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Spectral characterisation of oxazol-5(4*H*)-ones containing a furan and/or benzene ring in conjugation with the azlactone system†

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Oxazol-5(4*H*)-ones containing a furan and/or benzene ring in conjugation with the azlactone system have been investigated by IR and NMR spectroscopy. The IR absorption bands in the region of the C=O stretching vibrations measured in $CHCl_3$ revealed a clear splitting due to Fermi resonance interaction. Compounds with a furan-2-yl substituent exert multilevel resonance when the first overtone of an in-plane scissoring deformation γ of the furan ring interacts with the fundamental carbonyl stretching mode. A correlation has been found between the wavenumbers of the C=N stretching vibration and the ^{13}C NMR chemical shifts of the carbon in the C=N bond. Spectral characterisation (UV-VIS, ^1H and ^{13}C NMR), configurations and optimum conformations of these compounds are given.

Keywords: oxazolones, IR, Fermi resonance, NMR, reactivity

Oxazol-5(4*H*)-ones with aromatic substituents in position 2- and 4- of the azlactone ring have attracted much attention since their first preparation at the end of 19th century.[1] Their potential use includes selective organic synthesis and several photochemical and photophysical applications because the energy of the *E*-isomer is found to be higher than the *Z*-isomer by more than 2 kcal mol^{-1} and this energy difference can be overcome only on a photochemical path.[2,3,4] Azlactone dyes have been used as optical sensors[5] and fluorescent indicators.[6,7]

Hydrolysis and the corresponding ring opening of oxazol-5(4*H*)-ones provides an useful reaction route to aromatic α-aminoacids, peptides and related compounds.[8] Alkaline hydrolysis of (*Z*)-4-benzylidene-2-phenyloxazol-5(4*H*)-ones leads in the first step to a ring opening according to Scheme 1. The reaction rate is controlled by substituent effects[9,10] and it is very sensitive to the structural changes on the aromatic system in the position 2- of the γ-lactone ring. The reaction is enhanced by electron acceptor substituents, yielding the reaction constant $\rho=0.74$ (at 304.4 K).[10] The kinetic coefficient remarkably correlates with the carbonyl stretching frequencies for a wide range of *o*-, *m*- and *p*-substituents. Studies of IR absorption bands of substituted (*Z*)-4-benzylidene-2-phenyl-oxazol-5(4*H*)-ones measured in $CHCl_3$ revealed a clear splitting due to the strong two-level Fermi resonance interaction between the C=O stretching mode and the first overtone of an out-of-plane deformation vibration mode of C–H group.[9,10]

Oxazol-5(4*H*)-ones with furan-2-yl substituents, prepared recently,[11] are intermediates to furan containing aminoacids and peptides.

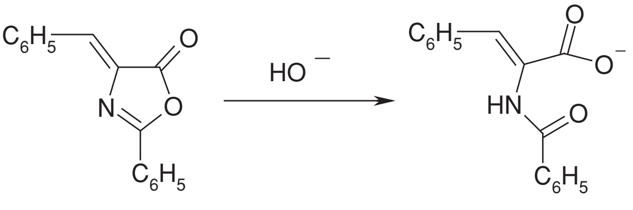
In the present work, we discuss structural and spectral properties of oxazol-5(4*H*)-ones with the furan ring in conjugation with the azlactone system. Six structural derivates with furan-2-yl, furan-2-ylmethylene and furan-2-ylvinyl substituents (Scheme 2) were investigated by AM1 method,[12] IR, ^1H NMR, ^{13}C NMR and UV-VIS spectroscopy in order to reveal the influence of furan ring on the spectral properties.

Results and discussion

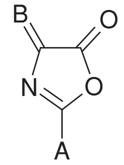
Configuration and conformation

Each of the compounds I–III may exist in one of the two configurations E or Z with respect to the exocyclic C=C double bond (Scheme 3). As confirmed previously by several authors,[2,9] the Z-configuration is more stable. Calculations of the Frank–Condon triplet of the azlactone molecule show the existence of a considerable excess of spin density on the methylenic C=C double bond at position 4 of the oxazolone ring – the so called "twisted triplet" state typical of most ethylenic compounds. Upon returning to the ground state, both Z and E isomers can be formed and the photochemical E-Z transformation from the triplet state is the main photoprocess.[2]

