Experimental IR, and computational *ab initio* and DFT B3LYP studies on spectral and structural changes, caused by the conversion of methyl cyanoacetate into carbanion

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Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

Spectral and structural changes, caused by the conversion of methyl cyanoacetate molecule into carbanion, have been studied applying a combined IRS experimental/*ab initio*, DFT computational approach. A good agreement has been found between experimental and scaled B3LYP/6-31++G** vibrational frequencies; the relationship between the corresponding band intensities has been only qualitative. In agreement between theory and experiment, the conversion of methyl cyanoacetate into carbanion causes strong decreases in the cyano and carbonyl stretching frequencies (with 109 and 127 cm^{-1}, respectively), a dramatic integrated intensity increase (51.3 fold) of the cyano stretching band and other essential IRS changes. According to both steric and electronic structure computations, the carbonyl group is conjugated with the carbanionic center more strongly than the cyano group. Except the methyl group hydrogen atoms, the whole carbanion is planar.

Key words: IR spectra, *ab initio* HF, DFT B3LYP method, structure, methyl cyanoacetate, carbanion.

INTRODUCTION

Methyl cyanoacetate NC–CH$_2$–COOCH$_3$ was first prepared by Walden in the twenties of 20th century; the detailed description of this synthesis was reported in 1934 in the patent of I. G. Farbenindustrie [1]. Methyl cyanoacetate is used nowadays as precursor in industrial synthesis of pharmaceuticals, herbicides and fungicides, cyanoacrylic polymers, dies for leather and polyesters, etc. [2, 3] (and references therein).

Vibrational spectra of methyl cyanoacetate have repeatedly been studied [2–10]; a part of these studies has been related to real and possible conformers of the molecule [2–5, 6, 9, 10]. This problem has also been approached by computational methods: PCILO [8], *ab initio* HF/4-21G [9], HF/6-31 G [2], MP2/6-31 G, DFT B3LYP 6-31G* [3], VDZ and MP2/6-31++G** [10]. All the used methods have predicted both little energy differences between the conformers and low energy barriers of the corresponding conformational conversions.

The vibrational spectra or structure of the carbanion of methyl cyannoacetate have not been studied either experimentally or theoretically, so the aim of the present studies is: (a) to obtain data for the carbanion and (b) to compare them with those for the molecule. This comparison will make it possible to determine spectral and structural changes accompanying the conversion of methyl cyanoacetate molecule into carbanion, using both experimental and computational methods.

EXPERIMENTAL

Methyl cyanoacetate (Aldrich, spectroscopic purity grade) was used without any additional purification. Its carbanion was prepared by adding dimethyl sulfoxide (DMSO/ DMSO-d$_6$) solutions of the parent compound to excess of dry CD$_3$O$^-$Na$^+$ under argon, and collecting the clear carbanion solution with a syringe-filter. We prepared the sample of CD$_3$O$^-$Na$^+$ itself by reacting CD$_3$OD (Fluka, 99 at.% enrichment) with Na and evapo-rating the excess of methanol *in vacuo*. The methyl cyanoacetate reacted with CD$_3$O$^-$Na$^+$ to form the carbanion in DMSO/DMSO-d$_6$ promptly (within 1–2 min) and practically completely: no bands of the parent compound were seen in the spectra after metalation. The IR spectra were recorded on a Bruker IFS 113v and Tensor 27 Standard System FTIR spectrophotometers in a CaF$_2$ cell of 0.129 mm path length, at a resolution of 1 cm^{-1} and 64 scans.

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COMPUTATIONS

The *ab initio* force field computations (full optimization) of the studied species were performed using the GAMESS software [11] at the Hartree-Fock HF/6-31++G** level. The GAUSSIAN 98 program package [12] was used for the same procedure within the same basis set, but applying the Density Functional Theory (DFT). This theory was the groundwork of a series of cost-effective methods to approximate electron correlation effects [13]. We applied the B3LYP functional, which combined Becke's three-parameter nonlocal exchange with the correlation functional of Lee, Yang and Parr [14, 15], adopting a 6-31++G** basis set without any symmetry restrictions. For every structure, the stationary points found on the molecular potentional energy supersurfaces (PEHS) were characterized using the standard harmonic vibrational analysis. The absence of any irrational frequencies or negative eigenvalues in the second-derivative matrix confirmed that the stationary points corresponded to global minima on PEHS [13]. The use of 6-31++G** basis sets both in *ab initio* and in DFT computations has recently resulted in better or equally good structural predictions, compared with other basis sets both for molecules and for anions [16–20] (and references therein). No scaling in the ab initio or density functional theory force fields was done. A standard least-squares program was used to calculate the single-parameter linear regression indices.

