

## IR spectra and structure of 1,1,3,3-tetracyanopropane and its carbanions: experimental and quantum chemical study

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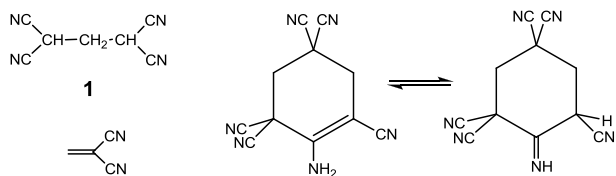
Dedicated to Acad. Dimiter Ivanov on the occasion of his 120<sup>th</sup> birth anniversary

A combined IR experimental/DFT computational approach has been applied to follow the spectral and structural changes, caused by the conversion of 1,1,3,3-tetracyanopropane in mono-, di-, and trianion. The conversion of molecule into carbanion has shown a weak effect on the cyano stretching band  $\nu(\text{C}\equiv\text{N})$  of cyanogroups remote of anionic center (down to  $13\text{ cm}^{-1}$ ) and strong on the cyano stretching band  $\nu(\text{C}\equiv\text{N})$  of cyanogroups which are directly bonded with anionic center (down to  $140\text{ cm}^{-1}$ ). The carbanionic charge is distributed mainly at anionic centre and cyanogroups which are directly bonded to it (overall  $0.85\text{ e}^-$ ). The conversion of the molecule into di- and trianion are pursued with stronger lowering of  $\nu(\text{C}\equiv\text{N})$  down to  $300\text{ cm}^{-1}$ . A very good agreement between experimental and theoretical data has been found. According to the computations the anionic charge formed by second and third step of deprotonation is distributed nearly uniformly over all fragments.

**Key words:** IR spectra, DFT B3LYP, structure, 1,1,3,3-tetracyanopropane, anion

### INTRODUCTION

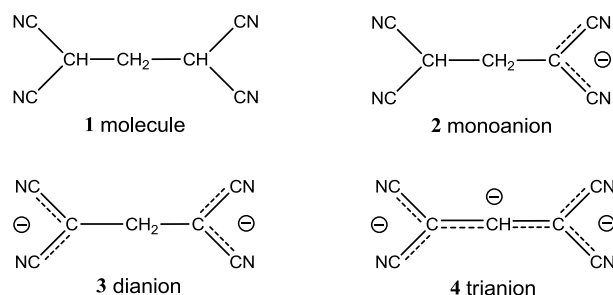
1,1,3,3-Tetracyanopropane (methylene-bis-malononitrile) **1** in Scheme 1 was synthesized for the first time by Diels as early as in 1922 [1] from formaldehyde and malononitrile, with vinylidene cyanide **2** (1,1-dicyanoetan) as intermediate [1-3].



**Scheme 1.** Methylene-bis-malononitrile **1** and some possible products of its decomposition.

Compound **1** and its derivatives undergo reaction of cyclo-dimerization (Michael-Thorpe) [2-5], leading to the formation of cyano-containing cyclohexane amines and imines (see Scheme 1) or decomposition to vinylidene cyanide ("reverse" Michael) [2]. There are complexes of **1** with transition metals such as Au and Pt [6,7]. A detailed study of the structure on **1** by IR, Raman, mass spectra and X-ray diffraction has been reported [8]. Although the structure, chemistry and covalent complexes of methylene-bis-malononitrile with

transition metals are studied, there are no data about its anions available in the literature.



**Scheme 2.** Methylene-bis-malononitrile **1** and its anions **2-4**.

Its mono- and dianion **2, 3** (Fig. 1) are clearly intermediates in many of the above reactions. The purpose of the present study is to generate the anions of methylene-bis-malono-nitrile and investigate their structure and IR spectra on the basis of experimental/DFT computational approach.

### EXPERIMENTAL

#### Synthesis of neutral compound

Malononitrile is highly reactive and polymerize on being kept. For this reason commercial malono-

