

SHORT  
COMMUNICATIONS

## Stability of the *Z* and *E* Isomers of 4-Alkoxyethylidene- and 4-Halomethylidene-2-phenyl-4,5-dihydrooxazol-5-ones. Reassignment of Their Fundamental Vibration Frequencies

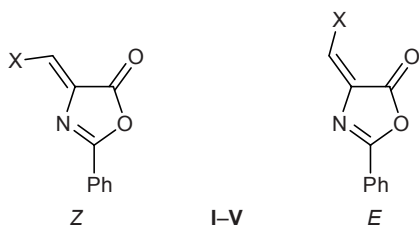
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The present communication reports on the results of quantum-chemical study on the stability and characteristic vibration frequencies of the *Z* and *E* isomers of 4-alkoxyethylidene- and 4-halomethylidene-2-phenyl-4,5-dihydrooxazol-5-ones **I–V**.



**I**, X = EtO; **II**, X = HO; **III**, X = Cl; **IV**, X = Br; **V**, X = I.

The calculations were performed with full geometry optimization using PC GAMESS program [1] from GAMESS (US) QC software package [2]. The accuracy of the optimization process was set simultaneously by two parameters, mean-square gradient (0.004 kcal/Å) and maximal gradient (0.012 kcal/Å). The Vosko–Wilk–Nusair (VWN#5) correlation potential was used in B3LYP calculations [3]. The accuracy in the calculation of vibrational frequencies of compounds **I–V** was limited only by positive shift of the Cartesian coordinates of atoms.

The results are summarized in table. The high energy of the  $\pi$ -contribution to the double C=C bond and the positive Hessian definition for the *Z* and *E* isomers of **I–V** suggest that these structures are kinetically stable. The *Z* configuration is more stable than *E* for all the examined compounds by 0.2–2.1 kcal/mol, regardless of the level of theory (semiempirical or

nonempirical), calculation procedure, and hybrid potential used. This is consistent with published data [4], according to which oxazolones **I–V** exist preferentially as *Z* isomers, except for two compounds of this series, chloro and bromo derivatives **III** and **IV**; the latter were isolated as less stable *E* isomers [5, 7]. The corresponding reaction mixtures contained both isomers: compound **III** crystallized by 67 wt % as *E* isomer [5], while compound **IV** gave two spots on thin-layer chromatogram [7]. The *E* isomers of **III** and **IV** are likely to be formed upon crystallization of their *Z/E*-isomer mixtures from nonpolar solvents (from tetrahydrofuran and diethyl ether–hexane, respectively). According to the calculations, nonpolar solvents favor crystallization of more polar *E* isomer ( $\mu$  3.97 and 3.67 D for the *E* and *Z* isomers, respectively; see table). The reverse pattern is observed upon isolation of the *Z* isomers of **I** (from propan-2-ol), **V** (from methylene chloride), and **II** (liquid substance). The kinetic stability of the isomers is confirmed by the fact that only irradiation of the preliminarily isolated *E* isomer of **III** in methylene chloride at  $\lambda$  310 nm (which corresponds to a photon energy of ~96 kcal; this value exceeds the energy of  $\pi$ -contribution of a classical double C=C bond, equal to 65.4 kcal in ethylene [8]) over a period of three days leads to formation of an equilibrium mixture of the *Z* and *E* isomers (~1:1 as determined by  $^1\text{H}$  NMR spectroscopy from the intensity ratio of signals from the vinyl protons,  $\delta$  7.2 and 5.3 ppm for the *E* and *Z* isomers, respectively [5]).

Analysis of the calculated [B3LYP/6-31G(*d,p*)] modes and intensities of characteristic vibrations of the *Z* and *E* isomers of **I–V** showed that the strong band at

Energy differences ( $\Delta$ , kcal/mol), dipole moments ( $\mu$ , D), characteristic vibration frequencies<sup>a</sup> ( $\nu$ ,  $\text{cm}^{-1}$ ), and experimental IR frequencies of the Z and E isomers of oxazolones I–V, calculated at the B3LYP/6-31G(*d,p*) level