The second exocyclic C=C bond present in the structure of compounds Ia and Ib gives rise to two other configurations E and Z (Scheme 3). We investigated this geometric isomerism both theoretically and spectroscopically. AM1 total energy calculations of the molecules in vacuum are given in Table 1. ^1H NMR chemical shifts of ethylenic protons measured in $CDCl_3$ together with corresponding coupling constants are listed in Table 2. Both proton coupling constants (*J*=12–16 Hz) and calculations prove that the *E*-form is present. The large energetical difference between (*Z*,*Z*) and (*Z*,*E*) isomers (658 kJ mol^{-1} for Ia, 318 kJ mol^{-1} for Ib) has to be assigned to the steric hindrance because when the benzene residue is



Scheme 1



	A	B
Ia	Phenylvinyl	Phenylmethylene
Ib	Furan-2-ylvinyl	Phenylmethylene
IIa	2,4-Dichlorphenyl	Phenylmethylene
IIb	2,4-Dichlorphenyl	Furan-2-ylmethylene
IIIa	Furan-2-yl	Phenylmethylene
IIIb	Furan-2-yl	4-Metoxyphenylmethylene

Scheme 2

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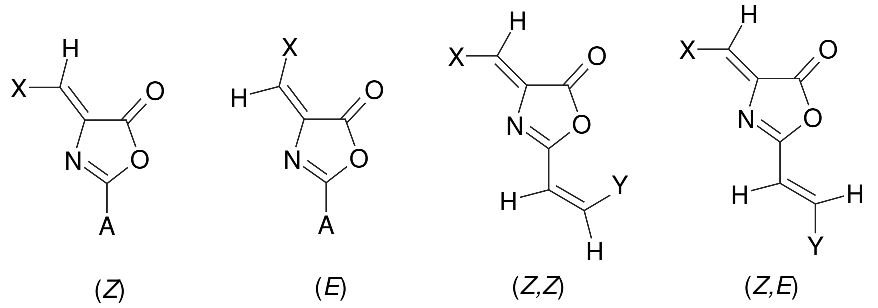
† This work is dedicated to Assoc. Prof. Dr. Alexander Perjéssy (1942–2003), *in memoriam.*



(*Z*) (*E*) (*Z,Z*) (*Z,E*)

Scheme 3

Table 1 Calculated AM1 energies (in kJ mol^{-1}) of the various configurations^a for compounds I, II and III in vacuum

Cmpd	–*E*	Cmpd.	–*E*
Ia(*Z,E*)	**3914.7**	**IIb(*Z*,1)**	**3062.0**
Ia(*Z,Z*)	3256.1	IIb(*Z*,2)	3060.3
Ib(*Z,E*,1)	3529.6	**IIIa(*Z*,1)**	**3095.5**
Ib(*Z,E*,2)	**3530.9**	IIIa(*Z*,2)	3093.9
Ib(*Z,Z*,1)	3211.4	**IIIb(*Z*,1)**	**3460.1**
Ib(*Z,Z*,2)	3455.2	IIIb(*Z*,2)	3458.5

^{a}For labelling see Schemes 3 and 4.

exchanged with the smaller furan molecule it results in the smaller energetical difference.

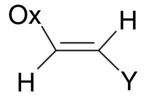
The presence of the conjugated system was further investigated by UV-VIS spectroscopy. Spectra measured in 70% (v/v) aqueous dioxane reveals an intensive absorption band in the region of 350–450 nm, log ε ~ 4 (Table 3). We observed that the presence of a furan molecule constitutes a significant shift in the peak positions. A shift of +20 nm is observed when the furan molecule is bonded in the position A and a shift of even +30 nm is observed when it is bonded in the position B (compare IIa and IIb or Ia and Ib). The extension of the conjugated system by one CH=CH produces a positive increase of +8 nm in the peak wavelength. This absorption band therefore belongs to a π–π* transition.

The presence of the furan ring in the structures Ib, IIb, IIIa and IIIb gives rise to conformation isomers because of the rotation of a heterocyclic ring along the C–C axis. These can be represented by structures **1** and **2** (Scheme 4). The spatial distance between the heterocyclic oxygen in the furan molecule and other heteroatoms in the oxazolone ring is not reflected in the energetical difference between isomers (less than 2 kJ mol^{-1}, see Table 1) and the rotation along the C–C axis is not sterically blocked.

Tables 4 and 5 show net charges, bond orders and bond lengths calculated by the AM1 method for the optimal configuration and the conformation of each derivative.

