FULL PAPER

Experimental Evidence of Intramolecular C_{Ar}–H···O=C Hydrogen Bonds in the Structure of (Diaryl)tetrahydrofuranones Using Spectroscopic Tools

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The occurrence of bifurcate H-bonds C_{Ar}–H···O=C in the structure of (diaryl)-tetrahydrofuranones was experimentally demonstrated using different methods and techniques. The consistent increasing spin–spin coupling constants ^1J(C,H) of the *ortho*-H-atoms and low-field shift of $\nu_{C=O}$ in IR spectra of 2,2-(diaryl)tetrahydrofuran-3(2*H*)-ones relative to their 5,5-diaryl counterparts, as well as pronounced dependence of the *ortho*-C–H H-atoms chemical shifts on the temperature and solvent polarity along with X-ray diffraction analysis data unambiguously point to the existence of weak C_{Ar}–H···O=C H-bonds in these molecules.

Keywords: Weak hydrogen bond, Furanones, Diazoketones, Variable-temperature NMR, IR Spectroscopy, X-ray diffraction analyses.

Introduction

Weak or 'non-classical' H-bonds of the type C–H···X (X = O, N, S, Hal, π) along with the classical H-bonds play an important role in many biological systems [1], including, for example, protein folding [1d], protein–DNA recognition [1e], conformation stabilization of cyclitol derivatives [1b], and other biochemical processes [1a][2]. In recent years, the possibility of their effect on the chemical properties of 'small molecules' are actively studied, and discussed by researchers in the area of organic chemistry and adjacent fields [3].

One of the least understood (and not accepted by many experts in this field) are 'non-classical' H-bonds of aryl H-atoms with O-atoms of different O-containing substrates (C_{Ar}–H···O). As far as we know, only a limited number of structures, which presumably exhibited H-bonds of this kind, have been mentioned in the literature. Thus, it was demonstrated using an X-ray diffraction analysis [1a][4] that the distances between aromatic H-atoms and O-atoms of the C=O or ester groups for several organic molecules **A** – **C** (*Fig. 1*) comprise 2.2 – 2.9 Å which are within the range of the classical H-bonds [1a]. These results obtained with the considered structures were treated by the authors as an indication on the intramolecular C_{Ar}-H···O H-bonding in the structure of these molecules [1a]. Nevertheless, employment of only one method of investigation for identification of 'non-classical' H-bonds of this kind puts the existence of them in doubt and does not allow to make a confidential conclusion on this matter.

Besides the X-ray diffraction analysis, the formation of intramolecular C_{Ar}–H···O bonds was established by the other present day methods and techniques. First and foremost is the NMR spectroscopy [5], where a high-frequency shift of the H-atom signal along with increasing the associated ^1J(C,H) constants [5d] and heteronuclear *Overhauser* effect [5e] are an essential criteria for identification of C–H···X (X = O, N, S) H-bonding. The IR spectroscopy [6] and DFT calculations [5a,d][7] were also found to be very useful in the studies of weak C–H···X interactions. However, in those rare events when authors were concerned with the proposed C_{Ar}–H···O bonds, their assumptions were based only on the data of 2 – 3 spectroscopic methods.

During our research on the reactivity of dihydrofuranone derivatives, the suggestion has been made on the existence of weak C_{Ar}–H···O H-bonds in the molecules of tetrahydrofuran-3(2*H*)-ones and related diazo compounds [8]. In this connection, a detailed experimental study of spectroscopic features of these compounds was undertaken using eight different spectroscopic methods and techniques. Herein, the major results of this study are presented.

Two pairs of regioisomeric 2,2-(diaryl) and 5,5-(diaryl) dihydrofuran-3(2*H*)-ones **1a**,**b** and **2a**,**b** were selected as the major subjects for the current research (*Fig. 2*). It was assumed that, in the structure of 2,2-(diaryl)substituted

 DOI: 10.1002/hlca.201600149

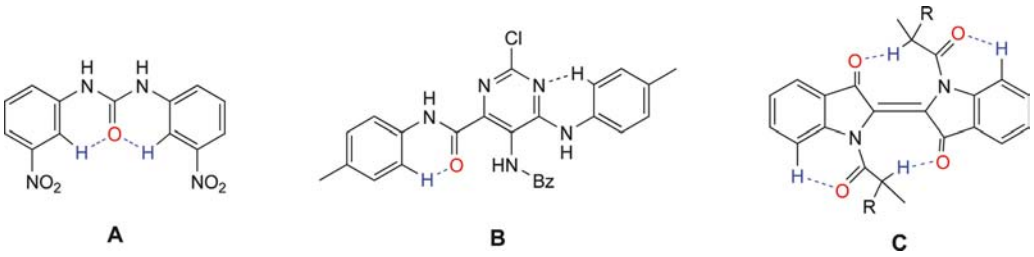


Fig. 1. Several examples of compounds with intramolecular C_{Ar}–H···O=C H-bonding [1a].

