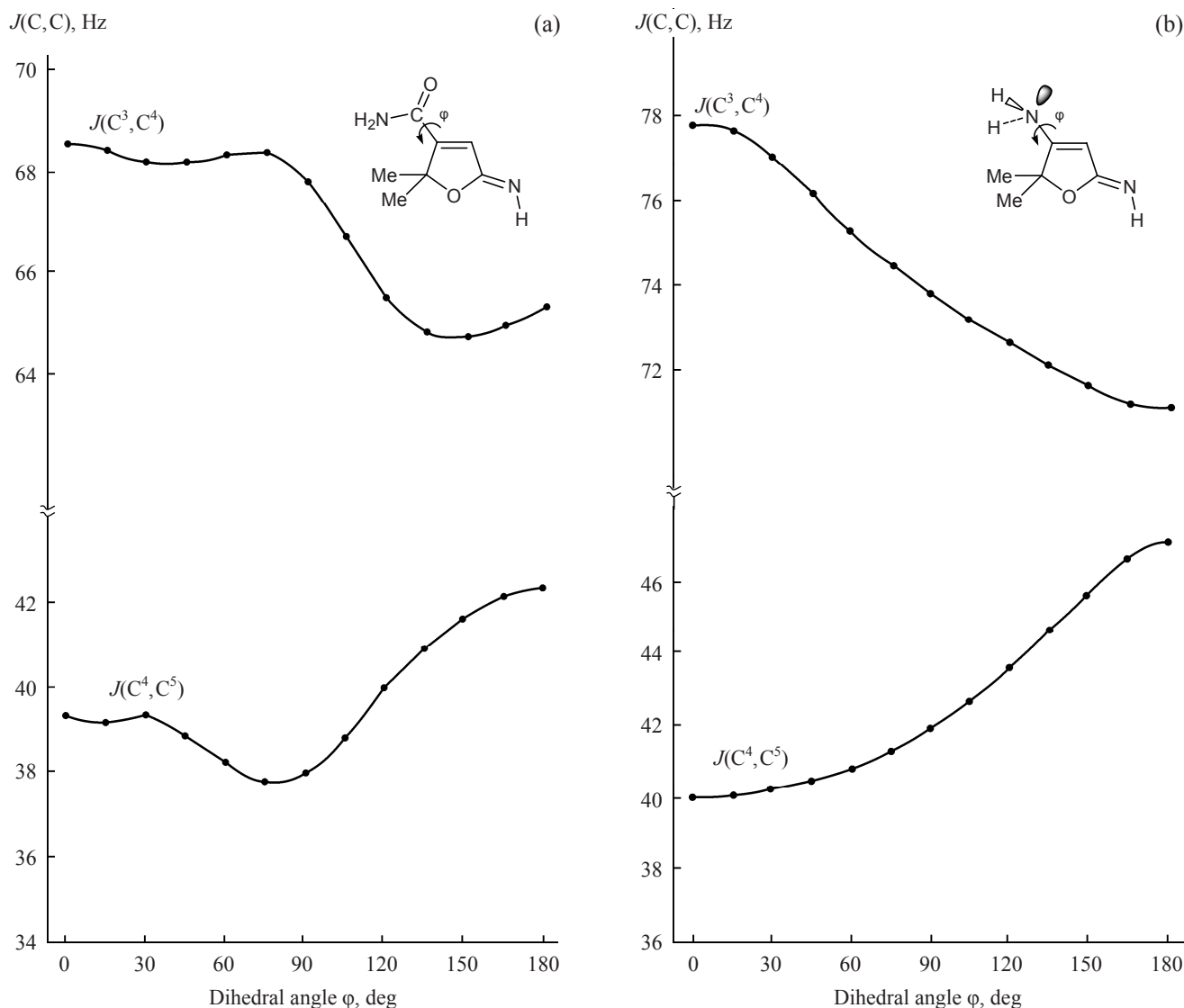


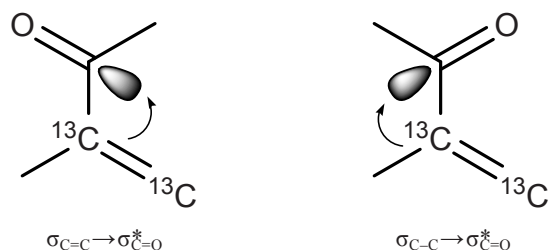
Fig. 3. Dependences of the ^{13}C - ^{13}C coupling constants for internal rotation in the molecules of (a) 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-carboxamide (**I**) and (b) 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-amine (**IV**) according to the SOPPA calculations with optimization of geometric parameters (MP2/6-311G*) at each rotational point.

shows that all these compounds exist preferentially as orthogonal conformers.

