1H NMR Dynamic study of thermal Z/E isomerization of 5-substituted 2-alkylidene-4-oxothiazolidine derivatives: Barriers to rotation about C=C bond

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Abstract

The rotational barriers between the configurational isomers of two structurally related push–pull 4-oxothiazolidines, differing in the number of exocyclic C=C bonds, have been determined by dynamic 1H NMR spectroscopy. The equilibrium mixture of (5-ethoxy-carbonylmethyl-4-oxothiazolidin-2-ylidene)-1-phenylethanone (1a) in CDCl 3 at room temperature to 333 K consists of the E- and Z-isomers which are separated by an energy barrier ΔG# 98.5 kJ/mol (at 298 K). The variable-temperature 1H NMR data for the isomerization of ethyl (5-ethoxycarbonylmethylidene-4-oxothiazolidin-2-ylidene)ethanoate (2b) in DMSO-d 6, possessing the two exocyclic C=C bonds at the C(2)- and C(5)-positions, indicate that the rotational barrier ΔG# separating the (2E,5Z)-2b and (2Z,5Z)-2b isomers is 100.2 kJ/mol (at 298 K). In a polar solvent-dependent equilibrium the major (2Z,5Z)-form (>90%) is stabilized by the intermolecular resonance-assisted hydrogen bonding and strong 1,5-type S−(O) interactions within the S=S=C−C=O entity.

The 13C NMR ΔδC(2)C(2') values, ranging from 58 to 69 ppm in 1a-d and 49-58 ppm in 2a-d, correlate with the degree of the push-pull character of the exocyclic C(2)=C(2') bond, which increases with the electron withdrawing ability of the substituents at the vinylic C(2') position in the following order: COPh > COEt > CONHPh > CONHCH 2CH 2Ph. The decrease of the ΔδC(2)C(2') values in 2a-d has been discussed for the first time in terms of an estimation of the electron donor capacity of the −S− fragment on the polarization of the C=C bonds.

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1. Introduction

Since the concept of push–pull alkenes was reviewed by Sandström [1], the physicochemical properties and chemical reactivity of numerous functionalized compounds of that type have been extensively studied [2–7]. 5-Substituted 4-oxothiazolidines 1 and 2 with one and two exocyclic double bonds attached to thiazolidine ring, respectively, exemplify typical push–pull compounds which can exist in different configurational and conformational forms. Stereodefined 4-oxothiazolidines 1 and 4, synthesized according to procedures reported by us [8,9], attracted our attention due to their potential biological activity [10,11]. In addition, they exhibit interesting chemical properties related, for example, to regiospecific bromination-rearrangement process of selected 4-oxothiazolidines 1 [12] and pyridine-assisted bromine transfer from the C=C bond to the C(5) position, followed by the formation of the pyridinium salts via nucleophilic substitution [13].

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They also represent an excellent model for investigation of the effects of weak noncovalent interactions on structure-reactivity relationship in solution and in the solid state [14–20]. The equilibrated mixtures of structurally related 4-oxothiazolidines 1a–d consist of the intramolecularly H-bonded (E)-isomer and intermolecularly H-bonded (Z)-isomer in varying proportions which depend on the solvent polarity [21,22]. The upfield chemical shift of the NH proton of the (Z)-1a isomer, observed during the Z/E process in CDCl 3 as a function of temperature increase, is explained in terms of a decrease of intermolecular H-bonding, resulting in a greater amount of a free or unassociated Z-isomer [23,24]. During the course of the Z/E isomerization of (Z)-1a in nonpolar CDCl 3 an equilibrated mixture is formed, enriched in the E-isomer (Z/E ratio ~ 10/90 at room temperature). Additionally, temperature-dependent chemical shift differences expressed as Δδ/ΔT coefficients serve as a parameter for distinction between the intermolecularly hydrogen-bonded (Z)-1a isomer and free NH groups in derivative 1a. In principle, the variable-temperature NMR data of that type provide information regarding the hydrogen bonding patterns (inter- vs intra-) in our model system and also in related amides and peptides [23–26]. In light of these results, we wish to report here (i) detailed NMR spectroscopic investigation of the stereodynamic behavior of 4-oxothiazolidines 1 and 2 associated with the kinetics of the configurational isomerization of the stereodefined (Z)-1a in CDCl 3 and (2E,5Z)-2b in DMSO-d 6 and (ii) determination of the energy barriers separating the configurational isomers of substrates 1a and 2b. In order to obtain additional structural information regarding the push-pull nature of the 4-oxothiazolidine derivatives, the IR data for selected compounds 1–4 were also analyzed in terms of vibrational interactions between the electron-donor(s), electron-acceptor and intervening exocyclic C=C bond.