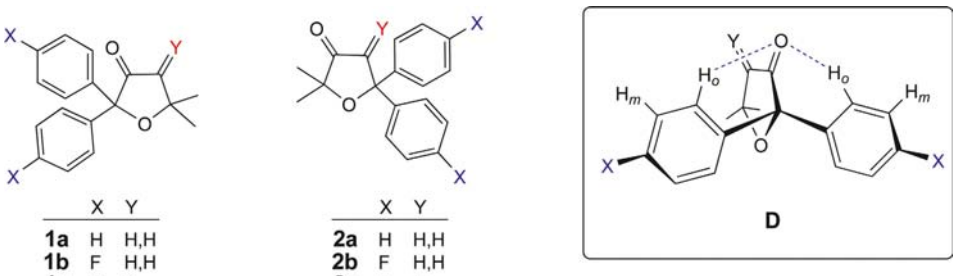


Fig. 2. Objects of investigation **1a** – **d**, **2a** – **d** and assumed interactions between *ortho*-C_{Ar}–H H-atoms and O-atoms of C=O group (structure **D**).

regioisomers **1a**,**b**, the intramolecular C_{Ar}–H···O bonds between *ortho*-H-atoms of aromatic ring (H_o) and O-atom of the closely located C=O group could be involved (*Fig. 2*; drawing **D**). By contrast, the formation of such H-bonds in the molecules of 5,5-(diaryl)substituted regioisomers **2a**,**b** was unlikely.

Hence, by changing the location of C=O group in the structure of heterocycles **1** and **2**, we can at our discretion 'switch on' or 'switch off' H-bonds in these molecules, thus providing a confident answer on the question regarding existence of C_{Ar}–H···O H-bonds in the structure of these compounds. It should be also noted that due to a reasonable 'rigidity' of furane ring, compounds **1** and **2** represent one of the simplest systems for monitoring intramolecular bifurcate H-bonds of the type C_{Ar}–H···O in the molecule by 'switching effect'.

To elucidate the generality of the aforementioned phenomenon besides dihydrofuranones **1a**,**b** and **2a**,**b** in many cases, the spectroscopic properties of two regioisomeric pairs of diazoketones **1c**,**d** and **2c**,**d** were also examined. However, due to the low thermal and acidic stability of diazo compounds **1c**,**d** and **2c**,**d**, their studies was limited to the ^{1}H-NMR and IR spectroscopy measurements at room temperature.

The investigation was performed using the ^{1}H-NMR spectroscopy, including measurements of the heteronuclear indirect (scalar) coupling constants ^1J(C,H) between *ortho*-H-atom and adjacent C-atom, effect of solvent polarity, temperature, additives of the proton donors and acceptors (CF_3COOH, DMSO, *etc.*) on the chemical shifts of the C_{Ar}–H H-atoms in the ^{1}H-NMR spectra, as well as in the IR spectroscopy and X-ray diffraction analysis.

Results and Discussion

Chemical Shifts of Aromatic H-Atoms in the ^{1}H-NMR Spectra of Regioisomers **1** *and* **2**

According to the literature data, C–H···O bonding of a H-atom typically causes a decrease in diamagnetic shielding around it, which results in the downfield shift of the H-atom signal in a range of $\Delta\delta$ = 0.1 – 1.0 ppm [9]. The results of our measurements of ^{1}H-NMR spectra of regioisomeric **1a** – **d** and **2a** – **d** in the $CDCl_3$ solutions at room temperature are represented in *Table 1*.

As it is evident from these data that the signals of *ortho*-H-atoms of aromatic ring (H_o) of regioisomer **1** are markedly shifted in the low field when compared to corresponding signals of the regioisomers **2** ($\Delta\delta$ up to 0.16 ppm), whereas such a shift for the other H-atoms (H_m and H_p) does not exceed 0.06 ppm. In this connection, it may be assumed that C_{Ar}–H···O=C interactions in the structures **1a** – **d** cause deshielding the *ortho*-H-atoms of aryl groups relative to their *meta*- and *para*-counterparts of the isomer **1** as well as to all H-atoms of aromatic rings of the compounds **2a** – **d**. This intramolecular interaction leads to the downfield shift the signals of *ortho*-H-atoms in the ^{1}H-NMR spectra of regioisomers **1**, similar to that observed in the systems with classical H-bonds [5a][10].

Further studies have demonstrated that the effect of C_{Ar}–H···O H-bonding on the chemical shift of atom H_o in the ^{1}H-NMR spectra of the regioisomers **1** and **2** was solvent sensitive (*Table 2*).