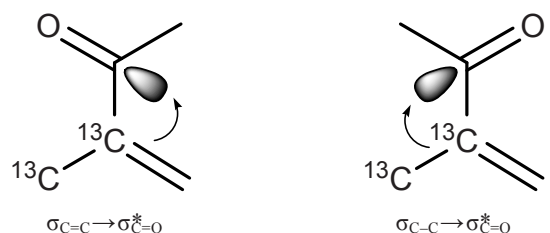
Thus the calculated dihedral dependences of the coupling constants $J(\text{C}^3, \text{C}^4)$ and $J(\text{C}^4, \text{C}^5)$ in **IV** are readily interpreted in terms of the well known orientational effect of the nitrogen LEP [7, 8] which was discussed in detail above. Quite different factors are responsible for the stereochemical behavior of $J(\text{C}^3, \text{C}^4)$ and $J(\text{C}^4, \text{C}^5)$ related to rotation of the amide fragment relative to the C^4 - $\text{C}(\text{O})$ bond in molecule **I** (Fig. 3a).

Decrease in the coupling constant $J(\text{C}^3, \text{C}^4)$ and increase in $J(\text{C}^4, \text{C}^5)$ in going from the *s-cis* conformer of **I** to the *s-trans* conformer (rotation of the amide fragment by $\sim 180^\circ$; Fig. 3a) should be assigned to dif-

ference in hyperconjugation interactions in these conformers (see [12] and references therein). In keeping with the data of [12], hyperconjugation like $\sigma_{\text{C}=\text{C}} \rightarrow \sigma_{\text{C}=\text{O}}^*$ for the *s-trans* orientation of the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds should reduce the corresponding ^{13}C - ^{13}C coupling constant as a result of electron density transfer from the bonding $\sigma_{\text{C}=\text{C}}$ orbital to the antibonding $\sigma_{\text{C}=\text{O}}^*$ orbital. On the other hand, $\sigma_{\text{C}-\text{C}} \rightarrow \sigma_{\text{C}=\text{O}}^*$ hyperconjugation in the *s-cis* conformer should increase the corresponding ^{13}C - ^{13}C coupling constant due to electron density transfer from the bonding σ orbital formed by one carbon atom involved in the above coupling and carbon atom not involved in that coupling to the antibonding $\sigma_{\text{C}=\text{O}}^*$ orbital.



Analogous but opposite effects are produced by hyperconjugation interactions considered above ($\sigma_{C=C} \rightarrow \sigma_{C=O}^*$ and $\sigma_{C-C} \rightarrow \sigma_{C=O}^*$) on the ^{13}C - ^{13}C coupling constant between the single-bonded carbon atoms: the first of these interactions increases and the second reduces the coupling constant. A combination of the above hyperconjugation effects should appreciably reduce the ^{13}C - ^{13}C coupling constant in the *s-trans* conformer and increase it in the *s-cis* conformer. As a result, the difference between the ^{13}C - ^{13}C coupling constants for the *s-cis* and *s-trans* conformers becomes considerable (orientational effect of the C=O bond).

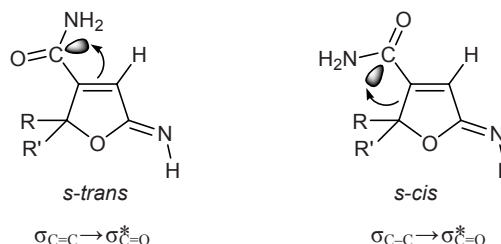


As applied to the series of amides **I–III**, analogous considerations led us to expect the following effect of hyperconjugation on $J(\text{C}^3, \text{C}^4)$ and $J(\text{C}^4, \text{C}^5)$ values. The overall hyperconjugation effect (orientational effect of the C=O bond) in compound **I** is estimated at ~ 3.5 Hz for $J(\text{C}^3, \text{C}^4)$ and ~ 2.5 Hz for $J(\text{C}^4, \text{C}^5)$ (Table 3). Comparison of the calculated coupling constants $J(\text{C}^3, \text{C}^4)$ and $J(\text{C}^4, \text{C}^5)$ for the *s-cis* and *s-trans* conformers of **I**

Table 3. Calculated (SOPPA) and experimental ^{13}C - ^{13}C coupling constants and calculated contributions thereto (Hz) for different conformers of 5-imino-2,2-dimethyl-2,5-dihydrofuran-3-carboxamide (**I**)

