

Conformational Mobility of Substituted 2-Methoxychalcones under the Action of Lanthanide Shift Reagents

A. V. Turov, S. P. Bondarenko, A. A. Tkachuk, and V. P. Khilya

Taras Shevchenko Kiev National University, ul. Vladimirskaya 64, Kiev, 01033 Ukraine
e-mail: vkhilya@hotmail.com

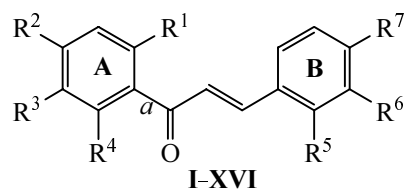
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Abstract—Various lanthanide shift reagents Ln(fod)₃ were found to affect the conformational composition of 2-methoxychalcones. Coordination of Yb(fod)₃ occurs mainly at the carbonyl oxygen atom of the substrate, while Eu(fod)₃ and shift reagents derived from other lanthanides coordinate substituted chalcones as bidentate ligands, giving rise to a secondary tetrachelate with the corresponding change of conformation of the substrate molecule. The possibility for chelation is determined by steric hindrances in the vicinity of the substrate coordination centers and concurrent coordination of other electron-donor groups present in the substrate molecule.

Lanthanide shift reagents (LSR) have long been used in structural and conformational analysis of organic compounds, studies of their chirality, and interpretation of the NMR spectra. Creation of superconducting spectrometers made it possible to solve many problems without involving LSR. In the recent years, new fields of application of LSR were found, e.g., enhancement of regioselectivity of organic reactions [1], analysis of ion–ion interactions [2], and experimental determination of the site of predominant charge localization in anions [3]. The effect of LSR on conformations of difunctional compounds was revealed recently [4]. Although this property of LSR can complicate their use as conformational probes, it may be helpful in modeling interactions between small molecules and biological macromolecules, where biological activity of a small molecule originates from variation of its conformation during association. Therefore, studies on the effect of LSR on molecular conformations in solution seem to be important.

Application of LSR is based on their ability to selectively coordinate electron-donor functional groups in the substrates and induce shifts of signals in the NMR spectra; the magnitude of the lanthanide-induced shifts depends on the structure of the LSR–substrate adduct and arrangement of magnetic nuclei in the substrate molecule relative to the coordination center [5, 6]. The structure of LSR adducts with monofunctional organic molecules was extensively studied [7].

Complex formation of LSR with difunctional compounds is characterized by some specific features. Most frequently, coordination centers present in a substrate molecule operate independently from each other, and the induced shifts are integral quantities for all possible adducts. If coordination centers in a substrate molecule are spatially close, chelation with LSR is possible to afford tetrakis-adducts in which the coordination number of lanthanide increases to 8 [8]. In order to study this mode of coordination in more detail, we synthesized a series of substituted 1-(2'-alkoxyphenyl)-3-phenyl-2-propenones



I–XVI, R^x = H, unless otherwise stated; **I**, R¹ = OCH₃, R³ = Cl, R⁷ = F; **II**, R¹ = OCH₃, R³ = R⁵ = Cl; **III**, R¹ = OCH₃, R³ = Br, R⁵ = Cl; **IV**, R¹ = OC₂H₅, R³ = R⁷ = Cl; **V**, R¹ = R⁵ = OCH₃, R³ = Cl; **VI**, R¹ = OCH₃, R³ = Cl, R⁶R⁷ = OCH₂O; **VII**, R¹ = OCH₃, R³ = Cl, R⁶R⁷ = OCH₂CH₂O; **VIII**, R¹ = R² = OCH₃, R⁴ = CH₃, R⁷ = NO₂; **IX**, R¹ = R² = R⁴ = OCH₃, R⁷ = Cl; **X**, R¹ = R² = R⁴ = OCH₃, R⁶ = NO₂; **XI**, R¹ = R⁶ = R⁷ = OCH₃, R³ = F; **XII**, R¹ = OCH(CH₃)₂, R³ = F, R⁶ = R⁷ = OCH₃; **XIII**, R¹ = R⁶ = R⁷ = OCH₃, R³ = Cl; **XIV**, R¹ = R⁶ = R⁷ = OCH₃, R³ = Br; **XV**, R¹ = R² = R⁶ = R⁷ = OCH₃, R⁴ = CH₃; **XVI**, R¹ = OC₂H₅, R³ = Cl, R⁶ = R⁷ = OCH₃.