The highest values of the parameter $\Delta\delta$, which characterizes the downfield shift of the *ortho*-H-atoms of the

Table 1. Chemical shifts of aromatic H-atoms in the ^{1}H-NMR spectra of regioisomers **1** and **2** (δ, ppm)

Entry	X; Y	**1**			**2**			$\Delta\delta$[a])		
		H_o	H_m	H_p	H_o	H_m	H_p	H_o	H_m	H_p
1	H; H,H (**a**)	7.54	7.29	7.23	7.41	7.31	7.24	+0.13	−0.02	−0.01
2	F; H,H (**b**)	7.49	6.99	–	7.35	7.00	–	+0.14	−0.01	–
3	H; N_2 (**c**)	7.49	7.30	7.27	7.36	7.34	7.30	+0.13	−0.04	−0.03
4	F; N_2 (**d**)	7.45	7.01	–	7.29	7.07	–	+0.16	−0.06	–

[a]) $\Delta\delta = \delta$ (**1**) – δ (**2**).

Table 2. Effect of solvent polarity (ε, D) on the relative chemical shifts of *ortho*-aromatic H-atoms of regioisomers **1a** – **d** and **2a** – **d**

Entry	Solvent	ε	D	$\Delta\delta$[a])			
				H; H,H (**a**)	F; H,H (**b**)	H; N_2 (**c**)	F; N_2 (**d**)
1	Hexane	1.9	0.1	0.20	0.21	0.22	0.21
2	CCl_4	2.2	0.0	0.14	0.15	0.13	0.16
3	$CDCl_3$	4.7	1.1	0.13	0.14	0.13	0.16
4	(D_6)Acetone	20.9	2.8	0.02	0.02	0.07	0.07
5	(D_6)DMSO	45	4.0	−0.03	−0.03	−0.01	0.03

[a]) $\Delta\delta = [\delta(H_{ortho})$ (**1**) – $\delta(H_{ortho})$ (**2**)], ppm.

regioisomers **1** relative to isomers **2**, were observed for the solvents with a low dielectric constant, such as hexane, where they amounted up to 0.20 – 0.22 ppm (*Entry 1*). In halomethanes solutions (*Entries 2* and *3*), this effect was significantly lower ($\Delta\delta$ = 0.13 – 0.16) than in hexane. In (D_6)acetone, the value of $\Delta\delta$ was 0.02 – 0.07 (*Entry 4*), and, in (D_6)DMSO, $\Delta\delta$ has attained negative values (*Entry 5*), which qualitatively agrees with the results of calculations of the chemical shifts using additive schemes for **1a**,**b** and **2a**,**b** (calculations led to $\Delta\delta$ = 0.1 ppm).

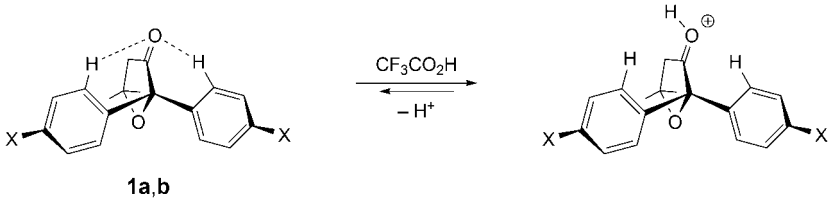
The peculiarity of H_o-H-atoms in the structure of regioisomers **1a** – **d** is also evident from the effect of solvent permittivity (ε) and dipole moment (D) on the difference in chemical shifts of the H_o- and H_m-H-atoms of regioisomers **1** and **2** (see SI, p. S4, *Figs 1* and *2*). For all *ortho*-H_o-atoms, the dependence of this difference on the permittivity of the solvent (macroscopic feature) is consistent with the logarithmic function $\Delta\delta = A \ln(\varepsilon) + B$, which is in a good agreement with the literature data for various H-bonding systems [11]. Similar dependence of a chemical shift on the dipole moments of solvents (microscopic property) is also in good agreement with literature data [11] and in a similar way has linear relationship $\Delta\delta = aD + b$. As for the *meta*-H-atoms, their chemical shifts are practically independent on the solvent polarity ($\Delta\delta(H_m) < 0.06$ ppm), while the dependence on the dielectric permittivity of the solvent can be fitted by the linear function (see SI, p. S4, Fig. *1*, left diagram).

The significant effect of the solvent nature on the chemical shifts of H_o-atoms can be apparently explained by the *intermolecular* interactions of the *ortho*-H-atoms of regioisomers **1a** – **d** with polar solvent, which compete with the *intramolecular* C_{Ar}–H···O=C interactions in compounds **1a** – **d** and, in (D_6)acetone and (D_6)DMSO, most likely completely replace it.

Effect of Trifluoroacetic Acid Addition

In principle, to weaken an intramolecular C–H···O=C H-bond, an acid can be added to a studied substrate. As a consequence, the acid would protonate the O-atom of the C=O group (*Scheme*) giving rise to weakening the intramolecular C–H···O=C H-bond. This should lead to an upfield shift of the corresponding C–H H-atom signal in the ^{1}H-NMR spectrum (*Scheme*).

Scheme. The assumed protonation of the C=O group of the ketones **1a**,**b** by CF_3COOH that should weaken the C_{Ar}–H···O=C H-bonding.