The structure of compounds I, II and III was also studied by ^{1}H and ^{13}C NMR spectroscopy. Individual chemical shifts were assigned by advanced correlation techniques.[13] Table 6 summarises the chemical shifts of the carbons forming the oxazol-5(4H)-one ring.

Table 2 ^{1}H NMR chemical shifts and corresponding coupling constants of vinyl group hygrogens in the structure of compounds Ia and Ib (Ox=oxazolone ring)

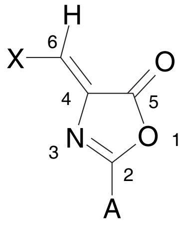


Cmpd	δ/ppm	J/Hz
Ia	6.90; 7.78	16.2
Ib	7.91; 8.10	12.2

Table 3 Wavelengths (in nm) of the peak maximum in 70% aqueous dioxane for compounds I–III

Cmpd.	λ_{max}
Ia	379
Ib	399
IIa	368
IIb	398
IIIa	391
IIIb	392

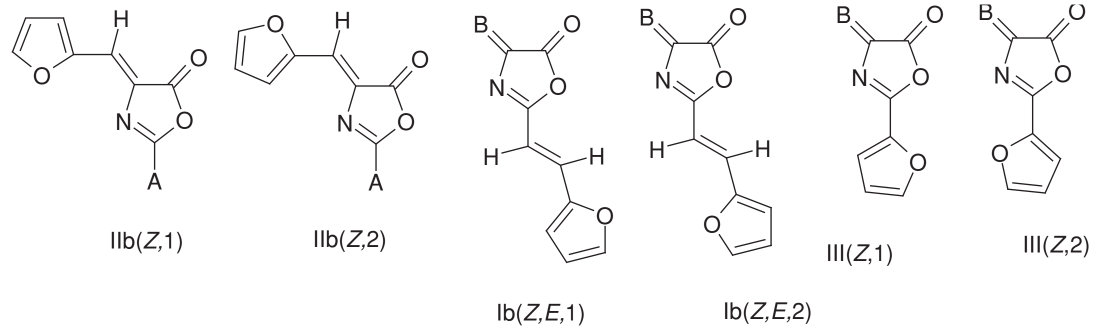
Table 4 Calculated values of the net atomic charges on atoms of oxazol-5(4*H*)-ones I–III



	c(O_1)	c(C_2)	c(N_3)	c(C_4)	c(C_5)
Ia	–0.235	0.126	–0.159	–0.147	0.308
Ib	–0.236	0.122	–0.151	–0.149	0.308
IIa	–0.212	0.135	–0.166	–0.148	0.307
IIb	–0.212	0.130	–0.142	–0.134	0.307
IIIa	–0.207	0.159	–0.152	–0.150	0.300
IIIb	–0.207	0.155	–0.151	–0.160	0.307

Table 5 Calculated bond orders (b) and bond lengths (l, in Å) of oxazol-5(4*H*)-ones I–III

	O_1-C_2		C_2-N_3		N_3-C_4		C_4-C_5		C_5-O_1	
	b	l	b	l	b	l	b	l	b	l
Ia	0.988	1.424	1.718	1.323	1.060	1.424	0.918	1.501	0.955	1.410
Ib	0.987	1.424	1.720	1.322	1.060	1.424	0.918	1.501	0.955	1.410
IIa	1.007	1.423	1.716	1.322	1.062	1.424	0.919	1.500	0.949	1.411
IIb	1.001	1.419	1.718	1.327	1.066	1.423	0.916	1.498	0.954	1.411
IIIa	1.004	1.418	1.708	1.324	1.059	1.425	0.918	1.501	0.951	1.413
IIIb	1.004	1.418	1.710	1.324	1.060	1.425	0.921	1.499	0.951	1.413



Scheme 4

Table 6 ^{13}C and ^{1}H NMR chemical shifts (in ppm) of compounds **I–III**[a]

Cmpd	C_2	C_4	C_5	C_6	H_6
Ia	163.3	133.6	167.2	131.3	7.27
Ib	166.2	133.8	167.2	132.5	6.92
IIa	160.3	132.9	166.4	(133.4)	7.37
IIb	159.9	129.7	166.1	120.1	7.39
IIIa	155.0	133.1	166.6	131.8	7.29
IIIb	154.2	141.3	166.9	132.1	7.27

[a] The value in brackets is of uncertain assignment.

