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Infrared Spectra and Theoretical Study of *E*-3-(2-*R*-vinyl)-2-benzothiazolinones

Alexander Perjéssy[a,]*, **Tran Thi Tuu**[a], **Dušan Loos**[b], and **Viktor Sutoris**[a]

[a] Department of Organic Chemistry, Komensky University,
CS-842 15 Bratislava, Czechoslovakia

[b] Institute of Chemistry, Komensky University,
CS-842 15 Bratislava, Czechoslovakia

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The C = O stretching frequencies of *E*-3-(2-*R*-vinyl)-2-benzothiazolinones (**1a**–**1p**) were measured in CCl_4 and $CHCl_3$ and correlated with σ, σ^+ and σ^* substituent constants. The $\nu(C=O)$ vs $\sigma^*(R)$ correlation was compared to an analogical relationship obtained with 3-*R*-2-benzothiazolinones (**2**). The electronic structure and geometry of compounds was investigated by CNDO/2 and PCILO methods. The results of both the spectral and theoretical studies showed for *E*-3-(2-*R*-vinyl)-2-benzothiazolinones a preference of the "N—C-*s-cis*" conformation (**3**), in which the substituent effects are transmitted to the C = O group very efficiently. The transmission factor for the CH = CH group was determined according to the definition of *Jaffé*. The role of inductive effects, delocalization of the nitrogen lone-pair electrons as well as the through-space interaction between the C = O and C = C bonds is discussed in terms of transmission mechanism and structural properties.

[Keywords: E-3-(2-R-vinyl)-2-benzothiazolinones; Infrared spectra; Conformation; Substituent effects; CNDO/2; PCILO]

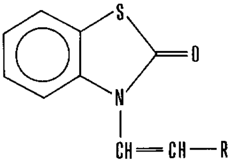
Infrarotspektren und theoretische Untersuchungen von E-3-(2-R-vinyl)-2-benzothiazolinonen

Es wurden die C = O-Streckfrequenzen von *E*-3-(2-*R*-vinyl)-2-benzothiazolinonen (**1a**—**1p**) in CCl_4 und $CHCl_3$ gemessen und mit σ-, σ^+- und σ^*-Substitutionskonstanten korreliert. Die $\nu(C=O)$-σ^*-Korrelation wurde mit einer analogen Beziehung für 3-*R*-Benzothiazolinonen (**2**) verglichen. Die elektronische Struktur und die Geometrie der Verbindungen wurden mittels CNDO/2- und PCILO-Berechnungen untersucht. Es ergab sich dabei sowohl aus den spektroskopischen als auch aus den theoretischen Ergebnissen eine „N—C-*s-cis*"-Konformation (**3**) für die *E*-3-(2-*R*-vinyl)-2-benzothiazolinone, da dies eine günstige Geometrie zur Übermittlung von Substitutionseffekten zur

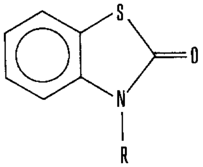
C=O-Gruppe ergibt. Der Transmissionsfaktor für die CH=CH-Gruppe wurde nach der Definition von *Jaffé* bestimmt. Die Rolle von induktiven Effekten, der Delokalisierung des freien Elektronenpaares am Stickstoff und der C=O....C=C-Wechselwirkungen durch den Raum wurde auf Basis von Transmissionsmechanismen und strukturellen Eigenschaften diskutiert.

Introduction

Previously [1] the C=O stretching frequencies of 3-substituted 2-benzothiazolinones were investigated. The correlation analysis and mutual comparison of spectral data enabled to determine or predict the fine structure and conformation of several compounds, which generally possess significant biological activity.