1a,**b**

In our study, CF_3COOH was tested as such as an external proton source. The dependence of *ortho*-H-atoms chemical shifts of regioisomers **1a**,**b** and **2a**,**b** in CCl_4 solution on the CF_3COOH concentration is presented in *Table 3* (and Fig. S3, p. S5) (diazoketones **1c**,**d** and **2c**,**d** were not used in this study due to their decomposition in the presence of CF_3COOH [8e]).

As expected, addition of CF_3COOH resulted in the significant upfield shift of the *ortho*-H-atoms signals in the ^{1}H-NMR spectra of regioisomers **1a**,**b** (*Table 3*; $\Delta\delta_{max}$ = 0.12 ppm for compounds **1a**, **1b**; see Fig. S3, p. S5). At the same time, chemical shifts of the similar *ortho*-H-atoms in the spectra of regioisomers **2** did not essentially change and were not dependent on the CF_3COOH concentration in solution of these compounds (*Table 3*; $\Delta\delta_{max}$ = 0.01 ppm for compounds **2a**, **2b**; see Fig. S3, p. S5).

It should be also noted that the values of chemical shifts of regioisomeric **1** and **2** H-atoms approached each other upon increasing CF_3COOH concentration in solution (*Table 3*, *Columns 3 – 5*). This observation can be considered as the evidence of significant decreasing the *intramolecular* C–H···O=C bonding in the molecules of regioisomers **1a**,**b** due to the effective competitive protonation by CF_3COOH of C=O O-atom at high concentrations of CF_3COOH.

Coupling Constants ^{13}C-^1H of Aromatic H-Atoms in the Spectra of Regioisomers **1** *and* **2**

It is well-known that increasing the values of the through one bond coupling constants ^1J(C,H) for the H-atoms, which participate in H-bonding, can also point to the existence of such specific interactions and provide a means for identification of a weak H-bond in the molecule studied [5d][12].

The results of the appropriate J(H,C) measurements for the compounds **1a** – **d** in $CDCl_3$ at room temperature performed in the INEPT [13] regime are given in *Table 4*. The obtained data demonstrate that the values of ^1J(H,C) of *ortho*-H-atoms of compounds **1a** – **c** far exceed those of regioisomers **2a** – **c** (ΔJ_{ortho} up to 2.4 Hz), whereas the differences in ^1J(C,H) of *meta*-H-atoms of regioisomers **1a** – **c** and **2a** – **c** are many times smaller (ΔJ_{meta} = 0.1 – 0.5 Hz). The maximum value of $\Delta J_{ortho}/\Delta J_{meta}$ ratio amounts up to 24:1 for the pair **1c**, **2c** (*Entry 3*).

Table 3. Chemical shits of *ortho*-H-atoms (H_o) of the ketones **1a**,**b** and **2a**,**b** in the presence of CF_3COOH

Compound	Mol. ratio CF_3COOH/compound and $\delta(H_o)$ [ppm]				$\Delta\delta_{max}$ [ppm]
	0	4	20	100	
1a	7.49	7.47	7.42	7.37	0.12
2a	7.35	7.35	7.35	7.34	0.01
1b	7.48	7.45	7.42	7.38	0.10
2b	7.33	7.33	7.33	7.33	0.00

Table 4. Values of ^1J(C,H) and ΔJ of aromatic H-atoms in the INEPT spectra of regioisomers **1** and **2**

Entry	X; Y	Coupling constant (^1J [Hz])				ΔJ [Hz][a])	
		1		**2**			
		o-CH	*m*-CH	*o*-CH	*m*-CH	ΔJ_{ortho}	ΔJ_{meta}
1	H; H,H (**a**)	162.0	160.8	160.4	160.7	+1.6	+0.1
2	F; H,H (**b**)	161.9	163.3	159.6	162.8	+2.3	+0.5
3	H; N_2 (**c**)	160.7	161.3	158.3	161.2	+2.4	+0.1
4	F; N_2 (**d**)	161.9	163.4	161.6	165.6	+0.3	−2.2

[a]) ΔJ = ^1J (**1**) – ^1J (**2**), Hz.

For the pair of diazo compounds **1d**,**2d**, however, the ΔJ_{ortho} difference is rather small (0.3 Hz; *Entry 4*), which either can point to the absence of H-bonding in diazo molecule **1d** or inapplicability of this approach for this pair of regioisomers.

Temperature Dependence of Chemical Shifts of H-Atoms of the Compounds **1a**,**b** *and* **2a**,**b** *in ^{1}H-NMR Spectra*

Variable-temperature NMR (VT-NMR) is a convenient method for estimation of the thermodynamic parameters of H-bonds, such as H-bond formation enthalpy ΔH^0 and enthalpy ΔS^0 [14]. To determine the thermodynamic C_{Ar}–H···O=C H-bond parameters for the ketones **1a**,**b**, we have studied temperature dependence of ^{1}H-NMR spectra of the regioisomeric ketones **1a**,**b** and **2a**,**b**[1]) in the temperature range from −45 to +140 °C (*Figs 3 – 5* and *Table 5*). Considering that the strongest C–H···O=C interactions were expected to be in nonpolar media (as it was shown above), the experiments were performed in nonane solutions.