Table 1. ^1H NMR spectra of compounds **I–XVI**, δ , ppm

Comp. no.	Ring A					Olefinic protons		Ring B				
	2'	3'	4'	5'	6'	α	β	2	3	4	5	6
I	3.89	7.55	7.67	–	7.58	7.25	7.65	7.7	7.00	–	7.00	7.7
II	3.89	6.94	7.38	–	7.6	7.3	8.03	6.71				
III	3.89	6.9	7.33	–	7.73	7.28	8.00	7.2–7.7				
IV	4.10, 1.42	6.91	7.34	–	7.62	7.74	7.53	7.2–7.6				
V	3.87	6.92	7.31	–	7.44	7.45	7.94	3.87	7.2–7.6			
VI	3.88	7.15	7.4	–	7.56	7.04	7.56	6.87	6.02	6.82	7.1	–
VII	3.87	7.01	7.3	–	7.54	7.04	7.53	4.28				
VIII	3.83	6.37	3.77	6.37	2.25	7.07	7.37	7.66	8.22	–	8.22	7.66
IX	3.76	6.15	3.85	6.15	3.76	6.91	7.42	7.45	7.31	–	7.31	7.45
X	3.87	6.15	3.85	6.15	3.87	6.91	7.33	7.45	7.47	–	7.47	7.45
XI	3.87	7.1	7.1	–	7.3	7.2	7.54	6.9	3.92	3.92	6.88	6.9
XII	4.54, 1.33	6.8–7.4		–	7.26	7.35	7.61	7.35		3.93	3.93	6.8–7.4
XIII	3.92	6.91	7.40	–	7.53	7.13	7.53	7.10	3.92	3.87	6.88	7.1
XIV	3.88	7.16	7.55	–	7.67	7.55	7.21	7.10	3.88	3.93	6.87	7.1
XV	3.83	6.37	3.75	6.37	2.23	6.84	7.25	7.06	3.9	3.9	7.06	6.87
XVI	4.07, 1.41	7.11	7.1	–	7.36	7.6	7.31	6.9	3.9	3.9	~6.9	

(chalcones) by alkaline condensation of the corresponding benzaldehydes with methoxyacetophenones (compounds **I–III**, **V–X**, and **XV**) or by alkylation of 2'-hydroxychalcones prepared by the same procedure (**IV**, **XI–XIV**, **XVI**). All compounds **I–XVI** contain both carbonyl and 2'-alkoxy groups, and the other substituents were selected so as to elucidate the effect of electronic and steric factors on the coordination with LSR.

The structure of products **I–XVI** was confirmed by the ^1H NMR spectra (Table 1). The chemical shifts and coupling constants for all protons were typical of the assumed structures. Signals from the olefinic protons were assigned on the basis of the spectra of specially synthesized α -deuterated analogs of chalcones **IV** and **XIII** in which the substituents in ring **B** strongly differ in electron-acceptor properties. In the ^1H NMR spectra of these compounds, the upfield olefinic proton signal disappeared as a result of H–D exchange, while the downfield signal appeared as a singlet. Therefore, in the spectra of all substituted chalcones, the downfield signal was assigned to the β -proton. Exceptions were compounds **IX** and **X** for which diamagnetic $\text{Eu}(\text{fod})_3$ -induced shifts were observed.

The molecules of substituted chalcones consist of two aromatic rings linked through an α,β -unsaturated ketone

bridge. The enone fragment in such compounds is known to be planar; this follows from both X-ray diffraction data [9] and theoretical molecular-mechanics calculations (MM+).