2. Experimental

The NMR spectra for characterization were obtained using a Varian Gemini 2000 instrument (1H at 200 MHz, 13C at 50.3 MHz). Chemical shifts are reported in parts per million (ppm) on the δ scale from TMS as an internal standard in the solvents specified. Variable-temperature 1H NMR measurements in the temperature range 273–343 K were carried out on a Bruker AC-300 spectrometer using CDCl 3 as a solvent which was dried over activated molecular sieves (4 Å) for one day. In the case of deuterated DMSO, the solvent was distilled from CaH 2 prior to use. The concentrations of CDCl 3 solutions were 0.011 or 0.016 M in the case of (Z)-1a and 0.010 M for (2E,5Z)-2b in DMSO, unless otherwise indicated. The variable-temperature was computer controlled employing the BVT 2000 unit. The internal temperature was calibrated with methanol and ethylene glycol using the Bruker Batman program. Caution was taken to increase the temperature slowly when using CDCl 3, especially at 333 K to avoid solvent evaporation.

The sample was equilibrated at the given temperature and a 128-scan spectrum was recorded with 0.5 Hz per point digital resolution. All chemical shifts were referenced to the solvent residual signal. Typical parameters were: acquisition time 1.892 s, spectral width 7997.6 Hz with 256 repetitions and 32 k data points. Melting points were determined on a Micro-Heitizts Boetius PHMK apparatus and Büchi apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer FT-IR 1725x spectrophotometer and are reported as wave numbers (cm⁻¹). Samples for IR spectral measurements were prepared as KBr disks. Low-resolution mass spectra were recorded using a Finnigan MAT 8230 BE spectrometer. Isobutane was used as the ionizing gas for the chemical ionization (CI) mass spectra. The UV spectra were measured on a Beckman DU-50 spectrophotometer. Analytical thin-layer chromatography (TLC) was carried out on Kieselgel G nach Stahl, and the spots were visualized by iodine. Column chromatography was carried out on SiO 2 (silica gel 60 Å, 12–26, ICN Biomedicals). Elemental analyses were performed at the microanalysis laboratory at the Faculty of Chemistry, University of Belgrade.

The structural assignments of all isolated products were made on the basis of spectroscopic data (IR, 1H and 13C NMR, MS, UV) and elemental analysis [8,9]. For the configurational isomers of derivatives 1a and 2b, used in the variable-temperature (VT) 1H NMR experiments, the following 1H NMR data are pertinent to the discussion.

2.1. (Z)-(5-Ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-1-phenylethanone (1a)

1H NMR (CDCl 3 ): δ 1.26 (t, 3H, CH 3, J = 7.2 Hz), 3.00 (dd, 1H, CH 2CH 3), 3.15 (dd, 1H, CH 3), 1.75 (HH, J 1A = 17.5 Hz, J 2X = 8.2 Hz), 4.19 (q, 2H, CH 2OCH 3), 4.22 (dd, 1H, CH 3S, J 1X = 8.2 Hz, J 2X = 4.3 Hz), 6.65 (s, 1H, = CH), 7.39–7.53 (m, 3H, m- and p-Ph), 7.88–7.93 (m, 2H, o-Ph), 8.88 (s, 1H, NH).
2.2. (E)-(5-Ethoxycarbonylmethyl-4-oxothiazolidin-2-yldiene)-1-phenylethanone (1a)