1a – 1p



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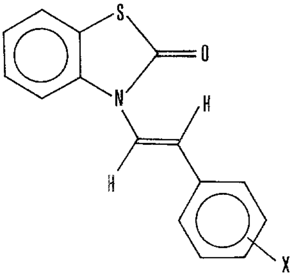
Recently [2] *E*-3-(2-*R*-vinyl)-2-benzothiazolinones (**1a–1p**) were synthesized and their herbicidal activity was studied. The series of compounds **1** in comparison with 3-*R*-2-benzothiazolinones (**2**) appeared to be suitable for investigation of conformation and transmission of electronic effects in the 2-benzothiazolinone system.

Continuing our previous investigations on substituent effects in heterocyclic systems containing endocyclic C=O groups [1, 3, 4] we decided to examine the electronic properties and geometry of *E*-3-(2-*R*-vinyl)-2-benzothiazolinones (**1**) by correlation analysis of infrared spectral data and theoretical methods. For this purpose the carbonyl stretching frequencies of tetrachloro- and trichloromethane solutions of compounds **1a–1p** were measured and correlated with substituent constants. For representative structures of compounds **1** and **2** (i.e. *R* = C_6H_5) charge densities and *Wiberg* indices were calculated by the CNDO/2 method with standard parametrization [5] using interatomic distances published in [6]. For calculation of the optimal geometry of compounds the PCILO method with standard parametrization was used



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[7–10]. The quasi-planar conformations **3** and **4** of compound **1e** ($R = C_6H_5$) as the structures with minimal total energy were obtained by rotating the linear part of molecule around the axis of N—C and C — *R* bonds by rotational angles α and β respectively.

Experimental

The preparation and some properties of compounds **1a–1p** are described [2]. The infrared spectra of CCl_4 and $CHCl_3$ solutions in the region of 1 800–1 600 cm^{-1} were recorded on a Perkin-Elmer 567 grating spectrophotometer at room temperature using NaCl cells 0.1, 1.0 and 5.0 mm thickness. The concentration of the measured solutions were chosen to give absorptions between 70%–75%. The spectra of *E*-3-(2-phenylvinyl)-2-benzothiazolinone were taken under the same conditions in *n*-heptane solutions. Peak positions were determined by averaging the results of three measurements and are believed to be accurate to ± 0.5 cm^{-1}. The instrument calibration was verified by using water vapor and indene standard spectra.

Results and Discussion

The configuration *E* (i.e. *trans*) with respect to the plane of C = C bond of 3-(2-*R*-vinyl)-2-benzothiazolinones (**1a–1p**) was determined [2] on the basis of intensive infrared absorption band in the region of 960–930 cm^{-1} corresponding to out-of plane deformation vibration of CH = CH.

The characteristic infrared spectral data measured for **1a–1p** are given in Table 1. In the region of 1 706–1 639 cm^{-1} two absorption bands can be observed. The solvent effect on the position of these bands in the case of *E*-3-(2-phenylvinyl)-2-benzothiazolinone (**1e**) is clearly documented in Table 2. It is evident that the higher frequency band is influenced by the solvent very markedly and consequently was assigned to the stretching vibration of the carbonyl group. A significant solvent effect on the

Table 1. *Characteristic infrared spectral data (in cm^{-1}) and substituent constants for E-3-(2-R-vinyl)-2-benzothiazolinones of type* **1**