RESULTS AND DISCUSSION

Conformational and energy analysis

The most stable conformations of the studied species are shown in Fig. 1. In these cases "s-cis" and "s-trans" indicate the co-position of the CN and CO groups. The energies of the studied species can be seen in Table 1. In a qualitative agreement with the results of earlier computations (see Introduction), the molecular conformer **1** is slightly more stable, by 1.10 kJ·mol⁻¹, than **2**. It is known [2, 4] that only the thermodynamically most stable **1** exists in the crystalline state; in the gas and liquid phase the methyl cyanoacetate exists as mixture of the two main conformers of similar energies **1** and **2** [2]. Reva *et al.* [10] have recently found on the basis of IR spectra of methyl cyanoacetate, isolated in low temperature inert gas matrices, that the results of the conformational cooling depend on:
  i) the nature of the matrix gas host;
  ii) the relative energies ΔE and the corresponding barriers;

  iii) the dipole moments of the conformers;
  iv) the temperature. For example, an increase in the temperature from 20 to 40 K results in a radical change of the conformational ratio [10].

According to our calculations (Table 1), the carbanion **3** is only by 0.57 kJ·mol⁻¹ more stable than **4**. The deprotonation energy of a given Broensted acid can be defined [18, 20] (and references therein) as $E^D = E^{corr.}$ (anion) $- E^{corr.}$ (molecule) (for the most stable conformers of these species). Georgieva and Velcheva have recently found that E^D's correlate fairly well with pKa values of Broensted acids, containing cyano or carbonyl groups, in DMSO solvent, according to Eqn. 1 [18]:

$$pKa \ (DMSO) = 0.11507 \ E^D \ (B3LYP/6\text{-}31\text{++}G^{**}) - 150.04 \qquad (1)$$

Table 1. Total energies E (in hartree) and differences between them ΔE (in kJ·mol⁻¹) of the species studied.

No.	Species	E (native)	E (corrected) [a]	ΔE [a, b]
1	Molecule s-trans 1	–360.642650	–360.553883	0
2	Molecule s-cis 2	–360.642134	–360.553463	1.10
3	Carbanion CH⁻ s-trans 3 [c]	–360.095170	–360.019854	1402.09
4	Carbanion CH⁻ s-cis 4 [c]	–360.094768	–360.019637	1402.66
5	Carbanion CH_2^- s-cis 5 [d]	–360.012041	–359.938965	1614.47
6	Carbanion CH_2^- s-trans 6 [d]	–360.011197	–359.938174	1616.54

[a] With corrections for zero-point vibrational energies (ZPVE).
[b] $\Delta E = E_n - E_1$. [c] Deprotonated in the methylene group.
[d] Deprotonated in the methyl group.

So, having in mind $E^{corr.}$ of **1** and **3** in Table 1, we can estimate pKa (DMSO) of methyl cyanoacetate to be near 11.3. Hence, this compound should be a moderately strong carbon acid, like dicyanomethane, 5,5-dimethylcyclohexane-1,3-dione and α-phenylsulfonyl acetophenone, whose pKa (DMSO) are 11.0, 11.2 and 11.4, respectively [21]. It was clear a priori that deprotonation in the methyl group of methyl cyanoacetate should be very disadvantageous. However, the data in Table 1 make it possible to estimate how much compound **5** is less stable than **3**. So, according to our calculations, **5** is by 213.37 kJ·mol⁻¹ less stable than **3**, i.e. (having in mind Eqn. 1) the deprotonation of methyl cyanoacetate in the methyl group should correspond to a very weak C–H acid, with pKa (DMSO) equal to 35.7. This hypothetic C–H "acid" should have a pKa by 24.4 units higher (or an acidity by 24.4 orders of magnitude lower) than that of methyl cyanoacetate.