The most pronounced temperature dependence was found to be with *ortho*-H-atoms of the ketones **1a**,**b**. In this case, increasing the temperature from −45 to +140 °C resulted in upfield shift of $\Delta\delta/\Delta T$ up to −0.38 ppb/K for regioisomer **1a** and −0.16 ppb/K for isomer **1b** (*Fig. 4*).

At the same time, the values of chemical shifts of *ortho*-H-atoms for regioisomer **2a**, as well as for *meta*- and *para*-H-atoms of both isomers **1** and **2**, did not in fact depend on the temperature ($\Delta\delta$ < 0.01 ppm and gradient $\Delta\delta/\Delta T$ did not exceed 0.04 ppb/K). This means that the observed temperature gradients for *ortho*-H-atoms of isomers **1** were 4.0 – 4.5 times greater than those for *ortho*-H-atoms of isomers **2** (*Fig.* 5).

Based on the temperature dependence data, one can estimate thermodynamic parameters of the weak intramolecular H-bond in compounds **1a**,**b** (*Table 5*) (see also SI, p. S7).

[1]) Diazoketones **1c**,**d** and **2c**,**d** were not used in these experiments since they are not stable at elevated temperatures [8e,f].

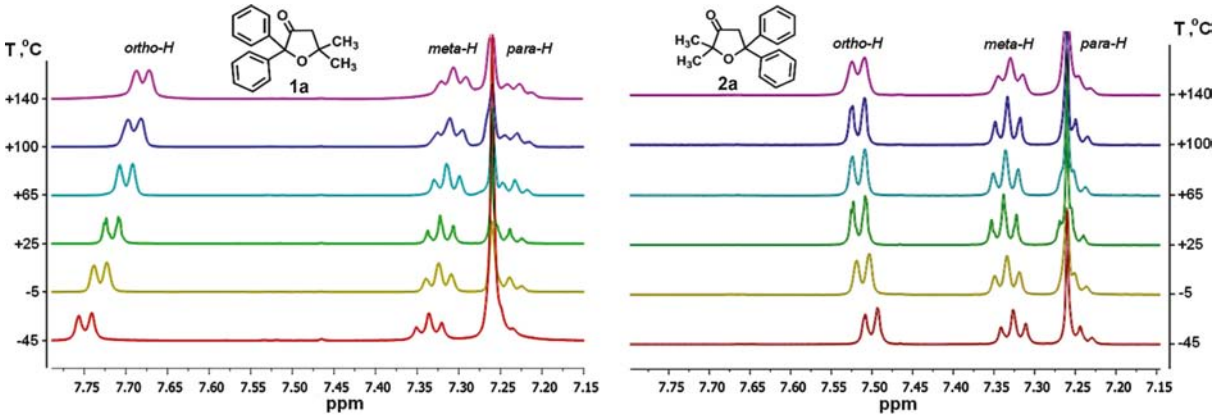


Fig. 3. Comparative temperature dependence of chemical shifts of aryl H-atoms of **1a** (left) and **2a** (right).

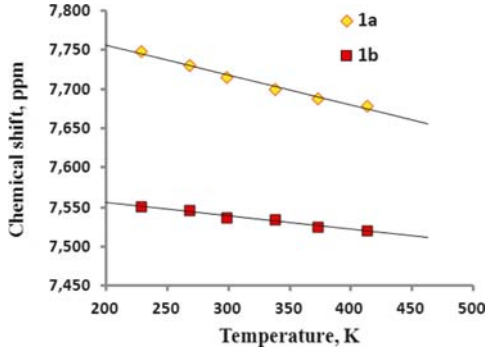


Fig. 4. Temperature dependence of chemical shifts of H_o for **1a** and **1b**.

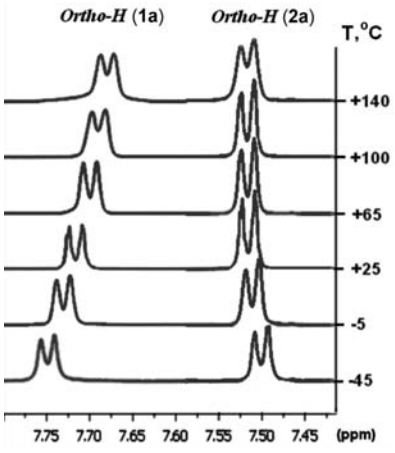


Fig. 5. Temperature dependence of chemical shifts of H_o for the isomers **1a** and **2a**.