As LSR we used tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)lanthanides $\text{Ln}(\text{fod})_3$. We examined reactions of all compounds **I–XVI** with $\text{Eu}(\text{fod})_3$ and $\text{Yb}(\text{fod})_3$ and of some substrates with other LSR. The lanthanide-induced shifts are collected in Tables 2 and 3. The results may be analyzed on a qualitative and quantitative level. Some interesting conclusions can be drawn even on a qualitative level. It is seen that the complex formation of compounds **I–XVI** with $\text{Eu}(\text{fod})_3$ is essentially different from the complex formation with $\text{Yb}(\text{fod})_3$. In the spectra of $\text{Yb}(\text{fod})_3$ adducts, the greatest shifts were observed for the 6'-H signal and olefinic proton signals, while complex formation with $\text{Eu}(\text{fod})_3$ induced the largest shift of the 2'-methoxy protons. Comparison of the LSR-induced shifts for differently substituted chalcones showed that steric effect is the crucial factor. For example, the shifts observed for 6'-methyl derivatives **VIII** and **XV** are much smaller than those found for their 6'-unsubstituted analogs. An appreciable effect on the induced shifts is produced by the substituents in ring **B**. Chalcones **II**, **III**, and **V** having an *ortho*-substituent in

Table 2. Lanthanide-induced shifts (δ , ppm) for compounds **I–X**^a

Comp. no.	LSR	2'-OCH ₃	3'-H	4'-H	5'-H	6'-H	α	β
I	Eu(fod) ₃	8.3	3.9	1.1	–	4.2	2.9	2.2
	Yb(fod) ₃	6.9	3.9	2.0	–	13.7	13.9	10.9
II	Eu(fod) ₃	7.2	4.2	1.3	–	2.8	2.3	1.3
	Yb(fod) ₃	5.2	4.2	2.2	–	8.3	8.2	7.2
III	Eu(fod) ₃	7.8	4.4	1.8	–	3.1	2.4	1.6
	Yb(fod) ₃	4.4	3.7	2.3	–	7.2	7.3	6.0
	Rr(fod) ₃	–14.8	–5.8	–0.3	–	–5.2	–7.0	–6.8
	Ho(fod) ₃	–20.3	–10.3	–2.8	–	–13.1	–14.0	–10.6
	Sm(fod) ₃	–15.4	–1.3	^b	–	–4.4	–7.6	–5.3
	Dy(fod) ₃	–143.4	–64.1	^b	–	–72.3	–88.3	–82.2
	Nd(fod) ₃	0.0	0.0	0.0	–	0.0	0.0	0.0
IV	Eu(fod) ₃	3.8, 2.2	2.2	1.0	–	5.4	5.3	3.5
	Yb(fod) ₃	3.7, 3.5	3.4	2.0	–	14.7	15.7	11.6
V	Eu(fod) ₃	12.1	6.9	2.0	–	3.9	2.3	1.4
	Yb(fod) ₃	12.3	10.0	4.4	–	15.4	13.7	12.3
VI	Eu(fod) ₃	10.5	5.1	1.7	–	4.3	3.0	1.9
	Yb(fod) ₃	9.6	7.7	6.4	–	18.4	18.1	14.7
VII	Eu(fod) ₃	14.6	7.4	3.0	–	5.8	4.2	2.3
	Yb(fod) ₃	12.9	8.9	5.7	–	21.2	19.8	17.9
VIII	Eu(fod) ₃	2.8	2.0	0.6	1.2	2.8	2.9	1.9
	Yb(fod) ₃	2.3	2.7	1.3	2.8	6.9	7.6	6.8
	Rr(fod) ₃	–10.2	–4.3	–0.5	–1.7	–4.2	–7.8	–6.4
	Ho(fod) ₃	–4.0	–2.3	0.0	–2.3	–5.0	–6.3	–5.0
	Sm(fod) ₃	–4.6	–2.4	–0.3	–1.2	–3.0	–3.1	–1.5
	Dy(fod) ₃	–34.5	–21.3	–3.1	–21.3	–37.9	–47.8	–37.2
	Nd(fod) ₃	–152.0	–73.1	–17.5	–73.1	–152.0	–125.0	–7.5
IX	Eu(fod) ₃	12.1	6.9	1.7	6.9	12.1	1.9	–2.8
	Yb(fod) ₃	18.5	15.4	4.7	15.4	18.5	17.3	–4.2
	Rr(fod) ₃	–13.6	–6.2	–0.9	–6.2	–13.6	–10.6	–3.0
	Ho(fod) ₃	–28.4	–15.6	–4.3	–15.6	–28.4	–23.4	7.7
	Sm(fod) ₃	–32.9	–17.2	–4.9	–17.2	–32.9	–11.7	20.5
X	Eu(fod) ₃	8.8	5.2	1.4	5.2	8.8	2.3	–2.2
	Yb(fod) ₃	15.5	13.2	4.1	13.2	15.5	12.9	–3.3