Compound	*R*[a]	CCl$_4$		CHCl$_3$		$\sigma(X)$[b]	$\sigma^+(X)$[c]	$\sigma^*(R)$[b]
		ν(C=O)	ν(C=C)	ν(C=O)	ν(C=C)			
1 a	2,4-(O*Me*)$_2$*Ph*	1 679.5	1 642.0	1 679.5	1 639.0	− 0.54	− 1.56	—
1 b	2-O*MePh*	1 699.0	1 649.0	1 682.5	1 648.0	− 0.27	− 0.78	0.42
1 c	2-*Fu*	1 698.0	1 650.0	1 683.5	1 652.5	− 0.10[d]	− 0.51[d]	—
1 d	3,4-O$_2$CH$_2$*Ph*	1 701.0	—[e]	1 681.5	1 647.5	− 0.16	—	—
1 e	*Ph*	1 700.5	1 645.0	1 684.5	1 644.0	0.00	0.00	0.60
1 f	2-Cl*Ph*	1 703.0	1 643.0	1 685.0	1 643.0	0.23	0.11	0.75
1 g	3,4-Cl$_2$*Ph*	1 705.5	1 648.0	1 687.0	1 646.0	0.60	0.51	—
1 h	2-NO$_2$*Ph*	1 701.0	1 646.0	1 687.5	1 645.0	0.78	0.79	—
1 i	3-NO$_2$*Ph*	1 699.5	—[e]	1 686.5	1 645.5	0.71	0.67	—
1 j	4-NO$_2$*Ph*	1 704.5	1 644.0	1 688.5	1 644.5	0.78	0.79	1.14
1 k	*Ph*CH=CH	1 697.0	1 639.0	1 683.5	1 639.0	—	—	—
1 l	4-Cl*Ph*	1 702.0	1 647.0	1 684.5	1 645.0	0.23	0.11	0.75
1 m	4-N*Me*$_2$*Ph*	1 697.0	—[e]	1 678.5	1 644.0	− 0.83	− 1.70	0.16
1 n	2-O*MePh*	1 700.0	1 641.5	1 681.0	1 642.0	− 0.27	− 0.78	0.42
1 o	3-*Py*	1 702.0	1 644.0	1 686.5	1 644.5	0.62[f]	—	—
1 p	5-(4-*MePh*)-2-*Fu*	1 695.0	1 650.5	1 681.5	1 650.0	− 0.17[g]	− 0.61[g]	—

[a] *Ph* phenyl, *Me* methyl, *Fu* furyl, *Py* pyridyl

[b] Taken from [11]

[c] Taken from [12]

[d] Taken from [13]

[e] The absorption band was not observed

[f] Taken from [14]

[g] Calculated according to equations derived on the basis of general formula published in [15]

Table 2. *Solvent effect of characteristic infrared spectral data (in* cm^{-1}*) of E-3-(2-phenylvinyl)-2-benzothiazolinone* (**1e**)

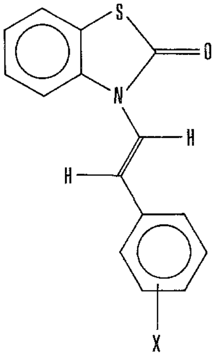
Solvent	$\nu(C=O)$	$\Delta\nu^a$	$\nu(C=C)$	$\Delta\nu^a$
n-heptane	1 709.5	0.0	1 647.5	0.0
CCl_4	1 700.5	9.0	1 646.0	1.5
$CHCl_3$	1 684.5	25.5	1 644.0	3.5

[a] $\Delta\nu = \nu_{n\text{-heptane}} - \nu_{\text{solvent}}$

$\nu(C=O)$ value ($\Delta\nu = 25\,cm^{-1}$, *n*-heptane → $CHCl_3$) shows that the carbonyl group in compounds **1** can be easily polarized and therefore it forms relatively strong intermolecular hydrogen bonds of the type $> C=O \ldots H—CCl_3$ with molecules of trichloromethane. On the other hand the less intensive lower frequency band of compound **1c** is practically insensitive to the solvent and thus can be attributed to the C =C stretching vibration of substituted vinyl moiety.