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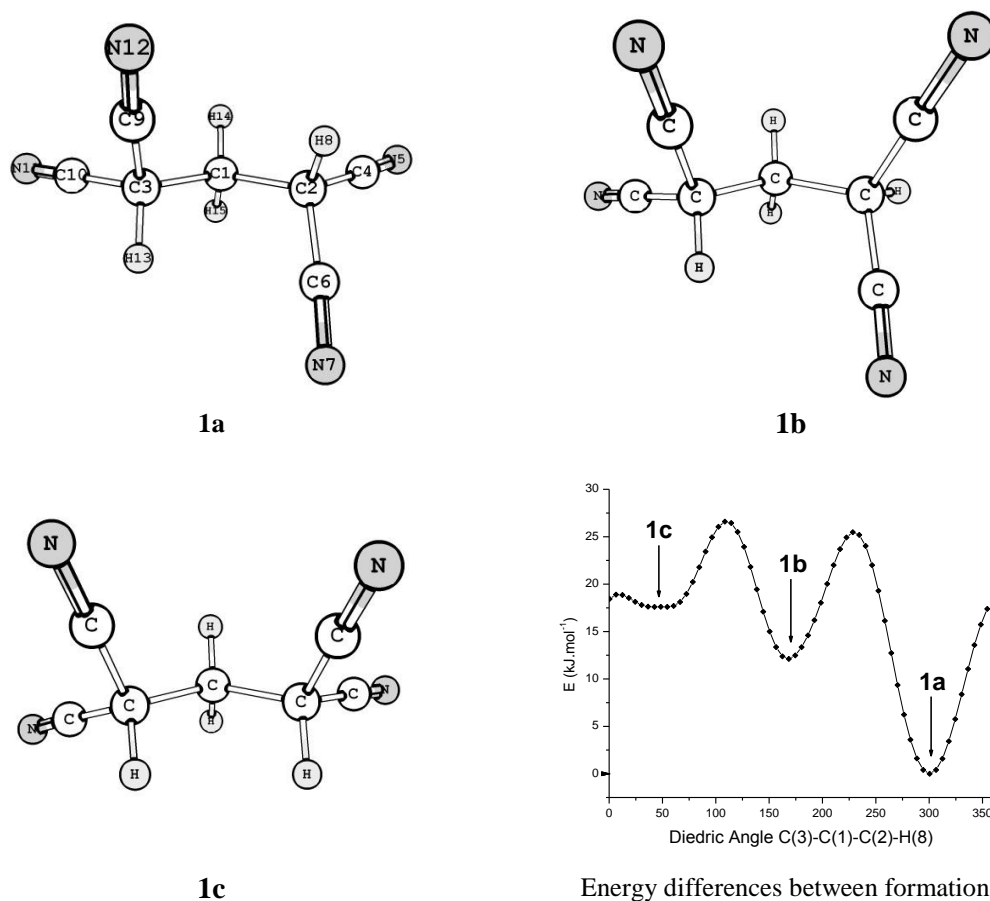
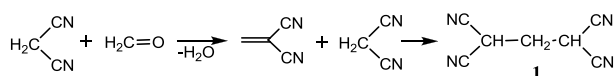


Fig. 1. Stability of conformers of methylene-bis-malononitrile **1**.

nitrile (Aldrich) was used in present study after purification by vacuum distillation. The resulting distillate was crystallized in colorless crystals of melting point 30°C. 1,1,3,3-Tetracyanopropane **1** was synthesized by modifying the method of Bell *et al.* [6] (Scheme 3).



Scheme 3. Synthesis of **1** by Bell *et al.* [6].

In a round bottom flask equipped with a stirrer and thermometer 7.5 ml 96% ethanol were mixed with 1.5 g (0.0227 mol) of purified malononitrile. The mixture was heated to 40°C and stirred until malononitrile was completely dissolved. The solution was cooled in ice bath to 10-12°C, and 0.86 ml (0.0144 mol) of 37% formaldehyde, and a few crystals of β-alanine as catalyst were added. The stirring was continued at this temperature, the solution became yellow (formation of vinylidene cyanide). When the solution became cloudy (app. 1

hour after the start) the reaction was stopped. 15 minutes after the crystallization started the mixture was filtered and washed several times with ice cold ethanol. The product was used without further purification. The product was dried and showed m. p. 132-135°C. The reaction is highly influenced by the temperature and stoichiometry and several adverse reactions such as polymerization and cyclo-dimerization to side products are possible to occur (Scheme 1).

#### Conversion of neutral compound into anions

The monoanion of methylene-bis-malononitrile (DMSO solution) was prepared by adding dimethyl sulfoxide solution of the parent compound to excess of dry CH<sub>3</sub>O<sup>-</sup> Na<sup>+</sup> under argon, stirring and collecting the clear anion solution with a syringe-filter. We prepared the sample of dry CH<sub>3</sub>O<sup>-</sup> Na<sup>+</sup> itself by reacting CH<sub>3</sub>OH with Na and evaporating the excess of methanol *in vacuo*. Methylene-bis-malononitrile **1** reacted with CH<sub>3</sub>O<sup>-</sup> Na<sup>+</sup> to form monoanion in DMSO promptly (within 1-2 min)

and practically completely: no bands of the parent compound were shown in the spectra after metalation. The IR spectra were recorded on Bruker Tensor 27 FTIR spectrometers in a CaF<sub>2</sub> cell of 0.129 mm path length, at a resolution of 1cm<sup>-1</sup> and 64 scans.