^a Given are the induced shifts extrapolated to an LSR–substrate ratio of 1 : 1; the shifts for protons in ring **B** are close to zero.

^b The shift was not determined owing to signal broadening.

ring **B** are characterized by smaller shifts than those possessing no substituent in the same position. Electron-acceptor power of the substituents in ring **B** also affects the LSR-induced shift, but to a weaker extent. The presence of electron-acceptor substituents reduces the

shift. Increase in the size of the 2'-alkoxy group in going from methoxy to isopropoxy derivatives has no considerable influence on the induced shift of the olefinic proton signals, presumably due to donor effect of alkyl groups, which facilitates coordination with LSR.

Table 3. Lanthanide-induced shifts (δ , ppm) found for chalcones **XI–XVI**

Comp. no.	LSR	2'-OCH ₃	3'-H	4'-H	5'-H	6'-H	α	β	2-H	3-OCH ₃	4-OCH ₃	5-H	6-H
XI	Eu(fod) ₃	8.8	2.5	1.7	–	4.7	4.0	3.5	3.9	3.8	3.0	4.9	4.9
	Yb(fod) ₃	12.2	10.6	5.6	–	27.1	24.0	23.3	~0	2.1	2.1	~0	~0
XII	Eu(fod) ₃	1.5, 1.2	0.7	0.7	–	3.8	5.4	4.5	6.0	7.5	7.5	6.0	6.0
	Yb(fod) ₃	8.2, 5.9	~0	–	33.9	33.3	26.4	~0	2.2	2.2	~0	~0	~0
XIII	Eu(fod) ₃	5.6	2.4	2.4	–	3.1	2.5	2.0	2.9	2.6	2.7	6.5	4.1
	Yb(fod) ₃	12.1	5.7	6.1	–	17.1	16.0	15.8	4.1	1.5	1.8	1.9	1.1
XIV	Eu(fod) ₃	7.5	3.4	1.3	–	3.2	3.6	2.2	4.5	3.5	3.5	2.8	2.9
	Yb(fod) ₃	12.2	4.7	2.7	–	20.7	19.9	18.3	6.9	2.1	2.1	0.3	0.3
XV	Eu(fod) ₃	2.9	2.0	0.8	1.0	1.9	3.5	2.0	4.7	3.6	3.8	1.0	2.9
	Yb(fod) ₃	0.7	0.9	0.5	0.9	2.0	2.5	2.0	0.5	0.3	0.2	0.2	0.6
XVI	Eu(fod) ₃	2.1	1.2	1.2	–	4.9	5.4	4.6	6.5	4.3	4.3	5.5	3.8
	Yb(fod) ₃	7.5, 5.6	4.8	8.1	–	29.0	29.3	21.8	6.2	2.2	2.2	6.2	6.2