The occurence of a single $\nu(C=O)$ absorption band in the region of 1 706–1 679 cm^{-1} (in CCl_4 and $CHCl_3$) indicates that *E*-3-(2-*R*-vinyl)-2-benzothiazolinones preferably exist in one of two theoretically possible planar, or quasi-planar conformations: "N—C—*s-cis*" (**3**), or "N—C—*s-trans*" (**4**). To determine the preferred conformation of compounds **1** we tried to interpret the value of $\nu(C=O) = 1\,700 \cdot 5\,cm^{-1}$ for **1e** against $\sigma^*(CH=CH—C_6H_5) = 0.41$ (taken from [11]) using Eq. (1) for 3-*R*-2-benzothiazolinones (**2**) [1].

$$\nu(C=O) = 7.02\,\sigma^*(R) + 1\,690.3 \qquad (1)$$



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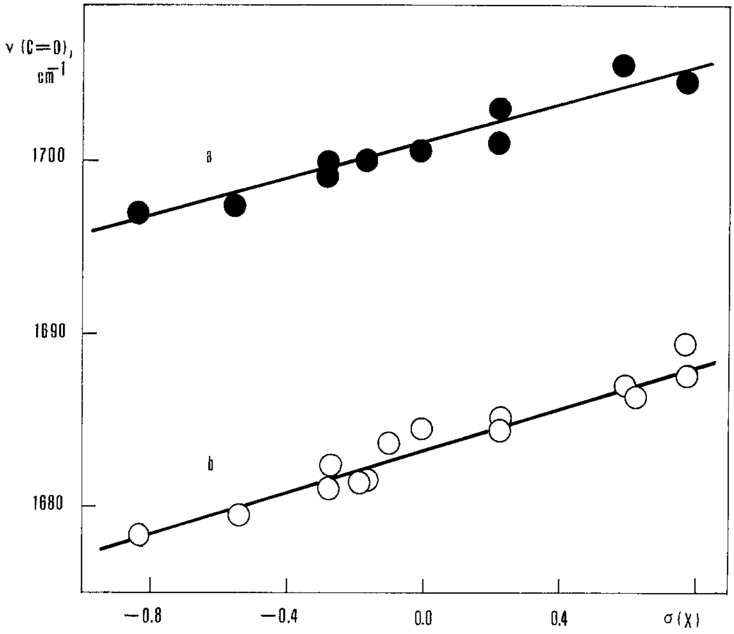

Fig. 1. The plot of $\nu(C=O)$ vs. $\sigma(X)$ for "N—C-*s-cis*"-*E*-3-(2-*R*-vinyl)-2-benzothiazolinones (**3**): *a* in CCl_4; *b* in $CHCl_3$

In this correlation a deviation was observed from the straight line of Eq. (1) by $7.5\,cm^{-1}$ to higher frequency values. Similar deviations were also found in the case of other compounds of series **1**. Such an increase of $\nu(C=O)$ values of compounds **1** compared to 3-*R*-2-benzothiazolinones (**2**) can be explained as the result of the through-space interaction (i.e. field effect) between the vibrating C=O and C=C groups, which operates only in the "*s-cis*" conformation shown in **3**. The results of the theoretical investigation by the PCILO method show a difference of $5\,kJ\,mol^{-1}$ between the energies of conformations **3** and **4** as well as the higher stability of **3**. The preference of conformation **3** can be documented well by comparison of isoenergetic curves in Fig. 2 constructed on the basis of the PCILO calculations. Moreover, it follows from Fig. 2 that the conformation **3** is not quite planar as the substituted vinyl group is twisted out of the plane of the 2-thiazolinone ring by 20°. The molecular diagram of conformation **3** containing values of charge densities and *Wiberg* indices calculated by CNDO/2 is illustrated in Fig. 3.

To investigate the transmission of electronic effects of substituents *R* and *X* in series **1** and **3**, respectively, the C=O stretching frequencies (in CCl_4 and $CHCl_3$) were correlated with *Hammett* σ, *Brown-Okamoto* σ^+