Correlation analysis

Comparison of B3LYP/6-31++G** vibrational frequencies, calculated for the conformer **1** with those measured experimentally in DMSO/DMSO-d$_6$ solvent gave the following linear correlation (Eqn. 2):

$$\nu_{(exp.)} = 0.92771\nu_{(exp.)} + 72.2 \quad (cm^{-1}) \qquad (2)$$

Correlation coefficient R = 0.99986, Standard deviation S. D. = 13.82 cm^{-1}; Number of data points n = 15.

According to Jaffe's classification [22], this correlation is *excellent*, as 0.99 < R < 1.00. We shall use Eqn. 2 for correlational scaling of the theoretical vibrational frequencies of the species studied in this work. As it was stated in Alcolea's review article [23] (and references therein), use of scaling equations instead of scale factors gave better results, especially in the low-frequency region. Correlational scaling is still used nowadays [3, 17, 20, 24–29] (and references therein).
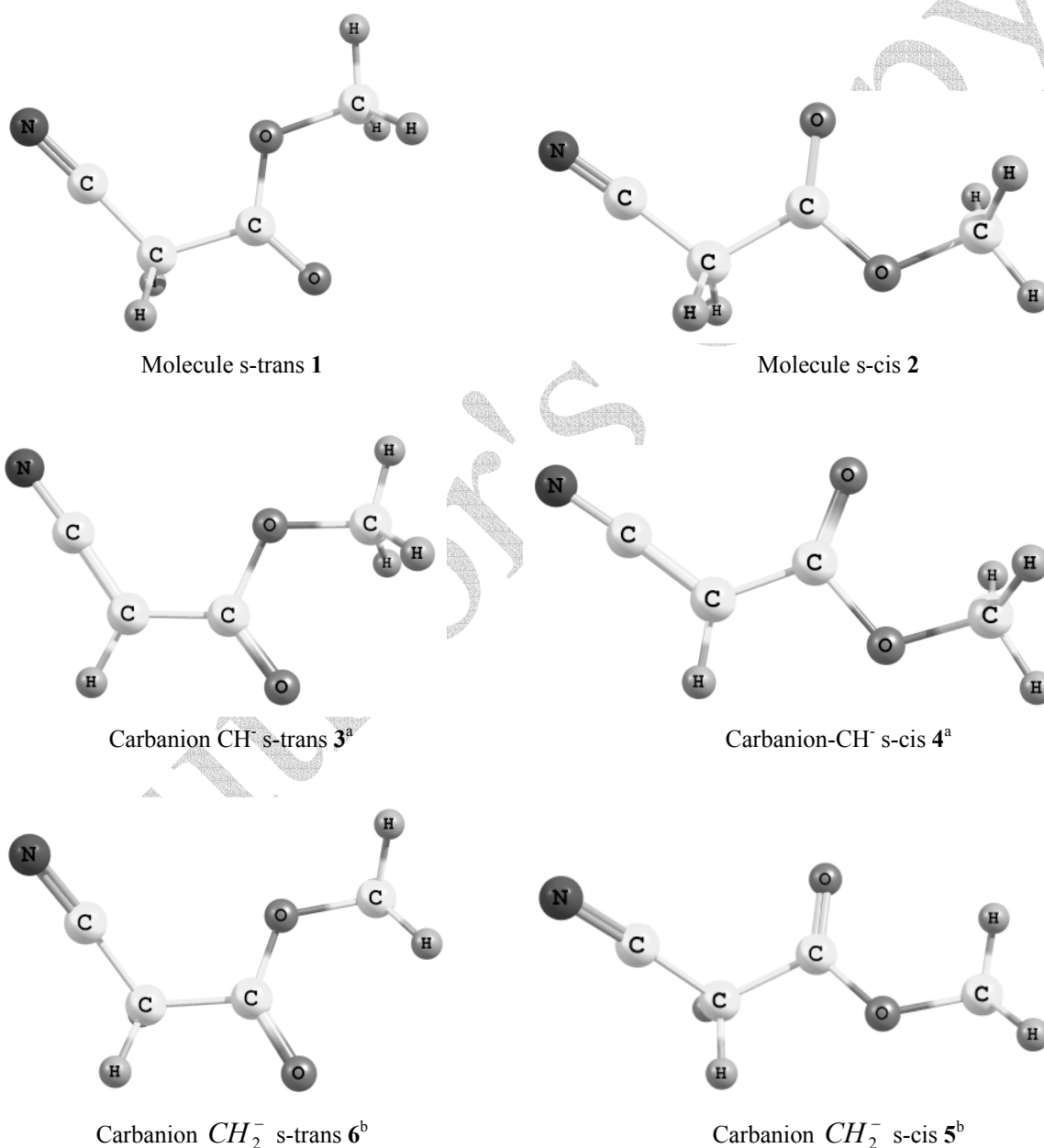