Table 4. Calculated structural parameters of LSR–substrate adducts^a

Compound no.	Most probable coordinates of Yb ³⁺ ion			Standard deviation	Yb–O bond length, Å
	x	y	z		
I	–2.27	0.01	–0.02	0.01359	2.27
II	–2.13	0.07	0.03	0.09562	2.13
III	–2.10	0.08	0.04	0.10285	2.10
IV	–2.69	0.25	0.06	0.08129	3.70
V	–2.07	0.09	0.03	0.16767	2.07
VI	–2.15	0.10	0.04	0.09728	2.15
VII	–2.19	0.07	0.04	0.09081	2.19
VIII	–2.44	2.17	0.07	0.06624	3.26
IX	–2.24	0.90	0.00	0.17820	2.41
X	–2.27	0.88	0.00	0.21270	2.43
XI	–2.32	0.12	0.05	0.06657	2.32
XII	–2.75	0.14	0.04	0.12990	2.03
XIII	–2.16	0.06	0.03	0.13118	2.16
XIV	–2.35	–0.09	–0.06	0.06103	2.35
XV	–2.55	1.99	0.10	0.07583	3.24
XVI	–2.49	1.24	0.00	0.11021	2.78

^a The molecule was assumed to lie in the *xy* plane; the carbonyl oxygen atom is located in the origin, and the C=O bond is directed along the *x* axis.

In order to elucidate the conformational composition of the compounds under study, we applied a calculation procedure based on the dipolar origin of lanthanide-induced shifts [3]. The Δ_{calc}^i value for an *i*th proton can be calculated using the McKonnel–Robertson equation which looks like Eq. (1) for axially symmetric adducts:

$$\Delta_{calc}^i = K(3 \cos^2\theta_i - 1)/r_i^3. \quad (1)$$

Here, r_i and θ_i are polar coordinates of an *i*th proton under the constraint that the coordination center is located in the origin, and K is a constant for all protons in the adduct. The geometric parameters were calculated by

Table 5. Yields, melting points, and analytical data of compounds **I–XVI**

Compound no.	Yield, %	mp, °C (solvent)	Calculated, %	Formula	Found, %
I	60	91–93 (MeOH)	Cl 12.19	C ₁₆ H ₁₂ ClFO ₂	Cl 11.89
II	47	111–112 (MeOH)	Cl 23.08	C ₁₆ H ₁₂ Cl ₂ O ₂	Cl 23.44
III	71	122–124 (MeOH)	Cl 10.08, Br 22.72	C ₁₆ H ₁₂ BrClO ₂	Cl 10.0, Br 22.73
IV	54	94–96 (MeOH)	Cl 22.07	C ₁₇ H ₁₄ Cl ₂ O ₂	Cl 22.14
V	64	72–73 (hexane)	Cl 11.29	C ₁₇ H ₁₅ ClO ₃	Cl 11.71
VI	69	140–141 (MeOH)	Cl 11.19	C ₁₇ H ₁₃ ClO ₄	Cl 11.16
VII	57	93–95 (EtOH)	Cl 10.72	C ₁₈ H ₁₅ ClO ₄	Cl 11.01
VIII	49	162–164 (MeOH, <i>i</i> -PrOH)	N 4.28	C ₁₈ H ₁₇ NO ₅	N 4.31
IX	51	129–131 (MeOH)	Cl 10.65	C ₁₈ H ₁₇ ClO ₄	Cl 11.08
X	55	140–142 (EtOH)	N 4.08	C ₁₈ H ₁₇ NO ₆	N 4.10
XI	59	94–96 (MeOH)	F 6.0	C ₁₈ H ₁₇ FO ₄	F 6.08
XII	63	79–80 (MeOH)	F 5.52	C ₂₀ H ₂₁ FO ₄	F 5.48
XIII	59	102–103 (MeOH)	Cl 10.65	C ₁₈ H ₁₇ ClO ₄	Cl 11.13
XIV	50	85–86 (MeOH, cyclohexane)	Br 21.18	C ₁₈ H ₁₇ BrO ₄	Br 21.25
XV	45	105–106 (cyclohexane)	C 70.17, H 6.43	C ₂₀ H ₂₂ O ₅	C 70.41, H 6.38
XVI	52	103–104 (EtOH)	F 5.75	C ₁₉ H ₁₉ FO ₄	F 5.81

