

**(E-Z) ISOMERIZATION OF UNSATURATED NITRILES**

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Equilibrium data of the title isomerization of  $X-CH=CH-CN$  nitriles ( $X = Cl, CN, OR, SR$ ) have been measured, and the respective  $\Delta G$  values have been compared with the energy difference calculated by the CNDO/2 method.

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So far the (*E-Z*) equilibria of the unsaturated nitriles  $X-CH=CH-CN$  have been determined for  $X = CH_3$  (refs<sup>1-5</sup>);  $C_2H_5$  (ref.<sup>3</sup>);  $(CH_3)_2CH$  and  $(CH_3)_3C$  (ref.<sup>6</sup>);  $C_6H_5CH_2$  (refs<sup>2,6</sup>) and  $C_6H_5$  (refs<sup>6,7</sup>). For other substituents literature only gives two dates of percentage of *Z*-isomer of  $NC-CH=CH-CN$ : 50 at 383 K (ref.<sup>8</sup>) and 34 at 453 K (ref.<sup>9</sup>). Also known is the equilibrium of prototropic isomerization for  $X = ClCH_2$  (ref.<sup>10</sup>) and that of photoisomerization of 3-chloropropenenitrile<sup>4</sup> and 3-bromopropenenitrile<sup>11</sup>. Our previous paper<sup>12</sup> gave data of the isomerization of methyl 3-cyanopropenoate. Investigation<sup>7</sup> of temperature dependence of the isomerization equilibrium constant showed slight dependence for  $X=C_6H_5$ ; for  $X = CH_3$  it was found  $\Delta H = 0.71 \pm 0.5 \text{ kJ mol}^{-1}$  and  $\Delta S = -1.63 \text{ kJ mol}^{-1}$ ; standard heats of combustion of a series of aliphatic nitriles are also known<sup>13,14</sup>.

This communication deals with equilibrium data of the (*E-Z*) isomerization for the substituents  $X = Cl, CN, CH_3O, C_4H_9O, (CH_3)_2CHO, C_4H_9S$ . The found values of Gibbs energy (Table I) have been interpreted on the basis of the MO CNDO/2 calculation. With respect to experimental error (slight temperature dependence of the equilibria) and the temperature range accessible experimentally, the  $\Delta H$  values are not sufficiently reliable. In the case of the branched alkyl groups of 3-alkoxy- and 3-alkylthiopropenenitriles, the equilibrium content of the (*Z*)-isomers was found to increase with sterical demands. This dependence was observed in isomerization of 1-alkoxypropenes<sup>15,16</sup> and was explained by entropy effects on position of the equilibrium. For the non-branched alkyl groups (Table I) the equilibrium data of 3-alkoxypropenenitriles differ but little, which indicates predominance of one conformer in the series of non-branched alkyl groups. Table II gives electronic energy values of the unsaturated nitriles calculated by the CNDO/2 procedure, and Table III gives a comparison with  $\Delta G_{453}$  values.

The calculated energy difference  $-5.0 \text{ kJ mol}^{-1}$  between the isomeric 1,2-dicyanoethenes can be interpreted as a difference of bicentric interactions given in Eq.

(1). Denoted are the substantial differences of the bicentric interactions ( $Z-E$ ) of the identically numbered atoms, positive sign being used for antibonding interaction. In all, it can be concluded that the two isomers have close energies due to compensation of antibonding interactions.

The overall energy difference of the 3-chloropropenenitrile isomers is  $0.1 \text{ kJ mol}^{-1}$  according to the calculation with  $sp$ -basis. The main bicentric interactions are given in Eq. (2); the decisive component cannot be determined, and no significant change in bond strength is manifested to which we could ascribe changes in delocalization in systems of the two isomers. In the case of the substituents  $X = \text{CH}_3, \text{OCH}_3, \text{SCH}_3$ , low-energy conformation had to be found first. The energy difference between  $ap$  and  $sp$  conformations of  $\text{C}=\text{C}-\text{C}-\text{H}$  bonds was calculated for  $X = \text{CH}_3$  (Eqs (3) and (4) give the more significant interactions,  $\sum_{6,7}$  means sum of  $\text{C}\cdots\text{C}$  and  $\text{C}\cdots\text{H}$  interactions). Rotation barriers around  $\text{H}_3\text{C}-\text{C}=\text{C}$  bond in 2-butenitriles are known<sup>17,18</sup> from microwave spectra ( $8.8$  and  $5.8 \text{ kJ mol}^{-1}$  for the ( $E$ )- and ( $Z$ )-isomers, respectively, in gas phase). According to the calculations, predominant conformation of the both 2-butenitrile isomers (and propene, too) has a hydrogen atom synperiplanar to double bond. If stabilizing factors to the individual conformations are analyzed, at first, with the ( $E$ )-isomer (Scheme 3), then the predominance of  $sp$ -conformation can be due to interaction of two hydrogen atoms of the methyl group with carbon ( $20.2 \text{ kJ mol}^{-1}$ ) as compared with that of one hydrogen atom in  $sp$ -conformation ( $16.5 \text{ kJ mol}^{-1}$ ). In addition,  $sp$ -position of the ( $Z$ )-isomer exhibits further interactions which, however, are compensated by a changed  $=\text{C}-\text{CH}_3$  bond strength. In  $ap$ -position of hydrogen atom, the interactions of two remaining hydrogen atoms of  $\text{CH}_3$  group of the ( $Z$ )-isomer are negligible. With respect to approximately equal energy differences of the two conformers ( $4.9$  and  $5.5 \text{ kJ mol}^{-1}$  with the ( $E$ )- and ( $Z$ )-isomer, respectively), the equilibrium should