The dianion of the methylene-bis-malononitrile was prepared by reacting with dimsyl sodium (Sodium salt of dimethylsulfoxide). Dimsyl sodium was formed by reacting sodium metal with excess of DMSO. The solution of this reagent (excess) was added to the solution of the neutral compound **1** and transferred to IR cell, previously flushed with argon. The conversion was nearly complete. The IR bands, corresponding to dianion strongly dominate over those, corresponding to monoanion. The latter bands appeared like little shoulders.

Trianions of methylene-bis-malononitrile **1** were prepared by reacting with red naphthalene lithium, naphthalene sodium and naphthalene potassium in THF solution. Alkali reagents (dianions of naphthalene) were formed previously in ampulla with excess of alkali metals in dry THF. The metal reagents (more than 3-fold excess) were added to the solution of neutral compound **1** and were transferred immediately into IR cell, previously flushed with argon. The conversion into trianions

was incomplete, as in all spectra bands corresponding to their dianions appeared.

## COMPUTATIONS

Full optimization of geometries was done using Gaussian-98 program package [9]. We performed DFT B3LYP computations, the latter combined Becke's three-parameter nonlocal exchange [10] with the correlational functional of Lee, Yang and Parr [11-12], adopting a 6-31++G\*\* basis set without any symmetry restrictions. The stationary points found on the potential energy hypersurfaces for each structure, were characterized using the standard harmonic vibrational analysis. The absence of imaginary frequencies confirmed that the stationary points corresponded to local minima on the potential hypersurfaces. A standard least-squares program was used to calculate the single-parameter linear regression indices.

## RESULTS AND DISCUSSION

### Energy analysis

B3LYP/6-31++G\*\* theoretical level has been chosen to perform all computations. This level

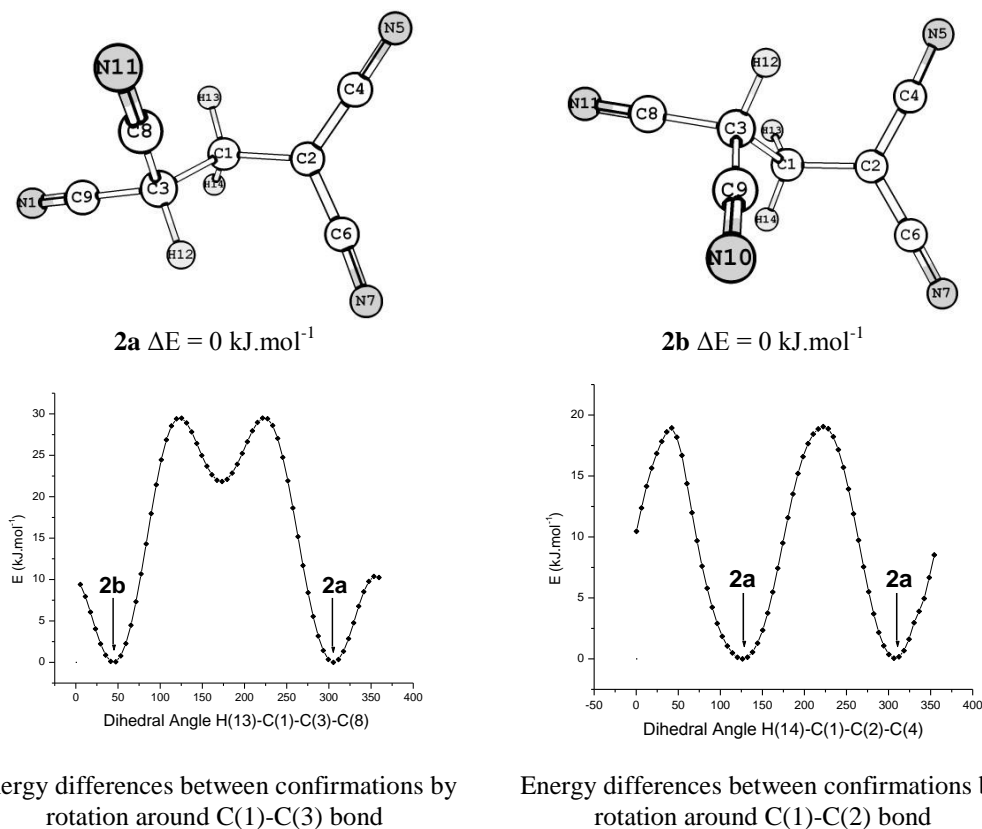


Fig. 2. Stabilities of the conformers of methylene-bis-malononitrile carbanion **2**.