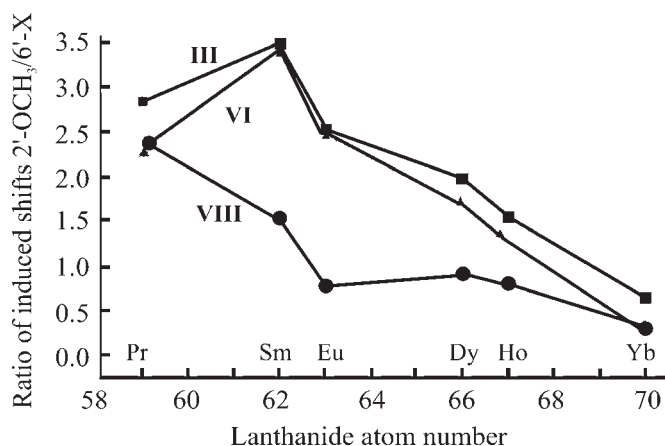
the molecular-mechanics method. Using the gradient descend technique, we localized a point in the vicinity of the coordination center, for which the dispersion of the K values calculated by Eq. (1) for LRS-induced proton shifts was minimal. Just that point was characterized by the best agreement between the calculated and experimental lanthanide-induced shifts [7]. We succeeded in determining the structure of Yb(fod)₃ adducts with chalcones **I–XVI** with a high statistical reliability. A good agreement between Δ_{calc}^i and Δ_{exp}^i was observed for planar arrangement of the conjugated bond sequence and E configuration of bond a (antiperiplanar orientation of the AlkO and C=O groups). The Yb ion in the adducts lies in the molecular plane at a distance of 2.2–3.2 Å from the carbonyl oxygen atom, most commonly in the vicinity of the C=O bond extension (Table 4).

The planar structure of molecules **IX** and **X** in the adducts follows from the diamagnetic shift of the β -H signal. This is explained by displacement of the lanthanide ion in the adduct toward β -H, which is caused by steric hindrances to complex formation with Yb(fod)₃ created by the 6'-methoxy group in ring **A**. Here, the β -H proton falls into the area shielded by Yb³⁺ ion since the angle between the O–Yb and Yb– β -H axes exceeds 54°. We can conclude that the examined chalcones are coordinated to Yb(fod)₃ as unidentate ligands. The

structure of the LSR–substrate adducts can readily be determined and is typical of unsymmetrical ketones [10].

The results of calculations of the structure of adducts formed by chalcones **I–XVI** and Eu(fod)₃ turned out to be much less accurate than those obtained for Yb(fod)₃ adducts. The reason is that the complex formation with Eu(fod)₃ involves both potential coordination centers in molecules **I–XVI**, the carbonyl oxygen atom and oxygen atom of the 2'-methoxy group. Taking into account that alkoxy phenols having no other coordination center almost do not react with LSR (the lanthanide-induced shift of the methoxy group protons in molecule **V**, where the methoxy group is remote from the carbonyl group, is close to zero), considerable shifts of the methoxy protons in compounds **I–IV** indicate simultaneous coordination of Eu(fod)₃ at the carbonyl and methoxy groups, i.e., formation of a chelate structure. However, we failed to find a model which could describe the induced shifts for the adducts with Eu(fod)₃ on a quantitative level. Presumably, the McConnell–Robertson equation cannot be applied to complexes formed by eight-coordinate europium atom and four dissimilar bidentate ligands owing to magnetic anisotropy.

Table 2 contains data which make it possible to analyze complex formation of a wider series of LSR with the same substrate. Here, the results obtained for Ln(fod)₃



Relative ability of chalcones **III**, **VI**, and **VIII** to form chelates with different LSR.

adducts with chalcones **III**, **VIII**, and **IX** are given. The largest lanthanide-induced shifts were observed for adducts with $\text{Dy}(\text{fod})_3$ and $\text{No}(\text{fod})_3$. However, in these cases the complex formation was accompanied by strong broadening of signals. We succeeded in making most signals narrower by carrying out experiments at a temperature near the boiling point of chloroform (340 K). The data given in Table 2 were obtained using this technique.