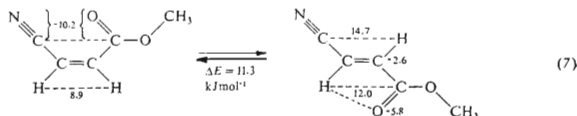
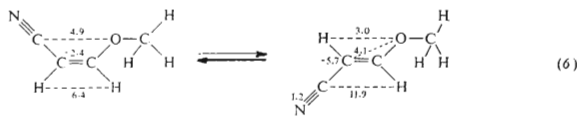
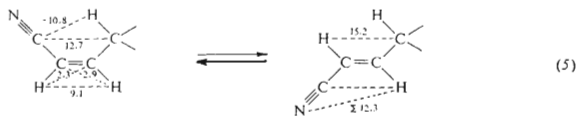
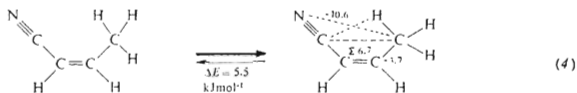
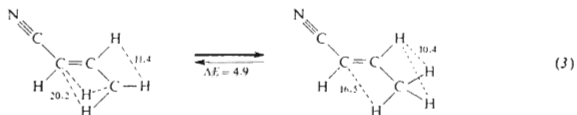
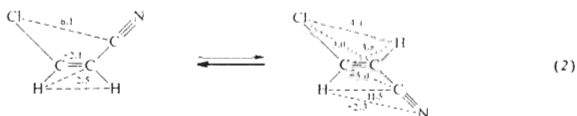
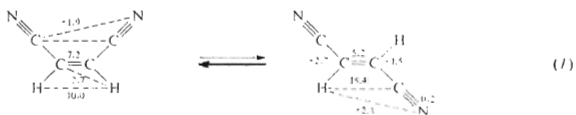
TABLE I

Results of isomerization of nitriles  $\text{X}-\text{CH}=\text{CH}-\text{CN}$  (453 K, chlorobenzene, catalysis by iodine)

X	% ( $Z$ )-isomer	$K(Z/E)$	$\Delta G, \text{ kJ mol}^{-1}$
Cl	$61.3 \pm 0.5$	$1.54 \pm 0.04$	$-1.62$
CN	$50 \pm 1$	$1.0 \pm 0.04$	$0.0$
$\text{CH}_3\text{O}$	$36 \pm 2$	$0.56 \pm 0.05$	$2.18$
$\text{C}_4\text{H}_9\text{O}$	$40 \pm 2$	$0.67 \pm 0.05$	$-1.45$
$(\text{CH}_3)_2\text{CHO}$	$59 \pm 3$	$1.44 \pm 0.16$	$-0.4$
$\text{C}_4\text{H}_9\text{S}$	$53 \pm 2$	$1.33 \pm 0.12$	$-0.46$
$(\text{CH}_3)_3\text{CS}^a$	$66 \pm 1$	$1.94 \pm 0.4$	$-2.5$
$\text{COOCH}_3$	$89.2 \pm 0.5^b$	$8.25$	$-8.3$

<sup>a</sup> The equilibrium was only approached from the side of the ( $E$ )-isomer; <sup>b</sup> 473 K, 1,4-dioxane<sup>12</sup>.

not be influenced by conformation of CH<sub>3</sub> group. The higher bonding energy of (Z)-isomer of 2-butenitrile, which causes its predominance in the equilibrium (the calculated energy difference is 6.9 kJ mol<sup>-1</sup>), is due to different interactions in Eq. (5).



Particularly the bonding interaction  $\text{NC}\cdots\text{H}-\text{CH}_2$  in the (*Z*)-isomer makes itself felt.