Molecule s-trans **1**

Molecule s-cis **2**

Carbanion CH$^-$ s-trans **3**[a]

Carbanion-CH$^-$ s-cis **4**[a]

Carbanion CH_2^- s-trans **6**[b]

Carbanion CH_2^- s-cis **5**[b]

Fig. 1. DFT/B3LYP 6-31++G** conformers of the molecule and carbanions of methylcyanoacetate. [a] Deprotonated in the methylene group. [b] Deprotonated in the methyl group.

Spectral analysis

Table 2 contains IRS data for the methyl cyano-acetate *molecule*. A good agreement between experimental and scaled theoretical frequencies can be seen there. The mean absolute deviation

$$m.a.d. = n^{-1} \sum_{i=1}^{n} \left| v^i_{theor} - v^i_{exp} \right|$$

is 8.7 cm^{-1}, a little bit lower (i.e. better value) than the interval of 9–20 cm^{-1}, typical for the DFT calculations for molecules containing cyano or carbonyl groups [20, 28–31] (and references therein). The approximate description of the vibrations in Table 2

is not far from those of the authors [2, 4]. The cyano stretching band shows no peculiarity: high $v_{C\equiv N}$ frequency and low $A_{C\equiv N}$ intensity, as the cyano group is not conjugated. As it can be expected, the stretching vibration of the carbonyl group is represented by a very strong band (see also Fig. 2). The various CH$_3$ and CH$_2$ bendings are listed below in Table 2 (Nos, 8–12, 14). A moderate band at 1211 cm^{-1} corresponds to the v^{as}_{COC} vibration in methyl cyanoacetate molecule. There are cases where this band is comparable in intensity to the $v_{C=O}$ one [32].

Table 2. Theoretical (B3LYP 6-31++G (d,p) and experimental (solvent DMSO/DMSO-d$_6$) IRS frequencies (cm^{-1}) and integrated intensities (km·mol^{-1}) of methyl cyanoacetate.

No	B3LYP 6-31++G (d, p)			Approximate description [c]	Experimental data [a]	
	v	v [b]	A		v	A
1	3186	3028	9.7	$v^{as}_{CH_3}$	3039[d]	2.0
2	3154	2998	13.9	$v^{as}_{CH_3}$	3012[d]	4.0
3	3104	2952	0.4	$v^{as}_{CH_3}$	2955	11.4
4	3071	2921	24.9	$v^{s}_{CH_3}$	2932[d]	4.8
5	3065	2916	3.5	$v^{s}_{CH_2}$	2897	1.8
6	2375	2275	5.6	$v_{C\equiv N}$	2256	3.0
7	1825	1766	236.8	$v_{C=O}$	1749	151.2
8	1500	1464	11.0	$\delta^{as}_{CH_3}$	–[e]	–
9	1489	1453	9.8	$\delta^{as}_{CH_3}$	1448	vw
10	1475	1441	13.9	$\delta^{as}_{CH_3}$	1439	12.2
11	1446	1413	19.8	$\delta^{sc}_{CH_2}$	1403	7.9
12	1364	1338	103.7	τ_{CH_2}, v_{CCC}, $\delta^{s}_{CH_3}$	1343	34.2
					1268[f]	m
13	1226	1209	291.2	v^{as}_{COC}, $\delta^{wag}_{CH_2}$, $\delta^{as}_{CH_3}$,	1211	55.0
14	1225	1209	3.2	$\delta^{rock}_{CH_2}$	1211	55.0
15	1200	1185	115.6	τ_{CH_3}, v_{COC}, $\delta^{wag}_{CH_2}$	1183	44.3
16 [g]	1174	1161	0.9	$\delta^{tw}_{CH_2}$	–[e]	–