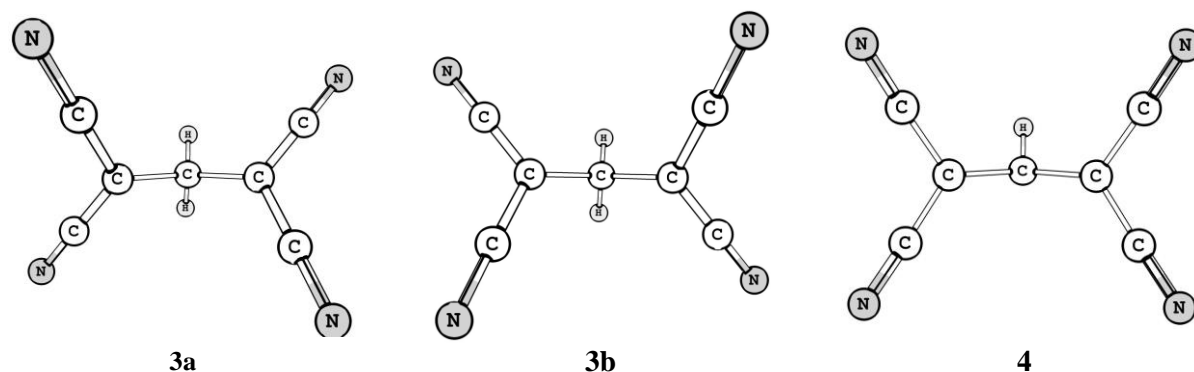


Fig. 3. Optimized structures of di- **3a-3b** and trianion **4** of methylene-bis-malononitrile.

shows a good prediction of IR spectra of nitriles and their anions [13-19]. The mean absolute deviation (MAD) of predicted values of cyano stretching frequencies for a large series of nitriles is  $6\text{ cm}^{-1}$  and  $11\text{ cm}^{-1}$  in a series of nitrile anions [19]. Different conformations of the molecule of methylene-bis-malononitrile **1** by rotation around C(1)-C(3) and C(1)-C(2) bonds in steps of  $6^\circ$  are presented in Fig 1. According to the theoretical calculations, among all possible conformations of the molecule **1** the three most stable conformers **1a-1c** should exist. **1a** possess the lowest energy among them, and the energy difference between **1a** and the other two is approximately 12 and 17  $\text{kJ}\cdot\text{mol}^{-1}$ . According to the X-ray diffraction [8], only **1a** exists in the crystalline state. IR spectra measured in DMSO, THF and  $\text{CHCl}_3$  solutions show no evidences for the presence of more than one conformer. So, we can assume, that only **1a** exists in solution. We have calculated the energy of the different conformations of the anion **2** (Fig. 2), by rotation around C(1)-C(3) and C(1)-C(2) bonds in steps of  $6^\circ$ . Four minima were found by this procedure. By reason of symmetry of anionic dicyanomethanide fragment three of them correspond to identical structure - **2a**. The fourth structure **2b** in fact is a chiral conformer of **2a**, which is energetically degenerated. For di- and trianion **3-4** there is only one stable conformer (Fig 3). However, **3** possesses a chiral axis and two enantiomers **3a** and **3b**.

#### Spectral analysis

In Table 1 the theoretical and experimental frequencies of the molecule of methylene-bis-malononitrile **1** measured in solid state are presented. They show a very good correlation: correlation coefficient  $R=0.99985$ ; standard deviation  $SD = 14.75$ ; number of points  $n = 28$ . The

resulting correlation Equation (1) is used for scaling the theoretical frequencies:

$$\nu^{\text{scaled}} = 0.94388\nu^{\text{native}} + 43.0 \quad (1)$$

The mean absolute deviation (MAD) is  $11\text{ cm}^{-1}$ . This value lies within the range  $9\text{-}25\text{ cm}^{-1}$ , typical for molecules and anions containing cyano and carbonyl groups [20-24].