1H NMR (CDCl3): δ 1.29 (t, 3H, CH3, J = 7.2 Hz), 2.91 (dd, 1H, CH3H2CH3S, JAB = 17.6 Hz, JAX = 10.1 Hz), 3.28 (dd, 1H, CH3H2CH3S, JAB = 17.6 Hz, JBX = 3.7 Hz), 4.22 (q, 2H, CH2O, J = 7.2 Hz), 4.29 (dd, 1H, CH3S, JAX = 10.1 Hz, JBX = 3.7 Hz), 6.32 (s, 1H, = CH), 7.41–7.59 (m, 3H, m- and p-Ph), 7.88–7.93 (m, 2H, o-Ph). Anal. Calcd for C11H13NO5S: C, 48.73; H, 4.79; N, 5.16. Found: C, 48.61; H, 4.84; N, 5.02. 

2.3. (2E,5Z)-Ethyl (5-ethoxycarbonylmethylidene-4-oxothiazolidin-2-ylidene)ethanoate (2b)

1H NMR (CDCl3): 1.30 (t, 3H, CH3, J = 7.1 Hz), 1.35 (t, 3H, CH3, J = 7.1 Hz), 4.22 (q, 2H, CH2O, J = 7.1 Hz), 4.31 (q, 2H, CH2O, J = 7.1 Hz), 5.35 (s, 1H, = CH (C2)), 6.88 [s, 1H, = CH (C5)], 10.82 (s, 1H, NH). 

2.4. (2Z,5Z)-Ethyl (5-ethoxycarbonylmethylidene-4-oxothiazolidin-2-ylidene)ethanoate (2b)

1H NMR (CDCl3): 1.32 (t, 3H, CH3, J = 7.0 Hz), 1.35 (s, 3H, CH3, J = 7.0 Hz), 4.25 (q, 2H, CH2O, J = 7.0 Hz), 4.32 (q, 2H, CH2O, J = 7.0 Hz), 5.83 [s, 1H, = CH (C5)], 10.54 (s, 1H, NH). Anal. Calcd for C11H13NO5S: C, 48.73; H, 4.79; N, 5.16. Found: C, 48.61; H, 4.84; N, 5.27. 

3. Results and discussion

3.1. Stereodynamic behavior of push-pull thiazolidine derivatives 1a and 2b

The configurational isomerization of the stereodefined (Z)-1a in nonpolar CDCl3 and (2E,5Z)-2b in DMSO-d6 is characteristic process for push-pull alkenes [1,27,28]. It is based on a lowering of the rotational barrier of the C==C bond at the C(2)-position as a consequence of the electronic n,π-interactions between the two electron-donors (-NH and -S) and one electron-acceptor (the COPh group for 1a and CO2Et for 2b) through the π-conjugated bond (Scheme 1).

We have recently shown that the push-pull effect, i.e., the extent of the donor-acceptor interactions, has in combination with other electronic and steric effects, decisive influence on the chemical properties and reactivity of these heterocyclic compounds [12,20]. The ground-state structure of push–pull thiazolidines can be represented as a combination of the neutral resonance forms 1a and 2b and charge-separated dipolar resonance forms A–C. The push-pull character of thiazolidines 1 and 2, explained in terms of the resonance structures, reflects the extended delocalization in the molecule [15,27]. In this sense the 13C chemical shift difference (ΔδC2) between the two electron-donors provides an assessment of the degree of n,π-conjugation encompassing the N—C==C—O and S—C==C—O entities of derivatives 1a–d and 2a–d (Table 1) [29].