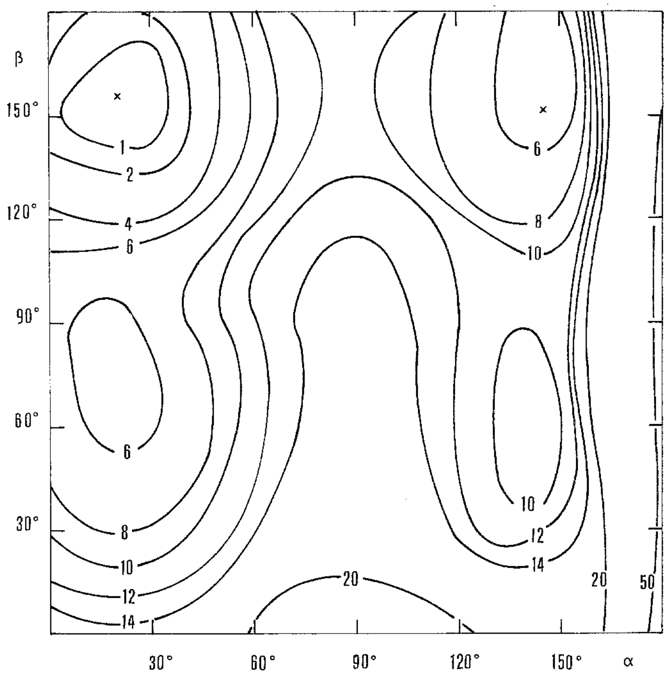

Fig. 2. Relationship between the total energy (in kJ mol^{-1}) of *E*-3-(2-phenylvinyl)-2-benzothiazolinone (**1e**) and rotational angles α and β

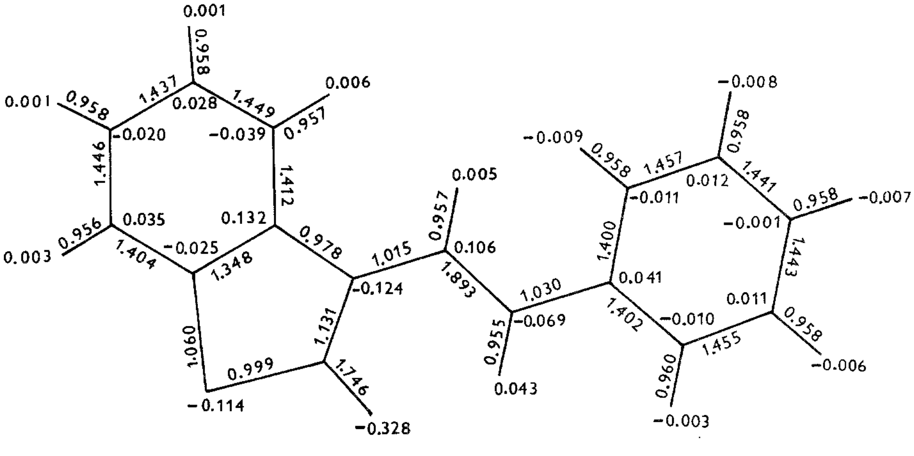

Fig. 3. Molecular diagram of "N—C-*s-cis*"-*E*-3-(2-phenylvinyl)-2-benzothiazolinone (3, $X = \mathrm{H}$)

Table 3. *Statistical treatment of linear correlations*

Series	Correlation	Solvent	n^a	r^b	ρ^c	q^d	s^e
3	$\nu(C=O)$ vs. $\sigma(X)$	$CHCl_3$	15	0.974	5.85 ± 0.38	1 683.2	0.72
3	$\nu(C=O)$ vs. $\sigma^+(X)$	$CHCl_3$	13	0.980	3.64 ± 0.22	1 684.7	0.65
3	$\nu(C=O)$ vs. $\sigma(X)$	CCl_4	10	0.967	5.47 ± 0.51	1 701.1	0.76
3	$\nu(C=O)$ vs. $\sigma^+(X)$	CCl_4	9	0.950	3.20 ± 0.40	1 702.2	1.00
1	$\nu(C=O)$ vs. $\sigma^*(R)$	CCl_4	7	0.973	7.81 ± 0.83	1 696.1	0.64