The values of ΔH^{298} appeared to be rather moderate, but negative (from −4.2 to −4.5 kJ/mol),[2]) which indicates that H-bonded state is enthalpy favored. This conclusion is in good agreement with the literature data for many similar systems studied by different methods where ΔH^{298} (C–H···O) was found to be in the range from −1.9 to −5.7 kJ/mol [15]. The negative ΔS^{298} values (10.5 – 13.2 J/mol/K) can be associated with the decrease in rotational and vibrational degrees of freedom in the H-bonded molecules. Equilibrium constants obtained at different temperatures (K_{228}, K_{413}; *Table 5*) demonstrated that H-bonded species are favored by low temperatures ($K_{228} > 1$ for **1a**, **1b**; *Table 5*), while increasing the temperature moves the equilibrium in the direction of H-nonbonded molecules ($K_{413} < 1$ for **1a**, **1b**; *Table 5*).

Measurement of Intramolecular C_{Ar}–H···O=C Interactions by Means of IR Spectroscopy [10]

According to the literature data [15a], the intramolecular C_{Ar}–H···O=C H-bonding should decrease the frequency of the C=O stretching vibrations in IR spectra of C=O compounds. Indeed, it was found that the ν_{CO} band of regioisomers **1** in CCl_4 solution was noticeably shifted to the lower frequencies as compared to their isomers **2** ($\Delta\nu_{CO} = \{\nu_{CO}(\mathbf{2}) - \nu_{CO}(\mathbf{1})\} \approx 5\ cm^{-1}$) (for **1a** and **2a**, see *Fig. 6a*).

Furthermore, it was shown that in the presence of 20-fold excess of DMSO in solution of regioisomers **1a** and **2a**, their IR spectra in the region of $\nu_{C=O}$ became almost identical (for **1a** and **2a**, see *Fig. 6b*; *Table 6*, last column).

The data mentioned above demonstrate that high-frequency shift of ν_{CO} band in IR spectra of isomers **1** in the presence of DMSO is most likely caused by the disruption of *intramolecular* C_{Ar}–H···O=C bond due to more effective *intermolecular* C_{Ar}–H···O=SMe_2 interaction of *ortho*-H-atoms with DMSO. As a result, ν(CO) band in the IR spectra of isomers **1** with DMSO corresponds to the frequencies of ν(CO) of the H-nonbonded C=O group and is close to that of regioisomers **2**, where formation of intramolecular H-bond is unlikely and their ν(CO) remains intact.

[2]) The calculations without assumption on the linear dependence of $\delta(H_o)$ resulted in slightly more negative values of enthalpy of *ortho*-C_{Ar}–H···O=C H-bond formation (*ca.* −7 kJ/mol; see SI, p. S7 – 11).

Table 5. Thermodynamic parameters of the compounds **1a** and **1b** obtained by VT-NMR spectroscopy

Compound	A (= δ_B)	B [ppm/K]	δ_N	T_N [K]	ΔH^{298} [kJ/mol]	ΔS^{298} [J/mol/K]	ΔG^{298} [kJ/mol]	K_{228}	K_{413}
1a	7.833	$-3.84\cdot10^{-4}$	7.545	750	−4.2	−10.5	−1.1	2.6	0.9
1b	7.590	$-1.70\cdot10^{-4}$	7.474	680	−4.5	−13.2	−0.6	2.1	0.7

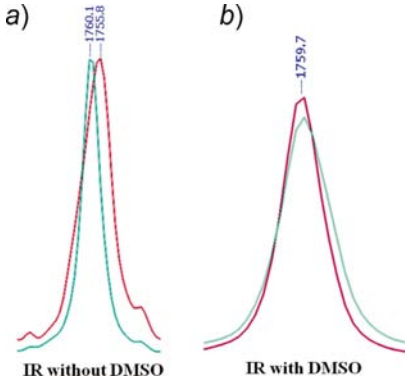


Fig. 6. IR Spectra (ν_{CO} region) of regioisomers **1a** (red line) and **2a** (blue line) in solution of CCl_4 without DMSO (left) and with addition of DMSO (right).

Therefore, the findings of IR spectroscopic study can be considered as one more argument in favor of the intramolecular H-bonding of *ortho*-H-atoms of aryl groups with C=O O-atom in the molecules of regioisomers **1**.

The Crystal Structure Features of Isomers **1** *and* **2**

As it was already mentioned, X-ray diffraction analyses is one of the most popular and significant methods to study the C_{Ar}–H···O=C H-bonds, which enables to draw a conclusion on the existence of H-bonding in the compound essentially based on the crystal structure parameters such as O···H bond distances and C–H···O angles of a molecule [4a]. Cutoff limits of the H-bond formation are typically assumed to be the distance d(O···H) ≤ 2.7 Å at the C–H···O angle > 90° [4a].

The structures of compounds **1a**,**b**,**d** and **2a**,**b**,**d** that were studied in the current research using the X-ray diffraction analysis are represented in *Fig. 7*; the X-ray analysis of the compounds **1c** and **2c** was performed previously [8b]. The main structural parameters obtained during these measurements (d(O···H), d(C···O), d(C–H), and angles C–H···O) as well as some discussion of these data are given in SI (p. S12 – S55).