In all thiazolidines 1a–d and 2a–d the high field 13C chemical shifts (88.9–97.3 ppm) for the acceptor-substituted C(2′) atoms, and low field shifts (145.0–161.6 ppm) for the donor-substituted C(2) atoms are typical [9]. The 13C NMR ΔδC2(C2′) values, ranging from 57.6 to 68.9 ppm in 1a–d and 48.5 to 58.0 ppm in 2a–d, indicate that the degree of the push-pull character of the exocyclic C(2)==C(2′) bond increases with the electron accepting ability of the substituents at the vinylic C(2′) position in the following order: COPh ~ COEt ~ CONHPh ~ CONHCH2CH3Ph. The larger numerical values of ΔδC2,C2′ in 1a–d, relative to the corresponding ΔδC2,C2′ values in 2a–d, correlate with a decrease of the charge polarization of the C(2)==C(2′) bond of the push–pull thiazolidines 2a–d [4,30]. A drop of the ΔδC2,C2′ values in compounds 2 for ~ 5–10 ppm reflects the influence of the C(5)==C(5′) bond in thiazolidines 2 on the lowering of the push-pull
effect of the C(2)==C(2') bond. The push-pull character of the C(5)==C(5') bond, with just one donor and one acceptor, is significantly reduced in comparison to the C(2)==C(2') bond, as demonstrated by \( \Delta \delta_{C5,C5'} \) values, ranging from 22.2 to 32.8 ppm (Table 1, entries 9–15). In addition, the donor capacity of the S– fragment in the thiazolidine series 2 – in contrast to series 1 – is being now dissipated between the two exocyclic C=C bonds. Accordingly, the decrease of the \( \Delta \delta_{C2,C2'} \) values of \( \sim 5\)–10 ppm in derivatives 2 with respect to these of the counterparts 1 must be roughly equal to the half of the total donor capacity of the sulfur atom. For example, the calculated \( \Delta \delta_{C2,C2'} \) values in CDCl\(_3\) for the isomers (\( E \))-1b and (\( 2E,5Z \))-2b with identical acceptor, the CO\(_2\)Et group, attached to the C=C bonds at the C(2) and C(5) positions, are 65.4 and 58.0 ppm, respectively (Table 1, entries 4 and 11). The two compounds show characteristic drop in \( \Delta \delta_{C2,C2'} \) values of 7.4 ppm and for the (\( Z \))-1b/(\( 2Z,5Z \))-2b pair the difference in CDCl\(_3\) is 7.8 ppm (Table 1, entries 3 and 10). The data in Table 1 exemplify also larger \( \Delta \delta_{C2,C2'} \) values in polar DMSO, which amount to 9.5 ppm for the derivative pair (\( Z \))-1c/(\( 2Z,5Z \))-2c (see entries 6 and 12) and 9 ppm for the pair (\( Z \))-1d/(\( 2Z,5Z \))-2d (entries 7 and 14). These data indicate that the electron-releasing power of the thioether moiety in the cyclic systems enhances the \( \pi \)-electron polarization, expressed through the \( \Delta \delta_{C,C} \) parameter, by approximately 15–19 ppm. The lower polarization of the (\( Z \))-C(5)==C(5') bond in thiazolidines 2, combined with the unfavorable steric and dipole-dipole interactions of the E-configurated C(5)-double bond, makes the 5Z-configuration fixed and not prone to the Z/E isomerization [9]. Recently, the reliable method of quantification of the push–pull effect in an extensive series of substituted alkenes, based on the quotient of the occupation numbers of \( \pi \) bonding and \( \pi^* \) antibonding orbitals of the C=C bond, instead of the \( \Delta \delta_{C,C} \) parameter, has been reported [31,32].