[a] Measured after having decomposed the complex bands into components; relative intensity: m, moderate; vw, very weak. [b] Scaled, according to correlation equation 2. [c] Vibrational modes: υ, stretching; δ, in-plane bending; τ, torsion. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; rock, rocking; wag, wagging; tw, twisting. [d] Solvent CDCl$_3$. [e] We did not detect this band. [f] The origin of this band is not clear. [g] Followed by 14 lower-frequency vibrations.
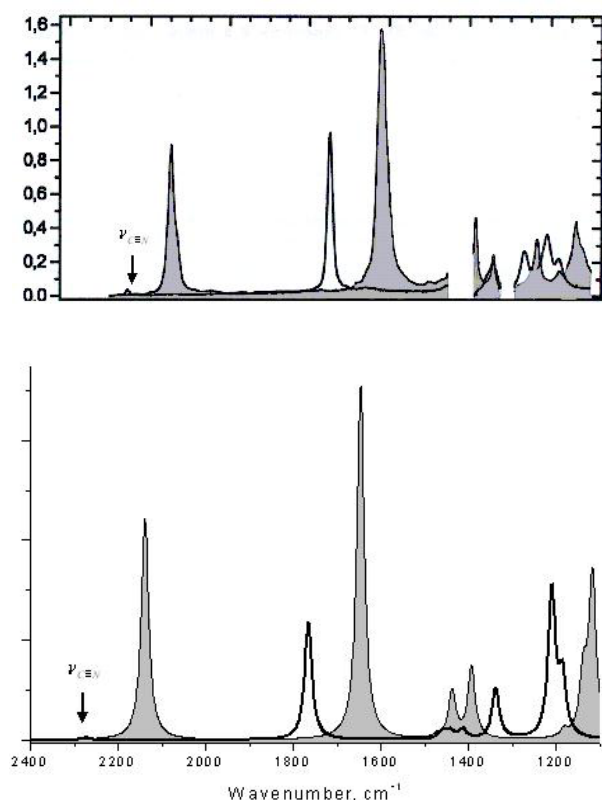
Fig. 2. Theoretical (bottom) and experimental (top) IR spectra of methyl cyanoacetate and its carbanion (solvent DMSO, counter ion Na$^+$, shaded).

We can see in Table 3 IRS data for the carbanion of methyl cyanoacetate. Like in the previous case, the agreement between experimental and scaled theoretical IRS frequencies is good. The main absolute deviation between them is only 8.1 cm^{-1}, lower than the corresponding interval of 9–25 cm^{-1}, typical for DFT calculations of frequencies for anions containing cyano or carbonyl groups [20, 28–31] (and references therein).

In agreement between theory and experiment, the conversion of methyl cyanoacetate into carbanion results in the following IR spectral changes (cf. Tables 2, 3 and Fig. 2).

- Strong decrease in $\nu_{C\equiv N}$: predicted 136 cm^{-1}, measured 109 cm^{-1}.
- Dramatic intensification of the corresponding IR band: calculated 79.0 fold measured 51.3 fold.
- Strong decrease in the $\nu_{C=O}$ frequency: predicted 119 cm^{-1}, measured 127 cm^{-1}.
- Increase in the intensity of the corresponding IR band: predicted 3.0 fold, measured 2.0 fold.
- Decrease in the ν_{COC}^{as} frequency: calculated 91 cm^{-1}, measured 56 cm^{-1}, as well as other IR spectral variations.

STRUCTURAL ANALYSIS

We did not found in the literature any experimental data on the *steric structure* of either methyl cyanoacetate or its carbanion. According to our calculations the conversion of the molecule into carbanion causes essential steric structure variations (Table 4), which take place *at* the carbanionic center and *next to* it. This rule is also valid for bond angles (Table 4).

Table 4. Selected B3LYP/6-31++G (d,p) bond lengths R (Å), bond angles A (degrees) and dihedral angles D (degrees) of methyl cyanoacetate and its carbanion.

Indices [a]	Molecule	Carbanion	Δ [b]
R (1,2)	1.16	1.18	0.02
R (2,3)	1.46	1.40	−0.06
R (3,4)	1.53	1.41	−0.12
R (4,5)	1.21	1.24	0.03
R (4,6)	1.35	1.42	0.07
R (6,7)	1.45	1.42	−0.03
A (1,2,3)	177.6	177.0	−0.6
A (2,3,4)	113.6	123.1	9.5
A (3,4,5)	126.0	130.7	4.7
A (5,4,6)	125.0	118.6	−6.4
A (4,6,7)	115.8	114.7	−1.1
D 3 (2,4,8)	121.8	180.0	58.2
D 4 (3,5,6)	180.0	180.0	0
D 4 (5,6,7)	0.0	−0.1	−0.1

[a] Atom numbering according to Scheme 1.
[b] Δ = Index (anion) – Index (molecule) (Å or degrees).