Fundamental carbonyl stretching frequencies

Figure 1 illustrates the IR absorption bands of compounds I, II and III in the region of the C=O stretching vibration. It is clear that the incorporation of the furan molecule is pronounced in the multiple splitting and the shifting of the peak positions. The spectral characterisation after the mathematical separation of overlapping bands is given in Table 7.

The most intensive absorption band belongs to the fundamental C=O stretching vibration.[14,15] The peak position and its intensity are perturbed due to the Fermi resonance interaction between two or more vibrational levels with the same group of symmetry and close in energy.[16,17] A correction resulting from the perturbation theory using the analytical relations of Langseth and Lord (developed for the two-level interaction) and improved by Nyquist *et al.* for the three-level interaction[18] is given in Table 8. The interaction constant W and the shift in the peak position Δν both reflect the strength of the interaction. This analysis is insufficient in the case of compounds IIIa and IIIb where the four-level interaction has to be considered. Table 5 shows only the estimation of the unperturbed bands based on the three-level model.

In order to assign all vibrational levels involved in the Fermi resonance, we measured the IR spectras in the region of 940–810 cm^{-1} where the deformation vibration ω of the C–H group is present[9]. Spectral patterns are summarised in Table 9.

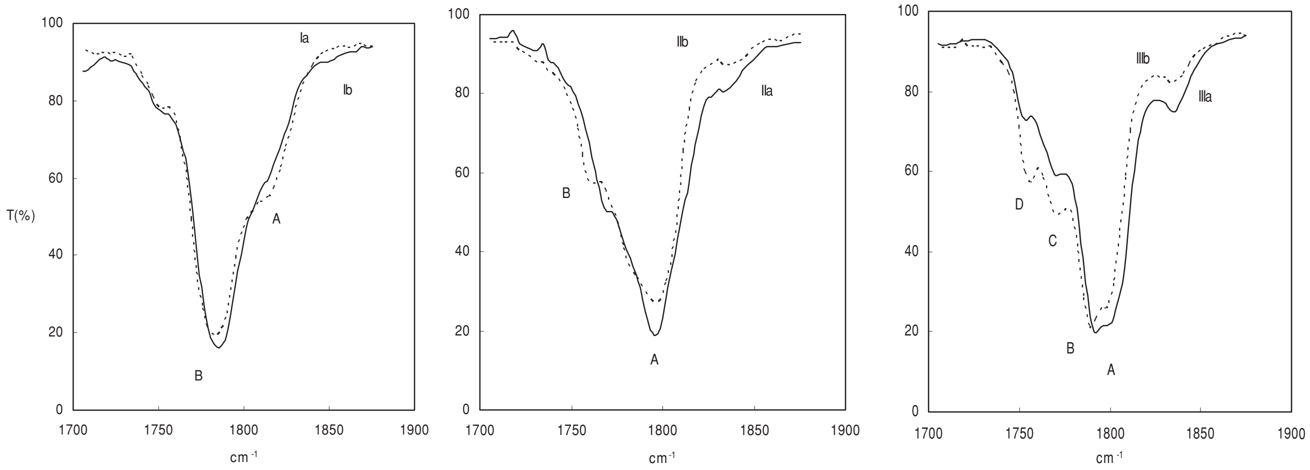


Fig. 1 IR absorption bands in the region of the carbonyl stretching vibration for compounds I–III in $CHCl_3$, c = 12 mmol dm^{-3}.

Table 7 IR absorption bands of oxazolones I–III in $CHCl_3$, c=0.012 mol dm^{-3} after the mathematical separation of overlapping bands, ν-peak wavenumber (cm^{-1}), A – absorbance in peak maximum, $\Delta\nu_{1/2}$ – half-peak width (cm^{-1}), ε – extinction coefficient ($dm^3mol^{-1}cm^{-1}$), I – integrated intensity ($dm^3mol^{-1}cm^2$).