The calculated optimum conformation of 3-methoxypropenenitrile has the  $\text{C}=\text{C}-\text{O}-\text{CH}_3$  dihedral angle about  $120^\circ$ . Although distribution of torsion vibration is not known, it can be presumed that the (*E*)-isomer enjoys free rotation around  $=\text{C}-\text{O}$  bond up to  $\pm 150^\circ$  from antiperiplanar position (at room temperature), whereas that of the (*Z*)-isomer is restricted to  $\pm 100^\circ$ , which would affect the entropy value. According to calculations, the two isomers should differ in extent of conjugation.

TABLE II

The energy values calculated by MO CNDO/2 for the unsaturated nitriles ( $\text{kJ mol}^{-1}$ )

Isomer	Part		$\Delta E$
	monocentric	bicentric	
1,2-Dicyanoethene			
<i>Z</i>	3 985.8	-15 917.7	-11 931.9
<i>E</i>	3 986.3	-15 913.2	-11 926.9
<i>Z-E</i>	-0.5	- 4.5	- 5.0
3-Chloropropenenitrile <i>sp</i> -basis			
<i>Z</i>	2 883.0	-11 418.7	- 8 535.7
<i>E</i>	2 880.2	-11 415.8	- 8 535.6
<i>Z-E</i>	2.8	- 2.9	- 0.1
2-Butenenitrile ( <i>sp</i> -conformation)			
<i>Z</i>	3 613.4	-15 763.5	-12 150.1
<i>E</i>	3 612.6	-15 755.9	-12 143.2
<i>Z-E</i>	0.7	- 7.6	- 6.9
3-Methoxypropenenitrile (optimum conformation)			
<i>Z</i>	4 209.4	-17 289.2	-13 079.8
<i>E</i>	4 206.2	-17 283.8	-13 077.6
<i>Z-E</i>	3.2	- 5.4	- 2.2
3-Methylbutiropenenitrile			
<i>Z</i>	3 758.5	-15 494.2	-11 735.7
<i>E</i>	3 756.5	-15 492.4	-11 735.9
<i>Z-E</i>	2.0	- 1.8	0.2

TABLE III

Comparison of  $\Delta E$  (*Z*-*E*) and  $\Delta G_{453}$  values for nitriles  $X-\text{CH}=\text{CH}-\text{CN}$  ( $\text{kJ mol}^{-1}$ )

X	$\Delta E$	$\Delta G_{453}$	$\Delta E - \Delta G_{453}$
Cl	-0.1	-1.6	1.5
CN	-5.0	0	-5.0
OCH <sub>3</sub>	-2.2	2.2	-4.4
SCH <sub>3</sub>	0.2	-0.4 <sup>a</sup>	0.6
CH <sub>3</sub>	-6.9	-1.4 <sup>b</sup>	-5.5
CO <sub>2</sub> CH <sub>3</sub>	-11.2	-8.3	-2.9

<sup>a</sup> The data for  $X = \text{SC}_4\text{H}_9$ ; <sup>b</sup>  $\Delta H_{f,298}^0 = -6.7 \text{ kJ mol}^{-1}$  (ref.<sup>13</sup>).

If the calculated optimum conformation of 3-methoxypropenenitrile is compared with literature<sup>19</sup> data for methoxythene (for which electron diffraction measurements at 473 K indicate an equilibrium of 64% *s-cis* and 36% *gauche* conformation with 80–110° angle), then the comparison indicates a suppression of the *s-cis* form on substitution with nitrile group in either isomer. In (*Z*)-1-alkoxypropene, refs<sup>20,21</sup> only presume *s-trans* i.e. antiperiplanar conformation.

Calculation in *sp*-basis for 3-methylthiopropenenitrile indicates the optimum conformation with *ap*-orientation between CH<sub>3</sub> group and C=C bond, the both isomers having, besides, another energy minimum in *sc* region (which is higher by 2.6 kJ mol<sup>-1</sup> with the (*E*)-isomer), and the energy difference of 9 kJ mol<sup>-1</sup> corresponds to a possible free rotation of CH<sub>3</sub>S group. The situation is analogous to the (*Z*)-isomer, the rotation only being restricted to the angles up to  $\pm 150^\circ$  from *ap*-position. The energy comparisons of the two isomers were based on calculations of the antiperiplanar conformations, the result being 0.2 kJ mol<sup>-1</sup> in favour of (*E*)-isomer (Eq. (6)). In the case of methyl 3-cyanopropenoate, planar C=C—C=O conformations were only presumed: both the calculation and comparison with conformations of other esters confirmed, as the most favourable arrangement, *sp*-conformation between OCH<sub>3</sub> and C=O groups and *sp*-conformation of the segment C=C—C=O. The higher stability of the (*Z*)-isomer is due, first of all, to attractive interaction between the groups C=O...C $\equiv$ N, the difference being decreased by higher bond energy of the series of bonds in the (*E*)-isomer (Eq. (7)).

## EXPERIMENTAL

### Preparation of the Substances

Structure of the (*E*)- and (*Z*)-isomers was assigned on the basis of literature data<sup>11,22</sup>; the melting points were determined with a Boetius apparatus (GDR).