Parameter	I			II			III			IV		V		
	calcd.		exptl. <sup>b</sup>	calcd.		exptl. <sup>b</sup>	calcd.		exptl. <sup>c</sup>	calcd.		calcd. <sup>d</sup>		exptl. <sup>e</sup>
	Z	E		Z	E		Z	E		Z	E	Z	E	
$\Delta^f$	0	1.51	Z	0	1.68	Z	0	2.10 <sup>g</sup>	E	0	1.79	0	1.57	Z
$\mu$	3.41	4.06	–	2.56	3.94	–	3.10	3.97	–	3.13	3.67	2.78	2.79	–
$\nu(\text{C=O})^h$	1805	1811	1785	1812	1820	1780	1825	1828 (6.01) <sup>i</sup>	1815 s	1823	1820	1783	1766	1780
$\nu(\text{C=C})^h$	1670	1660	1675	1695	1685	–	1633	1634 (6.75) <sup>i</sup>	1657 s	1640	1632	1629	1619	1620
$\nu(\text{C=N})^h$	1558	1558	–	1560	1560	–	1550	1550 (2.08) <sup>i</sup>	1569 m	1550	1548	1507	1506	1535

<sup>a</sup> Scaling factor 0.855.

<sup>b</sup> The IR spectrum was recorded in KBr [5]; the Z configuration was determined on the basis of the X-ray diffraction data for the  $\beta$ -acetoxy derivative [4].

<sup>c</sup> The IR spectrum was recorded in  $\text{CH}_2\text{Cl}_2$  ( $d = 0.1$  mm); the E configuration was determined on the basis of the  $^1\text{H}$  NMR data [5].

<sup>d</sup> B3LYP/3-21G(*d,p*) calculations.

<sup>e</sup> The IR spectrum was recorded from film (neat); Z configuration was assigned on the basis of the data of [4].

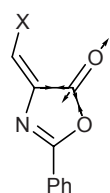
<sup>f</sup>  $\Delta = E(\text{E isomer}) - E(\text{Z isomer})$ , where E is the total energy with account taken of zero-point vibration energy.

<sup>g</sup>  $\Delta = 2.13$  {PBE96/6-31G(*d,p*) [6]}, 2.00 [6-31G(*d,p*)], 1.30 [3-21G(*d,p*)], 0.24 kcal/mol (MNDO).

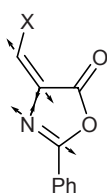
<sup>h</sup> Averaged calculated C=O, C=C, and C=N vibration modes for I–V, respectively: 0.23 (C), –0.14 (O); –0.15 ( $\text{C}^\beta$ ), 0.18 ( $\text{C}^\alpha$ ); 0.15 (C), –0.10 (N).

<sup>i</sup> Calculated intensity in  $\text{D}^2 \text{a.m.u.}^{-1} \text{A}^{-2}$ .

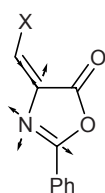
1650  $\text{cm}^{-1}$  [5] should be reassigned to stretching vibrations of the double C=C bond and that the low-frequency band at 1550  $\text{cm}^{-1}$  should be attributed to stretching vibrations of the five-membered heteroring (see table). The latter may be regarded as stretching vibration of the endocyclic double C=N bond, taking into account the maximal contribution thereto of the potential energy of the C=N bond.



$\nu(\text{C=O})$   
C=O, 42%  
C–C, 19%  
C–O, 18%



$\nu(\text{C=C})$   
C=C, 21%  
C=N, 11%  
C–N, 10%



$\nu_1 [\nu(\text{C=N})]$   
C=N, 20%  
C=C, 14%  
C–N, 11%

The  $\nu(\text{C=C})$  and  $\nu(\text{C=N})$  modes and the corresponding potential energy distributions (MNDO calculations), shown above for the E isomer of III (analogous patterns were observed for the other examined compounds), indicate considerable mixing of these vibrations. The stretching vibration spectrum of the oxazolone heteroring is characterized by the presence

of a single absorption band  $\nu_1^r$  at 1550  $\text{cm}^{-1}$  which is distant from the group of weak closely located bands in the region 1120–850  $\text{cm}^{-1}$ , belonging to four other ring vibrations ( $\nu_2^r$ – $\nu_5^r$ ).

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