Valuable information regarding the presence of various functionalities in 4-oxothiazolidine derivatives, and their push–pull character based on interactions between the electron-donor(s), electron-acceptor and intervening exocyclic C=C bond, were obtained by an analysis of the IR spectra of 1–4 (Table 2) recorded in the solid state. As a comparison, the principal frequencies of the IR spectra of 5-unsubstituted 4-oxothiazolidines (Z)-5 and (\( Z \))-6, previously reported by Taylor [33], are given (entries 7 and 8). All compounds 1–6 containing the five-membered lactam ring as a common skeletal fragment show weak to moderate NH band at 3165–3240 cm\(^{-1}\) and C=O stretching absorption band in the region of 1729–1689 cm\(^{-1}\). Thanks to its relatively constant position, high intensity and relative freedom from interfering bands, CO\(_{ring}\) band is one of the most typical in the IR spectra of heterocycles 1–6. Within the given range, the position of this band depends primarily on conjugation effect and nature of the neighboring lactam substituent (hydrogen or methyl group). Thus, the CO band of the parent compound (\( Z \))-1a, which appears at 1729 cm\(^{-1}\), is shifted in (\( 2E,5Z \))-2a to lower frequency (1689 cm\(^{-1}\)) due to the conjugation of the ring carbonyl with exocyclic C=C bond at the C-5 position (Table 2, entries 2, 9 and 10). As indicated in Table 2, strong CO\(_{ring}\) band of N-methyl-substituted 4-oxothiazolidine (Z)-3a at 1706 cm\(^{-1}\) is 23 cm\(^{-1}\) below that of the thiazolidine derivative (\( Z \))-1a. The lower frequency of CO\(_{ring}\) upon the replacement of NH by NMe correlates nicely with inductive effect of methyl group. It should be noted that the CO\(_{ring}\) frequency in (\( Z \))-1b is lower than that of the 5-unsubstituted analogue (\( Z \))-6 (Table 2, entries 5 and 8). A decrease of the CO\(_{ring}\) frequency for about 14 cm\(^{-1}\) can be rationalized by hydrogen bonding effect.

This is proved by the X-ray analysis of the (\( Z \))-1b isomer, which shows that the molecular packing is controlled by intermolecular hydrogen bonds between the NH group and the C-4 carbonyl of an adjacent molecule [20]. The existence of particularly favorable 1.5-type S–O interactions within the S–C=C–C=O subunit in (\( Z \))-1b nicely correlates with the shortening of the nonbonded distance.
S–O (2.873 Å) with respect to the sum of the van der Waals radii (3.22 Å).

The strong-intensity band in the IR spectra of 1a, 1b and 3a (Table 2, entries 1, 5 and 3, respectively), with the maximum at 1729 cm\(^{-1}\) for 1a, is assigned to the carbonyl fragment of the ethoxycarbonylmethyl group at the C-5 position. The lower frequency peak of this band in 2a, appearing at 1689 cm\(^{-1}\), indicates again the conjugation effect due to the presence of the exocyclic C=C group at the C-5 position. The IR spectra of 4-oxothiazolidine derivatives 1–6 show also a third medium strong peak within the 1618–1690 cm\(^{-1}\) region, which is assigned to the exocyclic CO group. It should be emphasized that the band overlapping of the CO\(_{\text{ring}}\) and CO\(_{\text{exo}}\) modes at 1729 and 1689 cm\(^{-1}\) is observed in compounds (Z)-1a and (2Z,5Z)-2a, respectively. The very strong and broad enamine band \([3,33,34]\), resulting from an asymmetric combination of the exocyclic C=C and C=N stretching motions, with a contribution of the in-plane N–H bending mode in case of the (Z)-1a, (2Z, 5Z)-2a and (Z)-4a and (Z)-5 isomers, is centered at about 1515 cm\(^{-1}\) in the IR spectra of all 4-oxothiazolidines with the COPh group at C-2' atom (Table 2, entries 1, 2, 4 and 7). In the case of compounds (Z)-1b, (2E,5Z)-2b and (Z)-6 (Table 2, entries 5, 6 and 8), containing the ethoxycarbonyl group at the same position, this band is shifted to higher frequency.