Maleic acid dinitrile was prepared by isomerization<sup>9,23</sup> of fumaric acid dinitrile<sup>24</sup>, the isomers were separated by preparative gas chromatography (10% Apiezon on Chromaton, 2.5 m column, 200°C). (*E*)-Isomer m.p. 101°C, b.p. 187°C/100 kPa; (*Z*)-isomer b.p. 120°C/2.7 kPa.

(*E*)- and (*Z*)-3-Chloropropenenitriles were prepared from isomeric 3-chloropropenoic acids<sup>25</sup> or by pyrolysis<sup>22</sup> of 2-acetoxy-3-chloropropenenitrile at 540°C giving a 1 : 1 *E/Z* mixture of 33% 3-chloropropenenitrile besides 28% 2-chloropropenenitrile. (*E*)-Isomer m.p. 45°C (diethyl ether), b.p. 118°C/100 kPa; (*Z*)-isomer b.p. 145–146°C/100 kPa.

Reaction of (*Z*)-3-chloropropenenitrile with sodium methoxide in methanol<sup>22</sup> at –20°C gave 75% yield of a *Z/E* 90/10% mixture of 3-methoxypropenenitriles; the same reaction of (*E*)-3-chloropropenenitrile gave 90% yield of a *E/Z* 95/5% mixture of 3-methoxypropenenitriles. The isomers were separated by preparative GC (3 m column with 10% Apiezon on Chromaton N, 180°C), (*Z*)-isomer b.p. 129–130°C/12.5 kPa, (*E*)-isomer 115°C/13 kPa. Similarly, with 95% retention of configuration, we prepared (*E*)-3-butoxypropenenitrile b.p. 139.5–140°C/7 kPa 93%, (*Z*)-isomer b.p. 151–152°C/7.5 kPa 85%. For C<sub>7</sub>H<sub>11</sub>NO (125.2) calculated: 67.1% C, 8.8% H; found: 67.0% C, 9.0% H.

Reaction with sodium 2-propoxide in 1 : 2 mixture of 2-propanol and diethyl ether at –35°C converted (*E*)-3-chloropropenenitrile into *E/Z* mixture 67/33% of 3-isopropoxypropenenitriles (total yield 35%), the (*Z*)-isomer being converted into *E/Z* mixture 70/30% (total yield 5%). Separation by preparative GC gave the (*Z*)-isomer with b.p. 140–141°C/12 kPa, whereas the (*E*)-isomer could only be enriched to a 76% mixture boiling at 132–134°C/12 kPa.

(*E*)- and (*Z*)-3-Butylthiopropenenitriles were prepared by reaction of 2 g (23 mmol) of the respective isomer of 3-chloropropenenitrile with 2.05 g (43 mmol) butanethiol in 60 ml diethyl ether and 2.35 g triethylamine at 0°C; after two days the reaction mixture was filtered and distilled. For C<sub>7</sub>H<sub>11</sub>NS (141.2) calculated: 59.5% C, 7.8% H, 9.9% N, 22.7% S; found: 59.4% C, 7.9% H, 10.0% N for the (*Z*)-isomer (b.p. 68°C/13.3 Pa; yield 68%), and 59.1% C, 8.0% H, 22.9% S for the (*E*)-isomer (b.p. 133–134°C/1.6 kPa; yield 65%).

Similarly (*E*)-3-(tert-butylthio)propenenitrile was prepared; b.p. 112–113°C/1.6 kPa, yield 43%. Elemental analysis: 59.4% C, 8.1% H. The corresponding (*Z*)-isomer could not be prepared, the reaction mixture undergoing polymerization; GC showed two compounds, one peak corresponding to the (*E*)-isomer, the other to the (*Z*)-isomer (identical retention time with that of the isomerization product).

## Methods

The equilibria were followed at 180°C in thick-walled 0.1 ml ampoules (5% solutions in chlorobenzene) under argon, the temperature was maintained within  $\pm 0.3^\circ\text{C}$ ; catalyst — 1% iodine. The equilibria were approached from both sides (except for that of 3-(tert-butylthio)propenenitrile) and evaluated by calibration of surface areas. The CNDO/2 calculations were carried out by the described method<sup>26</sup>, the bond lengths were chosen on the basis of literature data for propenenitrile, saturated halogeno derivatives, ethers and sulphides<sup>27</sup> ( $10^{-10}$  m): C=C 1.34, =C—H 1.083, =C—CN 1.43, C≡N 1.16, =C—Cl 1.72, =C—OR 1.36, =C—SR 1.74, C—S 1.806, C—O 1.44. The angles in degrees: Cl—C=C and C=C—CN 122, C—O—C 107, C—S—C 104.5, C=C—S 125.9.

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