[a] Number of compounds used in correlation
[b] Correlation coefficient
[c] Slope
[d] Intercept
[e] Standard deviation

and *Taft* σ^* constants. The corresponding substituent constants are given in Table 1, the statistical results of correlations are summarized in Table 3 and the $\nu(C=O)$ vs. $\sigma(X)$ correlation is illustrated in Fig. 1. It follows from data in Table 3 that the $\nu(C=O)$ values of **3** provide (in both solvents, CCl_4 and $CHCl_3$) correlations nearly of the same significance with both $\sigma(X)$ and $\sigma^+(X)$ substituent constants. The slopes of correlations (ρ) are practically not influenced by solvent. This can be explained by the fact the nitrogen atom lone-pair electrons in compounds **3** are delocalized and cannot form intermolecular hydrogen bonds with $CHCl_3$ molecules. This delocalization as well as the increased polarity of the $C=O$ bond of 2-thiazolinone ring is clearly illustrated in Fig. 3 by the separation of charge densities and values of *Wiberg* indices. A similar effect was observed also in the case of other compounds [16–18] containing nitrogen atoms as a unity of the transmission system.

As the structure of compounds **1** differ from that of compounds **2** only by $CH=CH$, it is convenient to employ the $\nu(C=O)$ vs. $\sigma^*(R)$ correlations for data in CCl_4 (Fig. 4) to determine the transmission factor of inductive effects $\pi'^*(CH=CH)$ according to the definition of *Jaffé* [14]. Taking the values $\rho(1) = 7.81$ for series **1** and $\rho(2) = 7.02$ for series **2** we obtained

$$\pi'^*(CH=CH) = \frac{\rho(\mathbf{1})}{\rho(\mathbf{2})} = 1.11$$

The magnitude of $\pi'^*(CH=CH)$ indicates that the presence of $CH=CH$ in the side-chain of 3-substituted 2-benzothiazolinones does practically not represent any hindrance in the transmission of substituent effects from the benzene ring to the carbonyl group. The relatively high transmissive

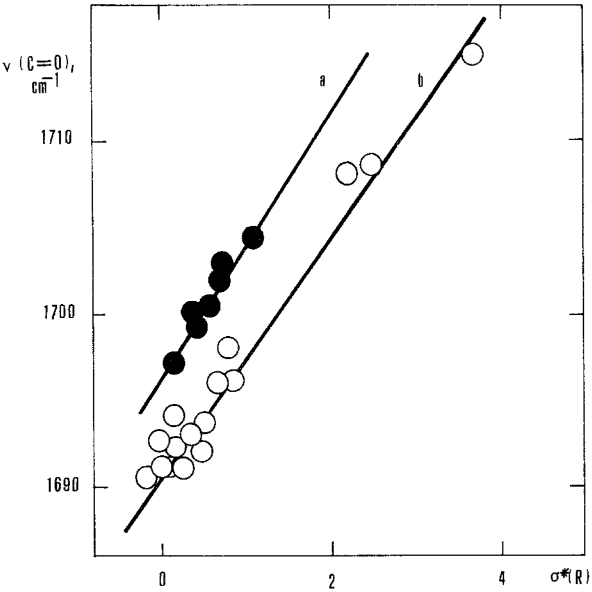

Fig. 4. Plot of $\nu(C=O)$ vs. $\sigma^*(R)$ in CCl_4 for: *a* *E*-3-(2-*R*-vinyl)-2-benzothiazolinones (**1**); *b* 3-*R*-2-benzothiazolinones (**2**)

efficiency to electronic effects in conformation **3** can be easily explained by the above discussed through-space interaction between the C=O and CH=CH groups as well as by delocalization of the nitrogen atom lone-pair electrons. The results of CNDO/2 calculations for representative structures of compounds **1** and **2** ($R = C_6H_5$) show that the presence of CH=CH in the side-chain has not a significant influence on the electronic structure of the 2-thiazolinone ring. Moreover, the separation of charge densities in Fig. 3 indicates that the inductive mechanism plays a significant role in transmission of substituent effects.

Acknowledgement

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