The stereodynamic behavior associated with the isomerization rate of (Z)-1a to (E)-1a at different temperatures in CDCl\(_3\) was followed by progressive disappearance of the singlet at \(\delta\) 6.85 ppm assigned to the olefinic proton of (Z)-1a and simultaneous appearance of the signal at \(\delta\) 6.32 ppm for the (E)-isomer (Table 3, entries 1 and 2).

In Fig. 1a typical resonances in the 6–9 ppm range in a set consisting of 25 \(^1\)H NMR spectra are shown \([21]\), when the Z/E process of 1a was monitored at 328 K at regular time intervals (15 min). In Fig. 1b plots are shown, correlating the decrease of the (Z)-1a isomer with the

### Table 2

Principal bands in the IR spectra of 2-alkylidene-4-oxothiazolidine derivatives 1–6 (KBr pellet)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>(\nu(N–H))</th>
<th>(\nu(C=\text{C}))(^a)</th>
<th>(\nu(C=\text{O})_{\text{ring}})</th>
<th>(\nu(C=\text{O})_{\text{exo}})</th>
<th>(\nu(C=\text{O})_{\text{ester}})</th>
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<tbody>
<tr>
<td>1</td>
<td>(Z)-1a</td>
<td>3239</td>
<td>1515</td>
<td>1729</td>
<td>1618</td>
<td>1729</td>
</tr>
<tr>
<td>2</td>
<td>(2Z,5Z)-2a</td>
<td>3165</td>
<td>1536</td>
<td>1689</td>
<td>1641</td>
<td>1689</td>
</tr>
<tr>
<td>3</td>
<td>(Z)-3a</td>
<td>–</td>
<td>1515</td>
<td>1706</td>
<td>1627</td>
<td>1731</td>
</tr>
<tr>
<td>4</td>
<td>(Z)-4a</td>
<td>3254</td>
<td>1522</td>
<td>1708</td>
<td>1627</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>(Z)-1b</td>
<td>3184</td>
<td>1604</td>
<td>1710</td>
<td>1690</td>
<td>1726</td>
</tr>
<tr>
<td>6</td>
<td>(2E,5Z)-2b</td>
<td>3256</td>
<td>1606</td>
<td>1696</td>
<td>1686</td>
<td>1696</td>
</tr>
<tr>
<td>7</td>
<td>(Z)-5</td>
<td>3210</td>
<td>1504</td>
<td>1728</td>
<td>1618</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>(Z)-6</td>
<td>3240</td>
<td>1568</td>
<td>1724</td>
<td>1665</td>
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</tr>
</tbody>
</table>

\(^a\) The enamine band arising from vibrational couplings of the C=C, C=N and N–H bonds.
1H NMR measurable time-dependent Z/E process conducted at different temperatures.

Fig. 2 depicts series of partial 1H NMR spectra of isomers (2E,5Z)-2b and (2Z,5Z)-2b (only the resonances of the olefinic protons are shown; see Table 3, entries 3 and 4) recorded in DMSO-d6 during the 2E,5Z/2Z,5Z-isomerization process at 298 K (part A) and 328 K (part B).

The ratios of the (2E,5Z)-2b versus (2Z,5Z)-2b isomers were calculated by the integration of the signals at δ 5.63 and 5.69 ppm, corresponding to the C(2°)-vinylic protons of the (2E,5Z)-2b and (2Z,5Z)-2b isomers, respectively. The kinetics of the isomerization at different temperatures can be also studied by the determination of the configurational ratio via integration of the C(5°)-H signals at δ 6.68 ppm [the (2E,5Z)-2b isomer] and 6.59 ppm [the (2Z,5Z)-2b isomer]. In Fig. 3, the decrease of the concentration of (2E,5Z)-2b is plotted as a function of time of the 2E,5Z/2Z,5Z-process at three different temperatures. The experimental values for t1/2, defined as the time required to reach the 50:50 ratio of isomers are 10.5 h at room temperature and less than 10 min at 328 K.