The ability of LSR to chelation can be estimated by the ratio $\Delta_{\text{exp}}(2'\text{-OCH}_3)/\Delta_{\text{exp}}(6'\text{-H})$, for chelation raises the induced shift of the $2'\text{-OCH}_3$ signal; otherwise, the shift of the signal from the $6'\text{-X}$ group increases. We used the above ratio to compare the chelating powers of different LSR. Figure shows the corresponding plots for compounds **III**, **VI**, and **VIII**. In the ^1H NMR spectra of adducts formed by compound **VI** with all the examined LSR, signals were strongly broadened, and we determined lanthanide-induced shifts only for $6'\text{-H}$ and $2'\text{-OCH}_3$. It is seen that the chelating power of lanthanides with respect to bidentate ligands decreases with rise in their atom number. The most efficient chelating agent are those based on samarium, europium, and praseodymium, while $\text{Yb}(\text{fod})_3$ is the least efficient.

Thus the results of our study showed that lanthanide shift reagents can be used to purposefully vary the predominant conformation of substituted chalcone molecules in solution. Addition of $\text{Yb}(\text{fod})_3$ stabilizes *anti*-periplanar orientation of the methoxy and carbonyl groups in 6-methoxychalcones, while $\text{Eu}(\text{fod})_3$ shifts the conformational equilibrium toward the corresponding *syn*-periplanar conformation. The revealed effect may be

useful in performing chemical reactions whose rate strongly depends on the molecular conformation.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker WP100-SY spectrometer at a frequency of 100 MHz. Commercial lanthanide shift reagents were used without additional purification.

Chalcones I–III, V–X, and XV. To a warm solution of 10 mmol of 2-methoxyacetophenone and 10 mmol of the corresponding substituted benzaldehyde in a minimal amount of ethanol we added 2.3 ml of a 50% solution of sodium hydroxide. The mixture was kept for 20–30 h at room temperature, the precipitate was filtered off and dispersed in water, and the resulting suspension was neutralized with 20% acetic acid. The precipitate was filtered off and recrystallized from appropriate solvent (Table 5).

Chalcones XI, XIII, and XIV. To a warm solution of 10 mmol of $2'\text{-hydroxychalcone}$ in a minimal amount of anhydrous acetone we added 4.14 g (30 mmol) of freshly calcined K_2CO_3 and 1.15 g (10 mmol) of dimethyl sulfate, and the mixture was heated for 5–7 h under reflux. The precipitate (inorganic salts) was filtered off and washed with acetone. The solvent was distilled off from the filtrate under reduced pressure (water-jet pump), and the residue was recrystallized from appropriate solvent (Table 5).

Chalcones **IV** and **XVI** were synthesized in a similar way using 1.3 ml (10 mmol) of diethyl sulfate instead of dimethyl sulfate.

Chalcone XII. To a warm solution of 10 mmol of the corresponding $2'\text{-hydroxychalcone}$ in a minimal amount of anhydrous acetone we added 4.14 g (30 mmol) of freshly calcined K_2CO_3 and 1 ml of isopropyl iodide, and the mixture was heated for 10 h under reflux. The inorganic precipitate was filtered off and washed with acetone, the solvent was distilled off from the filtrate under reduced pressure (water-jet pump), and the residue was recrystallized from methanol.

α -Deuterated analogs of chalcones IV and XIII. To a warm solution of 10 mmol of 2-methoxyacetophenone and 10 mmol of the corresponding benzaldehyde in a minimal amount of deuterated methanol (CD_3OD) we added 2.3 ml of a 50% solution of NaOD in D_2O . The mixture was kept for 20–30 h at room temperature, the precipitate was filtered off and dispersed in water, the resulting suspension was neutralized with CF_3COOD , and the precipitate was filtered off.

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