	Branch A					Branch B					Branch C					Branch D				
Cmpd	ν	A	$\Delta\nu_{1/2}$	ε	I	ν	A	$\Delta\nu_{1/2}$	ε	I	ν	A	$\Delta\nu_{1/2}$	ε	I	ν	A	$\Delta\nu_{1/2}$	ε	I
Ia	1813.4	0.211	26.5	176	1.86	1783.0	0.629	24.8	524	5.18										
Ib	1812.0	0.161	25.4	134	1.36	1784.7	0.695	23.5	579	4.44										
IIa	1795.5	0.583	27.7	486	5.37	1768.2	0.172	21.7	143	1.24										
IIb	1794.4	0.512	25.3	427	4.31	1767.4	0.188	27.2	157	1.70										
IIIa	1799.8	0.437	24.3	364	3.54	1791.4	0.293	18.8	244	1.83	1769.3	0.154	14.7	128	0.755	1754.4	0.07	12.6	58.3	0.293
IIIb	1799.3	0.399	17.3	333	2.30	1788.1	0.438	14.0	365	2.04	1771.1	0.246	13.7	205	1.12	1756.2	0.168	12.5	140	0.700

Table 8 IR absorption bands of oxazol-5(4*H*)-ones I–III after the correction for the Fermi resonance, ν-wavenumber (cm^{-1}) , W-interaction coefficient (cm^{-1})

Cmpd.	$\nu_1^{0\,a}$	$\Delta\nu^b$	$\nu_2^{0\,c}$	$\nu_3^{0\,d}$	$\nu_4^{0\,e}$	W_{12}	W_{13}	W_{23}	W_{24}	W_{34}
Ia	1791.0	8.0	1805.4			13.4				
Ib	1790.2	5.5	1806.5			10.9				
IIa	1790.4	–5.1	1773.3			10.7				
IIb	1786.8	–7.6	1775.0			12.2				
IIIa	1792.6	–7.2	1787.7	1781.1		3.34	6.51	7.76		
IIIa			1791.9	1765.6	1760.4			9.11	6.18	5.35
IIIb	1789.3	–10	1785.1	1781.9		2.92	7.33	4.14		
IIIb			1786.1	1768.1	1764.2			7.42	8.87	4.21

[a] $\nu_1^0=\nu^0(C{=}O)$; [b] $\Delta\nu=\nu^0(C{=}O)-\nu(C{=}O,\text{perturbed})$; [c] $\nu_2^0=2\omega(C–H)$; [d] $\nu_3^0=\omega(C–H)+\gamma(\text{furan})$; [e] $\nu_4^0=2\gamma(\text{furan})$

Table 9 Wavenumbers (cm^{-1}) of the out-of-plane C–H deformation vibration ω, the in-plane deformation vibration of the bonded furan molecule γ and the stretching vibration β of the C=N group together with the corresponding extinction coefficients (dm^{3}mol^{-1}cm^{-1})

	ω(C–H)		γ(furan)		β(C=N)	
Cmpd	ν	ε	ν	ε	ν	ε
Ia	912.0	333			1655.2	933
Ib	912.0	278	886.4	82.6	1651.2	973
IIa	886.4	103			1654.4	796
IIb	883.2	139	876.8	139	1659.0	641
IIIa	918.4	369	886.4	97.9	1664.0	535
IIIb	918.4	303	886.4	92.2	1664.0	722

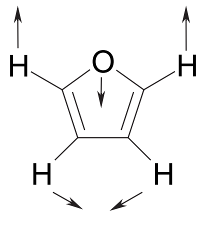
In the vibrational pattern of compounds I, we observed a broad single peak at ~910 cm^{-1}. Its first overtone, present at ~1820 cm^{-1}, is involved in the interaction with the fundamental stretching vibration of the carbonyl group. One can also see that there is a clear single peak present at ~880 cm^{-1} in the pattern of compound Ib but not in the IR spectrum of compound Ia (Fig. 2). This absorption band has to be attributed to one of the fundamental deformation vibrational modes of the bonded furan molecule.

Vibrational bands of the free furan molecule have been reported and assigned both in the vapour and in the liquid phase by several authors.[19–21] An intensive mode at 870.4 cm^{-1} was assigned to the in-plane scissoring deformation γ of the furan ring (group symmetry A_1, Scheme 5). Both the solvent effect and the presence of the bonded furan molecule in our case contribute to the observed shifting in the peak position of this vibration mode.

The vibrational spectrum of compound IIa reveals a single peak at ~880 cm^{-1}, belonging to the deformation vibration ω of the exocyclic methylene C–H group. Its first overtone is active in the Fermi resonance doublet with the C=O stretching mode.