In the IR spectra of methylene-bis-malononitrile **1** nitrile vibrations are four, two of them are symmetrical and degenerated and two are asymmetrical also degenerated (see Table 2). The splitting between them is only several  $\text{cm}^{-1}$ , so only a single band was observed in the solid-state and solution IR spectra. However a distinct high-frequency shoulder is present corresponding to  $\nu^s(\text{C}\equiv\text{N})$ . In the IR spectra measured in  $\text{DMSO-d}_6$  solution the bands responsible for  $\nu_{\text{C-H}}$  stretching vibrations decrease around  $30\text{-}70\text{ cm}^{-1}$  in comparison to the corresponding bands observed in KBr tablet. These shifts are due to hydrogen bonding with the molecules of solvent DMSO.

Similar to molecule **1** in the IR spectra of di- and trianions **3, 4**, the stretching vibrations of the cyano group have mixed origin (see Table 2). In the molecule the frequencies of both symmetric and asymmetric vibrations are very close to each other, and they have in phase and anti-phase components (Table 2). The differences in the frequencies are a bit larger in the free di- and trianion **3, 4** than observed in the molecule **1**. They also have in-phase and anti-phase components. Only in the free carbanion **2** the four nitrile vibrations are isolated. The  $\nu_{\text{C}\equiv\text{N}}$  in the anionic fragment are lower than those corresponding to the fragment which is remote from the anionic centre and they are strongly decoupled. The frequencies and intensities of former bands are very similar to those, observed in other dicyanomethanides [14,15,17,21-23]. They

interact much less with  $\nu_{C\equiv N}$  of the cyano groups remote from carbanion centre. In general, the relative intensities of the latter are very low and the frequencies are close to those observed in the molecule **1**.

Fig. 4 illustrates the experimental and theoretical spectral changes caused by the conversion of the molecule in the anions. Given the data in Table 2 and Figure 4, we can conclude that the conversion of the molecule **1** in anion **2** causes a decrease in nitrile frequencies of the cyano group in carbanion center predicted by theory as 98 ( $\nu^s C\equiv N$ ) and 139  $\text{cm}^{-1}$  ( $\nu^{as} C\equiv N$ ), and observed in practice - 96 and 135  $\text{cm}^{-1}$  respectively. The conversion of the carbanion **2** into dianion **3** leads to further decrease of nitrile frequencies. It is larger in the cyano group directly bonded to the second carb-

anionic center: predicted 128, measured 126  $\text{cm}^{-1}$ . The lowering of the nitrile frequency at the first carbanionic center is smaller: predicted 52, measured 35  $\text{cm}^{-1}$ . Theory provides further lowering in the nitrile frequencies at conversion of the dianion **3** into trianion **4** of about 50-70  $\text{cm}^{-1}$ . We could not obtain measurable amounts of trianion in DMSO solution, which generally can be expected to exist as free (uncoordinated) anion. However the IR spectra in THF solution show presence of mixture of di- and trianion. The conversion to trianion is significant when counterion is  $K^+$ , higher when counterion is  $Na^+$ , and dominant when counterion is  $Li^+$ . This fact allowed to decompose the complex bands into components. The polarity of THF as a

**Table 1.** B3LYP 6-31++G\*\* theoretical and experimental (KBr tablet) frequencies ( $\nu$  in  $\text{cm}^{-1}$ ) and relative intensities of methylene-bis-malononitrile molecule **1**.