3.2. Kinetic and thermodynamic aspects of the configurational isomerization

The mechanism of the (Z)-1a ⇌ (E)-1a isomerization in CDCl3 and (2E,5Z)-2b ⇌ (2Z,5Z)-2b isomerization in DMSO-d6 is:

\[ A \xrightleftharpoons[k_2]{k_1} A^* \xrightarrow{k_3} B \]

where A and B are concentrations of the configurational isomers and \( A^* \) is the concentration of the activated complex. Based on the steady state approximation and assuming that \( k_2 < k_1 \) reaction is further approximated to first order reaction. The rate constant, \( k \), is determined as the slope of the best straight line fitted through the first ten points, when ln\[A/A_0\] is plotted against time (t). The slope of the Arrhenius plot (Fig. 4) gives the energy of activation and the intercept at 1/\( T \)= 0 gives the frequency factor A (Table 4).

Thermodynamic and activation parameters calculated from the Eyring equation by substituting \( \Delta G^0 = \Delta H^0 - T\Delta S^0 \) are listed in Table 5.

As data indicate the barrier for rotation around the exocyclic C(2°)=C(2’) bond separating the (Z)-1a and (E)-1a isomers in CDCl3 is 98.52 kJ/mol. With respect to 1a,
slightly larger value of the rotational barrier has been determined in the case of thiazolidine derivative 2b for the isomerization $2E,5Z/2Z,5Z$-process in DMSO-$d_6$. Compounds 1a and 2b have similar rotational barriers in spite of the decreased push-pull nature of the C(2)═C(2') bond in 2b, as evidenced by the lower $\Delta\delta_{C2,C2'}$ value relative to that of 1b. This fact can be interpreted on the basis of the isomerization $2E,5Z/2Z,5Z$-process occurring via the polarized transition state which is increasingly stabilized by the solvation in the polar solvent [28]. It follows that the ability of the polar solvent molecules in terms of the transition state lowering in the case of 2b

![Diagram of molecular structures](image)

**Fig. 2.** Spectral evidence for the presence of the starting $(2E,5Z)$-2b isomer, based on the observation of the olefinic signals at $\sigma$ 5.63 and 6.68 ppm, and $(2Z,5Z)$-2b isomer (olefinic signals at $\sigma$ 5.69 and 6.59 ppm) in DMSO-$d_6$ at room temperature; 30 min interval (A) and 328 K; 5 min interval (B).

![Spectral data](image)

**Fig. 3.** Change of concentration of $(2E,5Z)$-2b with time at given temperatures.

![Arrhenius plots](image)

**Fig. 4.** Arrhenius plots of kinetic data for the interconversion around the C═C bonds in 1a and 2b.
counterbalances the opposing effect of the C(5)=C(5') bond. The negative activation entropy for the rotation in thiazolidine derivative 2b (-64.70 J/mol,K) is also attributed to a higher degree of order in the dipolar transition state which is more strongly solvated in comparison to the ground state.

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References


Table 4
Energy of activation for 1a and 2b

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<tr>
<th>Compound</th>
<th>$T$ [K]</th>
<th>$\Delta G^\circ$ [kJ mol$^{-1}$]</th>
<th>$\Delta H^\circ$ [kJ mol$^{-1}$]</th>
<th>$\Delta S^\circ$ [J K$^{-1}$mol$^{-1}$]</th>
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<tbody>
<tr>
<td>1a</td>
<td>298</td>
<td>98.5</td>
<td>39.3</td>
<td>-198.7</td>
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<tr>
<td>2b</td>
<td>298</td>
<td>100.2</td>
<td>80.9</td>
<td>-64.7</td>
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Table 5
Activation parameters for rotation around C(2)=C(2') bond in 4-oxothiazolidines 1a and 2b

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T$ [K]</th>
<th>$\Delta G^\circ$ [kJ mol$^{-1}$]</th>
<th>$\Delta H^\circ$ [kJ mol$^{-1}$]</th>
<th>$\Delta S^\circ$ [J K$^{-1}$mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>298</td>
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