The vibrational pattern of the compound IIb reveals a clear doublet present at ~875 cm^{-1}, representing the overlap of the out-of-plane C–H deformation vibration of the exocyclic methylene with the deformation vibration γ. Although only a 2-level Fermi resonance is observed, it can not be concluded that the vibrational overtone of the furan molecule bonded in the position B does not affect the vibration of the carbonyl group. Recent refinements of furfural carbonyl stretching bands clearly reveal that after the precise Fourier self-deconvolution, Fermi doublets can be splitted into quadruplets.[22]

The situation is more obvious in the case of compounds III. One can distinguish two single peaks – a stronger one at ~920 cm^{-1} belonging to the C–H deformation vibration of the methylene group and weaker one at ~880 cm^{-1} belonging to the in-plane deformation mode of the bonded furan molecule. From the situation given in Fig. 1 we conclude that both first overtones 2ω, 2γ and the combination mode γ+ω are active constituting the Fermi quadruplet with the fundamental C=O stretching mode. It was not possible for us to provide an exact calculation of wavenumbers before the interaction. Situations with multiple Fermi resonances were described recently by Belhayara *et al.* using the full quantum mechanical point of



Scheme 5

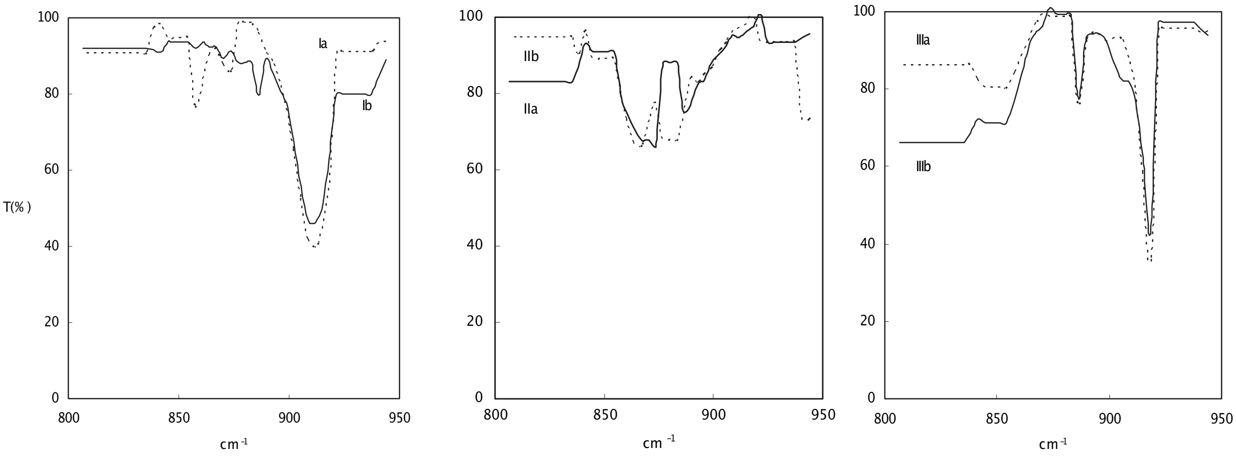


Fig. 2 IR absorption bands in the region of the C–H out-of-plane deformation vibration for compounds I–III in CHCl$_3$, c = 12 mmol dm^{-3}.

view.[23] They introduced a Fermi coupling parameter which can be extracted from IR spectral density widths with and without the Fermi coupling. They applied their model to the weak intermolecular interactions of H-bonding molecules. This approach normally requires the implementation of several algorithms and it is not yet accessible to average users.

Unperturbed carbonyl stretching frequencies for compounds I and II are given in Table 8. The presence of the furan ring in the B position lowers frequency of the C=O vibration down to 1786.8 cm^{-1} (compound IIb). We conclude that the furan ring in this position has a slightly stabilising effect on the carbonyl group (+M effect).

Fundamental stretching frequencies of the endocyclic C=N group

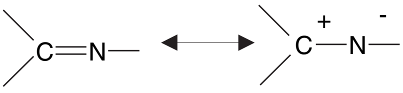
The stretching vibration of the endocyclic C=N group is present in the region of 1710–1620 cm^{-1}.[9] There is a single peak for each of the compounds but its frequency is strongly influenced by substituent effects (Table 9). The wavenumber of the C=N stretching vibration of (Z)-4-benzylidene-2-phenyloxazol-5(4H)-one is present at 1654.8 cm^{-1}.[9] The insertion of the furan ring into the position A (directly to the C=N group) is pronounced in the positive shift of +9.2 cm^{-1} and it may lead to the significant activation of the C=N bond (Scheme 6).