The obtained results enable one to conclude that all four *ortho*-H-atoms of each regioisomer **1a**,**c**,**d** interact with the both O-atoms of the proper molecule, resulting in stabilization of conformation with aromatic rings symmetrically located relative to the furan cycle (*Fig. 7*, regioisomers **1a**,**c**,**d**). The ketone **1b** probably have only two intramolecular H-bonds (C–H_o^1···O=C and C–H_o^2···O^1), which is not sufficient for stabilization of highly symmetrical conformation of aryl groups.

As regards regioisomers **2a** – **d**, the X-ray data presumably point to the H-bonding between only one of the *ortho*-H-atoms H_o^1 and O-atom of the furan heterocycle (SI, Table 24, p. S15, 16; H_o^1, *d*(O···H) = 2.35 – 2.71 Å; Entries 17 – 24). As a result, aryl rings of the regioisomers **2a** – **d** are orthogonal to each other similarly to isomer **1b** (*Fig. 7*, regioisomers **2a** – **d**).

Conclusions

The structural features of the regioisomeric 2,2-(diaryl)- and 5,5-(diaryl)tetrahydrofuran-3-ones were studied using a variety of experimental methods. It was shown that effect of solvent polarity, electrophile (acid) concentration, and temperature on the chemical shifts of *ortho*-H-atoms is considerably higher in 2,2-(diaryl)- than with 5,5-(diaryl)substituted regioisomers. Furthermore, 2,2-diarylisomers exhibit larger direct *ortho*-C_{Ar}–H spin–spin coupling constants, red-shifted $\nu_{C=O}$ in the IR spectra, and highly symmetrical conformation of aryl groups in the solid state, which meet the appropriate geometrical requirements for the formation of intramolecular H-bonds in the molecules of these compounds. The structural

Table 6. Frequencies of C=O stretching vibrations of the C=O group in IR spectra of **1a** – **d** and **2a** – **d** in CCl_4 solution

Entry	X; Y	ν(CO) [cm^{-1}]		$\Delta\nu$(CO)[a]	$\Delta\nu$(CO) (+DMSO) [b]
		1	**2**	[cm^{-1}]	[cm^{-1}]
1	H; H,H (**a**)	1755.8	1760.1	4.3	0.1
2	F; H,H (**b**)	1757.1	1762.0	4.9	3.3
3	H; N_2 (**c**)	1691.7	1695.3	3.6	0.4
4	F; N_2 (**d**)	1694.0	1699.0	5.0	2.5

[a]) $\Delta\nu(CO) = \nu_{CO}$ (**2**) – ν_{CO} (**1**). [b]) $\Delta\nu$(CO) in IR spectra for **1a** – **d** and **2a** – **d** in CCl_4 solution with additives of DMSO (the concentration of DMSO is 20 times larger than that of **1a** – **d** or **2a** – **d**).