For example, $|\Delta R(C–CO)|$ is twice larger than $|\Delta R(C–CN)|$ $|\Delta R(C=O)|$, is also larger than $|\Delta R(C\equiv N)|$, so it seems that the carbonyl group is more strongly conjugated with the carbanionic center than the cyano group. The largest bond angle deviation ΔA corresponds to C3, to indicate the transformation of the tetrahedral CH2 group of the molecule into a trigonal –CH group in the carbanion. The analysis of the dihedral angle changes shows that except for the methyl group hydrogen atoms, the whole carbanion is planar (Table 4, cf. Scheme 1).
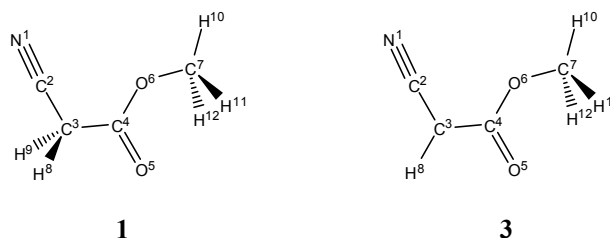
Scheme 1. Atom numbering of methyl cyanoacetate molecule **1** and its carbanion **3** within our both HF/and B3LYP/ 6-31++G** calculations.

Table 3. Theoretical (B3LYP++G(d,p)) and experimental (solvent DMSO/DMSO–d_6, counter ion Na$^+$) IRS frequencies (υ in cm^{-1}) and integrated intensities (A in km·mol^{-1}) of methyl cyanoacetate carbanion.

No.	B3LYP++G(d,p)				Experimental data [a]	
	υ	υ [b]	A	Approximate description [c]	υ	A
1	3203	3043	8.5	ν_{CH^-}	– [d]	–
2	3093	2942	57.7	$\nu_{CH_3}^{as}$	2945	vw
3	3065	2916	66.8	$\nu_{CH_3}^{as}$	2907	vw
4	3010	2865	120.8	$\nu_{CH_3}^{s}$	2840	vw
5	2228	2139	442.6	$\nu_{C\equiv N}$	2147	153.8
6	1698	1647	706.8	$\nu_{C=O}$	1622	299.1
7	1509	1472	6.5	$\nu_{CH_3}^{as}$	1469	6.2
8	1472	1438	89.7	$\delta_{CH_3}^{s}$	1440	m
9	1472	1438	3.93	$\delta_{CH_3}^{as}$	1440	m
10	1425	1394	143.7	$\delta_{CH_3}^{s}$, δ_{CH^-}	1389	24.2
					1239[e]	w
11	1197	1183	14.9	τ_{CH_3}, δ_{CH^-}, ν_{COC}	1185	4.1
12	1169	1157	0.3	τ_{CH_3}	– [d]	-
13	1149	1139	117.7	τ_{CH_3}, ν_{COC}, δ_{CH^-}	1135	47.8
14 [f]	1127	1118	322.9	ν_{COC}^{as}, δ_{CH^-}, τ_{CH_3}, ν_{CCC},	1127	30.7

[a] Measured after having decomposed the complex bands into components; relative intensity: m, moderate; vw, very weak. [b] Scaled, according to correlation equation 2 (Table 2). [c] Vibrational modes: ν, stretching; δ, in-plane bending; τ, torsion. Superscripts: s, symmetrical; as, asymmetrical. [d] These bands were not detected in the experimental spectrum. [e] The origin of this band is not clear. [f] Followed by 13 lower-frequency vibrations.