On the other hand, the presence of a furan-2-ylvinyl group results in a negative shift (–3.6 cm^{-1}). The effect of the furan ring on the C=N stretching vibration varies according to its position inside the molecule and therefore it reflects a π-electron conjugation inside the whole system (resonance effect). It decreases with the spatial distance – a lower positive shift (+4.2 cm^{-1}) is observed in the case of compound IIb.

Structure–spectra correlations

The statistical results for the linear correlations between the wavenumbers, the ^{13}C chemical shifts and the calculated AM1 bond parameters are summarised in Table 10. In these considerations we omitted frequencies of the C=O stretching vibrations of the compounds III. The value of the first two correlations is therefore lower comparing to the remaining five.

The correlation between the wavenumbers and the AM1 parameters is satisfactory, especially with the bond orders (Table 10). This agreement with our expectations is not surprising because the frequency of the stretching vibration reflects the strength of the chemical bond. The physical origin of the chemical shift is demonstrated by the successful correlation between the ^{13}C NMR shifts and the AM1 partial charges (Table 10).



Scheme 6

Table 10 Results of the linear correlation between the spectral parameters and the AM1 parameters for compounds I–III

y[a]	x	ρ	q	r[b]	n[c]	ex[d]
ν^0(C=O)	b(C=O)	574	583	0.587	4	IIIa,IIIb
ν^0(C=O)	δ(^{13}C=O)	–4.30	237×10^1	0.741	4	IIIa,IIIb
δ(^{13}C=O)	b(C=O)	–130	410	0.864	6	–
ν(C=N)	b(C=N)	–962	331×10^1	0.893	6	–
ν(C=N)	δ(^{13}C=N)	–1.08	183×10^1	0.956	6	–
δ(^{13}C=N)	b(C=N)	887	–136×10^1	0.933	6	–
δ(^{13}C=N)	c(C_2)	–287	199	0.952	6	–

[a] $y=\rho x+b$; [b] correlation coefficient; [c] number of independent variables; [d] compounds excluded from correlations.

The correlation between the wavenumbers of the C=N stretching vibration and the ^{13}C chemical shifts is statistically important (Fig. 3). When the chemical shift is decreased, the frequency of the vibration is increased. Therefore the reactivity of compounds III in the reactions located on the C=N group may be important. The reactivity of the C=N group has not been widely reported for oxazol-5(4H)-ones so far. However, the addition reactions of the isostructural 1,3-thiazolin-4-ones activated with fluorosubstituents in the position 2-, were described previously.[24] It has been shown that although the Diels–Alder reactions proceed preferentially via the exocyclic C=C double bond, the endocyclic C=N bond easily adds water or alcohols. Recently, K. Maekawa *et al.* reported a novel ring opening reaction of (Z)-2-methyl-4-arylmethyleneoxazol-5(4H)-ones with acylhydrazines.[25] They obtained 1,3,4-triazole substituted (Z)-α-dehydroaminoacids in high yields, irrespective of the substituents and the solvents examined. MM2 and PM5 calculations suggested that the triazole ring is constructed via the preferential nucleophilic addition of the hydrazino nitrogen to the C=N bond in the oxazolone ring.

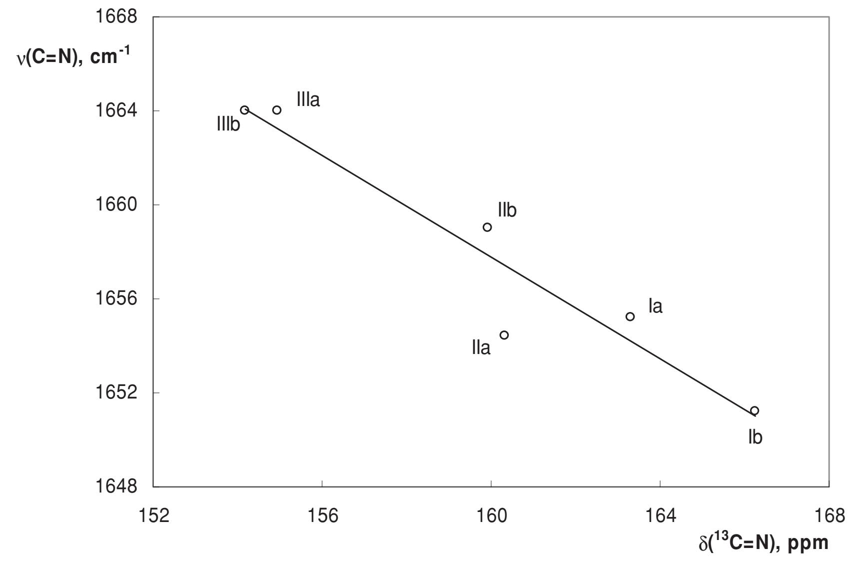
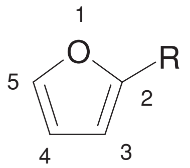


Fig. 3 Correlation between the ^{13}C NMR chemical shifts and the wavenumbers of the C=N stretching vibration for compounds I, II and III.