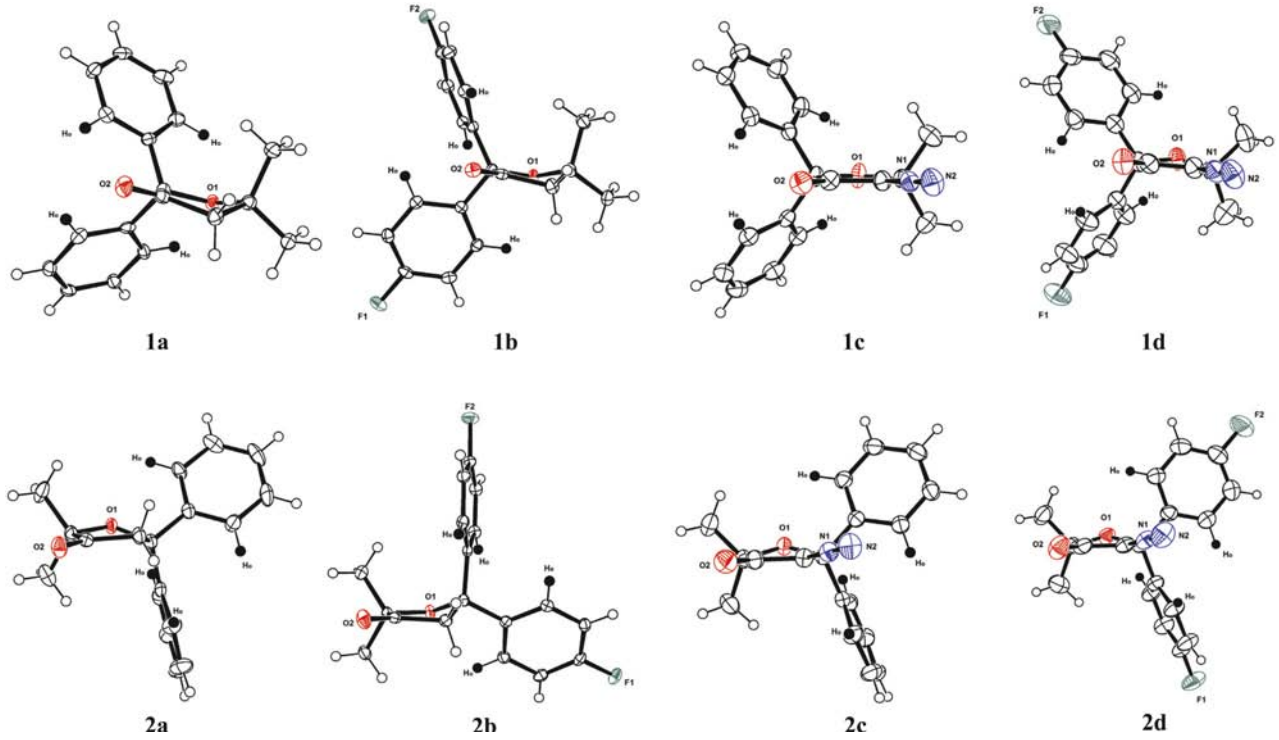


Fig. 7. ORTEP-generated [16] structures of regioisomers **1a** – **d** and **2a** – **d**. Thermal ellipsoids are drawn with the 50% probability.

parameters of 2,2-(diaryl)- and 5,5-(diaryl)tetrahydrofuran-3-ones derived from X-ray analyses in the solid state also provide support for the existence of the intramolecular weak *ortho*-H···O=C H-bonds in the structure of 2,2-(diaryl)tetrahydrofuran-3-ones with the energies estimated of 4 – 7 kJ/mol. One more important point in this comprehensive research is application of range of nonstandard techniques (besides classical tools), such as ^{1}H-NMR and IR spectroscopy with donor and acceptor additives, and employment of nonane instead of freons in the temperature-dependent experiments.

The authors express their gratitude to the SPbSU resource centers: 'Center for Magnetic Resonance' and 'Chemistry Educational Centre'. XRD studies of **1a**,**b**,**d** and **2a**,**b**,**d** were carried out at the 'Research Centre for X-ray diffraction Studies'. *A. S. M.* acknowledges the *Saint-Petersburg State University* for the financial support in the form of postdoctoral fellowship (No. 12.50.1562.2013). *J. J. M.* thanks 'UMNIK-2015' (contract No. 10093GU2/2015) and *RBFR* (mol_a No. 16-33-00059) foundation for the financial support of this project. *D. V. S.* acknowledges *F.A.S.I.E. Foundation* (contract No. 1074GC1/21867) for the financial support.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/hlca.201600149.

Experimental Part

IR spectra of the compounds were measured in CCl_4 solution by a compact size FT-IR spectrometer *TENSOR 37* (*Bruker*). ^{1}H-NMR spectra were measured using a *Bruker-400 Avance* NMR spectrometer with the internal Me_4Si standard unless otherwise stated. For ^{1}H-NMR measurements, sample weights were equal to 5 mg. Reproducibility of the chemical shifts, determined by the multiple measurements of the samples in a variety of solvents, was equal to ±0.002 ppm. For the NMR measurements, anh. solvents purified by standard methods were used. Scalar coupling constants ^1J(C,H) were measured by the INEPT method using a *Bruker-300-DPX* NMR spectrometer at r.t. in $CDCl_3$ solution. The values of coupling constants ^1J(C,H) were measured within the accuracy of 0.1 Hz.

For single crystal X-ray diffraction experiments of **1a**, **b**,**d** and **2a**,**b**,**d**, two types of diffractometers were used: an *Agilent Technologies Excalibur Eos* diffractometer with monochromated MoK_α radiation and an *Agilent Technologies Supernova Atlas* diffractometer employing microfocused monochromated CuK_α radiation. For diazoketones **1c** and **2c**, see [8b]. All samples **1a**,**b**,**d** and **2a**,**b**,**d** were measured at 100 K. The unit cell parameters were refined by least square techniques. The structures were solved by direct methods and refined by SHELXL-97 program [17] incorporated in the OLEX2 program package [18]. The C-bound H-atoms were placed in

calculated positions and were included in the refinement in the 'riding' model approximation with Uiso(H) set to 1.5 Ueq(C) and C–H 0.96 Å for Me groups, with Uiso(H) set to 1.2 Ueq(C) and C–H 0.97 Å for CH_2 groups, Uiso (H) set to 1.2 Ueq(C) and C–H 0.93 Å for the CH groups. Empirical absorption correction was applied in CrysAlisPro [19] program complex using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. It should be noted that the quality of the samples **1a** and **2a** was not sufficient to obtain a reasonably good data by single crystal X-ray diffraction so the information obtained could only be considered as a model.

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Received May 25, 2016
Accepted July 26, 2016