Conformation	Coupling	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	J_{exp}
<i>Z, s-cis</i>	$\text{C}^3\text{--C}^4$	0.32	−8.80	3.17	73.21	67.90	
	$\text{C}^4\text{--C}^5$	0.39	−1.33	0.72	39.17	38.95	
	$\text{C}^4\text{--CO}$	0.39	−1.30	0.75	66.24	66.10	
<i>Z, s-trans</i>	$\text{C}^3\text{--C}^4$	0.32	−8.78	3.22	69.79	64.55	65.1
	$\text{C}^4\text{--C}^5$	0.39	−1.47	0.74	41.95	41.61	41.7
	$\text{C}^4\text{--CO}$	0.40	−1.34	0.76	66.74	66.56	66.8

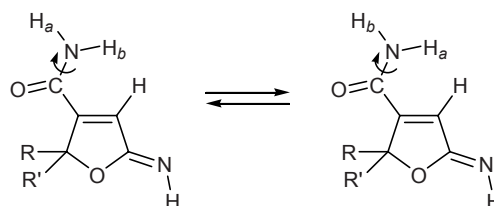
with the corresponding experimental values unambiguously indicates that the latter conformer is preferred. This conclusion is consistent with the calculated thermodynamic stabilities of the conformers (Fig. 1).



The data in Table 3 show that the coupling constant $J(\text{C}^4, \text{CO})$ for the *s-trans* conformer of **I** is larger by ~ 0.5 Hz. Although the difference is small, it nevertheless is quite understandable. It is well known that conjugation between two double bonds is more efficient when these bonds are oriented *s-trans*; such orientation favors increased π -order of the formally single bond between the double bonds. Therefore, the corresponding ^{13}C - ^{13}C coupling constant in the *s-trans* conformer should be larger. It follows that π -electronic effects related to rotation of the amide fragment about the $\text{C}^4\text{--C}(\text{O})$ bond in molecule **I** are weaker than hyperconjugation effects on the coupling constants $J(\text{C}^3, \text{C}^4)$ and $J(\text{C}^4, \text{C}^5)$, which were used for conformational analysis in the series of iminodihydrofurans.

Analysis of the experimental $J(\text{C}^3, \text{C}^4)$ and $J(\text{C}^4, \text{C}^5)$ values of amides **I–III** (Table 1) led us to conclude that these compounds exist preferentially as *s-trans* conformers with *Z* configuration of the exocyclic C=N bond (see above).

The third aspect of steric structure of the iminodihydrofurans under study implies restricted internal rotation about partially double C(O)–N bond in the amide fragment of compounds **I–III**, which gives rise to two rotamers. The ^1H NMR spectra of **I–III** characteristically display dynamic effects. The shape of signals from the amide protons changes upon variation of temperature, as shown using amide **I** as an example. Signals from protons in the amide fragment, located in the *s-cis* and *s-trans* positions with respect to the C=O bond in the two rotamers, were assigned using the two-



dimensional NOESY technique. The relevant data are available from the authors upon request by e-mail.

The rate of the exchange process at the coalescence temperature was estimated by the known formula $k = \pi\delta\nu/\sqrt{2}$ [13], and the Gibbs energy of activation (barrier to internal rotation) was calculated by the Eyring equation: it was found to be equal to ~16–17 kcal/mol for compounds **I–III**. In particular, the barrier to internal rotation about the CO–N bond in amide **I** is 16.3 kcal/mol.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were measured at 25°C on Bruker DPX-400 and Avance-400 spectrometers at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C using 5- and 10-mm NMR ampules. Samples were prepared as 10% solutions in CD_3OD or $\text{DMSO}-d_6$ containing HMDS as internal reference. The ^{13}C - ^{13}C coupling constants were determined using INADEQUATE pulse sequence with the following parameters: spectrum width 6 kHz, pulse duration 13.5 μs , relaxation delay 4 s, FID acquisition time 4 s, digital resolution 0.1 Hz per point, accumulation time 6 to 24 h. The ^{13}C - ^1H coupling constants were measured from the proton-coupled ^{13}C NMR spectra with periodically turning on broad-band decoupling from protons during relaxation delays (the spectral parameters were the same as above).

Quantum-chemical calculations were performed using GAMESS [14] and DALTON software packages [15]. The geometric parameters were optimized, and the total energies were calculated, in terms of the second-order perturbation theory (MP2/6-311G**). The ^{13}C - ^{13}C coupling constants were calculated in terms of the second-order polarization propagator approach (SOPPA) using either standard basis sets or those modified by the authors (for details, see [11]).

Compounds **I–III** [16], **IV–VI** [17], **VII**, **VIII**, **XI** [18], **IX**, **X** [19], and **XII** [20] were synthesized by known methods.

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