Table 11 Selected ^{13}C and ^{1}H NMR chemical shifts (in ppm) of the furan ring bonded in compounds I–III



Cmpd.	C_4	C_5	H_3	H_4	H_5
Ib	115.9	132.5	7.15(d)	7.32(dd)	7.77(d)
IIb	114.2	147.1	7.77(d)	6.80(dd)	7.82(d)
IIIa	112.7	147.8	7.52(d)	6.72(dd)	7.83(d)
IIIb	112.8	147.4	7.34(d)	6.71(dd)	7.80(d)

Conclusion

The main conclusions of this paper can be presented as follows:

(1) The presence of the conjugated π-electron system in the structure of compounds I–III was confirmed by the UV-VIS spectroscopy.

(2) The IR absorption patterns in the region of the carbonyl stretching frequency show a Fermi resonance interaction between the C=O fundamental stretching mode and the first overtone 2ω of the out-of-plane deformation vibration of the C–H group. The IR spectra of the compounds III reveal a four-level splitting. We assume that the first overtone of the in-plane deformation vibration γ of the furan molecule and the combination mode γ+ω contribute to the resonance.

(3) The correlation between the wavenumbers of the C=N stretching vibration and the ^{13}C NMR chemical shifts is statistically significant. We predict that due to the presence of the furan ring the endocyclic C=N group may be significantly activated in compounds III.

Experimental

(*Z*)-4-Arylidene-2-aryloxazol-5(4*H*)-ones (aryl = furan and/or benzene) were prepared by the cyclodehydration-condensation of the appropriate aldehyde and hippuric acid in dry acetic anhydride catalysed by acetate anion (Erlenmeyer-Plochl synthesis). Details of the experimental procedure can be found elsewhere.[1,3,9,11] The purity of the lactones was monitored by the IR and the NMR spectroscopy. Chemical shifts of the furan residue are listed in Table 11. Physical properties are given in Table 12.

IR measurements

The IR spectra of chloroform solutions of compounds I, II and III were recorded on a Zeiss Specord M-80 spectrometer at room temperature using NaCl cells of 0.01 cm thickness. The concentrations of compounds were 12.0 mmol dm^{-3}. $CHCl_3$ was of spectroscopic purity (Merck). The peak positions were referenced to the standard spectrum of polystyrene. The absorption intensities of the Fermi doublet components were determined after the mathematical deconvolution and the separation of overlapping bands. Curve analysis was carried out using a digital curve-fitting procedure.

NMR measurements

The ^{1}H and ^{13}C NMR spectra of compounds I, II and III were recorded for saturated $CDCl_3$ solutions at 300 K with a Bruker Avance DPX spectrometer working at 200.13 MHz for proton and 50.32 MHz for ^{13}C, respectively. The ^{1}H NMR chemical shifts were referenced to the signal of $CHCl_3$ ($\delta = 7.27$ ppm) and the ^{13}C NMR shifts to the signal of $CDCl_3$ ($\delta = 77.2$ ppm). In order to assign individual chemical shifts we employed experimental techniques DQF ^{1}H, ^{1}H COSY, APT, DEPT and ^{1}H, ^{13}C HMQC.[13]

Calculations

Optimum configurations and conformations were performed using the semiempirical AM1 Hamiltonian[12] within the program package HYPERCHEM 7.0.

Table 12 Physical properties of compounds I, II and III

Cmpd	M.p./°C	Recryst. solvent	Formula
Ia	130–132	Ethanol	$C_{18}H_{13}NO_2$
Ib	164–167	Benzene	$C_{16}H_{11}NO_3$
IIa	191–192	Benzene	$C_{16}H_9Cl_2NO_3$
IIb	208–210	Ethanol	$C_{14}H_7Cl_2NO_3$
IIIa	158–160	Ethanol	$C_{14}H_9NO_3$
IIIb	163–165	Ethanol	$C_{15}H_{11}NO_4$

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