We shall demonstrate the changes in the *electronic structure* of methyl cyanoacetate molecule, caused by its conversion into carbanion, on the basis of data on bond orders and net electric charges. The bond order variations (Table 5) are in agreement with the corresponding bond length changes (shorter bonds → higher bond orders, cf. Table 4). The largest (in absolute values) bond order changes (Table 5, values in bold) take place again at and next to the carbanionic center. The changes $|\Delta P(3,4)|$ and $|\Delta P(4,5)|$ are larger than $|\Delta P(2,3)|$ and $|\Delta P(1,2)|$, respectively. So, we can say as above that according to the computations, the carbonyl group is conjugated with the carbanionic center more strongly than the cyano one.
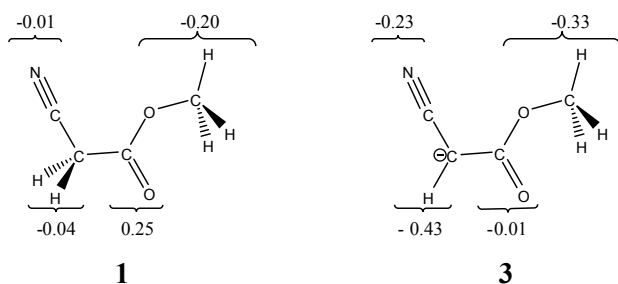
The net electric charges q_i of fragments of the molecule and carbanion of methyl cyanoacetate are shown in Scheme 2. The electric charge changes $\Delta q_i = q_i$(anion) – q_i(molecule) are usually quite informative to demonstrate the distribution of the new charge (carbanionic, azanionic, etc.) between individual fragments of anions [19, 33] (and references therein). According to the calculations (cf. Scheme 2), the anionic charge in the studied carbanion is distributed, as follows: 0.22, 0.26 and 0.13 e$^-$ are delocalized over the cyano, carbonyl and methoxy groups, respectively, and 0.39 e$^-$ of it remain localized in the carbanionic center. Δq(C=O) is larger than Δq(C≡N) i. e. the carbonyl group seems again to be better conjugated with the carbanionic center than the cyano one.

Table 5. *Ab initio* HF 6-31++G(d,p) bond orders *P* of methyl cyanoacetate molecule and carbanion.

Bonds [a]	Molecule	Carbanion	ΔP [b]
C^1≡N^2	2.89	2.82	–0.07
C^3–H^8	0.94	0.96	0.02
C^3–H^9	0.94	- [c]	– [c]
O^6–C^7	0.77	0.87	0.1
C^2–C^3	0.91	1.13	0.22
C^4–O^6	0.99	0.82	–0.17
C^3–C^4	0.95	1.34	0.39
C^4=O^5	1.84	1.62	–0.22
C^7–H^{10}	0.97	0.98	0.01
C^7–H^{11}	0.96	0.97	0.01
C^7–H^{12}	0.96	0.97	0.01

[a] Atom numbering according to Scheme 2. [b] $\Delta P = P_{anion} - P_{molecule}$. The largest $|\Delta P|$ values are given in bold. [c] There is no C^3–H^9 bond in the carbanion.

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Scheme 2. Natural Bond Orbital (NBO) net electric charges q_i over fragments of the most stable conformers of methyl cyanoacetate molecule **1** and carbanion **3**.

CONCLUSIONS

We found in this work a good agreement between experimental and B3LYP/6–31++G** data on the essential spectral changes, caused by the conversion of methyl cyanoacetate into the carbanion. So, we anticipate that the structural variations, computed by same method, should also be adequate.

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ЕКСПЕРИМЕНТАЛНИ ИЧ И ТЕОРЕТИЧНИ *AB INITIO* ХФ И ТФП B3LYP ИЗСЛЕДВАНИЯ НА СПЕКТРАЛНИТЕ И СТРУКТУРНИТЕ ПРОМЕНИ, ПРИЧИНЕНИ ОТ ПРЕВРЪЩАНЕТО НА МЕТИЛЦИАНОАЦЕТАТА В КАРБАНИОН

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(Резюме)

Спектралните и структурни промени, причинени от превръщането на метилцианоацетата в карбанион са изследвани с помощта на комбиниран ИЧ експериментален/*ab initio*, ТФП теоретичен подход. Установено е добро съответствие между експерименталните и скалираните B3LYP/6–31++G[**] вибрационни честоти; връзката между съответните интензивности на ИЧС ивици е само качествена. В съгласие между теория и експеримент, превръщането на метилцианоацетата в карбанион води до силно понижение на честотите на валентните трептения на циано- и на карбонилната групи (със 109 и 127 cm^{-1}, съответно), драстично повишение на интегралната интензивност (51.3 пъти) на вибрационната ивица на цианогрупата и други съществени промени в ИЧС спектър. В съгласие с изчислената пространствена и електронна структура, карбонилната група е спрегната по-здраво с карбанионния център в сравнение с цианогрупата. С изключение на водородните атоми на метиловата група, целият карбанион е планарен.