No.	Theoretical data			Experimental data <sup>a</sup>	
	$\nu^b$	A	Approximate description <sup>c</sup>	$\nu$	A <sup>d</sup>
1	3020	0.2	$\nu^{as}(\text{CH}_2)$	3020	m
2	2965	0.6	$\nu^s(\text{CH}_2)$	2959	m
3	2916	2.2	$\nu(\text{CH})$	}2912	vw
4	2915	4.9	$\nu(\text{CH})$		
5	2282	1.8	$\nu^s(\text{C}\equiv\text{N})$	}2278	sh
6	2281	0.1	$\nu^s(\text{C}\equiv\text{N})$		
7	2275	0.4	$\nu^{as}(\text{C}\equiv\text{N})$	}2266	m
8	2275	0.5	$\nu^{as}(\text{C}\equiv\text{N})$		
9	1452	6.7	$\delta^{\text{sciss}}(\text{CH}_2) + \delta(\text{CH})$	1450	s
10	1349	6.5	$\gamma^{\text{wag}}(\text{CH}_2) + \delta(\text{CH})$	1370	w
11	1325	5.3	$\gamma^{\text{twist}}(\text{CH}_2) + \delta(\text{CH})$	1340	w
12	1293	3.8	$\nu(\text{CC}) + \delta(\text{CH}) + \gamma^{\text{wag}}(\text{CH}_2)$	1293	m
13	1287	2.7	$\delta(\text{CH}) + \gamma^{\text{twist}}(\text{CH}_2)$	1284	m
14	1243	3.7	$\delta(\text{CH}) + \gamma^{\text{wag}}(\text{CH}_2)$	1247	s
15	1177	0.6	$\nu(\text{CC}) + \delta(\text{CH}) + \gamma^{\text{wag}}(\text{CH}_2)$	1181	m
16	1056	4.9	$\nu(\text{CC}) + \nu(\text{C-CN})$	1072	m
17	1054	7.7	$\nu(\text{CC}) + \nu(\text{C-CN})$	1072	m
18	1018	7.0	$\nu(\text{CC})$	1058	s
19	992	0.1	$\nu(\text{CC}) + \delta(\text{CH})$	1020	s
20	948	7.3	$\nu(\text{CC})$	953	m
21	854	0.1	$\nu(\text{C-CN}) + \nu(\text{CC})$	850	w
22	792	4.6	$\nu(\text{C-CN}) + \nu(\text{CC})$	787	w
23	621	7.4	$\delta(\text{C-CN}) + \delta(\text{skeletal})$	602	m
24	587	0.2	$\delta(\text{C-CN}) + \delta(\text{skeletal})$	571	m
25	585	0.4	$\delta(\text{C-CN}) + \delta(\text{skeletal})$	571	m
26	579	0.8	$\delta(\text{C-CN}) + \delta(\text{skeletal})$	562	m
27	500	0.6	$\delta(\text{skeletal}) + \delta(\text{C-CN})$	482	m
28 <sup>e</sup>	479	0.4	$\delta(\text{skeletal}) + \delta(\text{C-CN})$	464	m
<b>MAD<sup>f</sup></b>	<b>10.86</b>	-	-	-	-

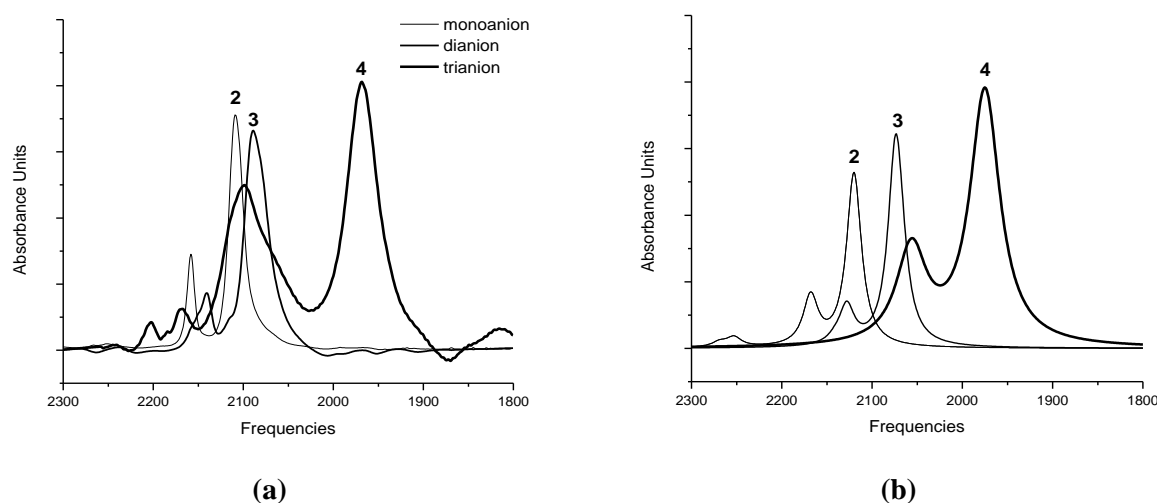
<sup>a</sup>Measured after having decomposed the complex bands into components. <sup>b</sup>Scaled, according to correlation Eqn. (1).

<sup>c</sup>Vibrational modes:  $\nu$ , stretching;  $\delta$ , in-plane bending;  $\gamma$ , out-of-plane bending; superscripts: s, symmetrical; as, asymmetrical; sciss, scissoring; wag, wagging. <sup>d</sup>Relative intensities: s, strong; m, moderate; w, weak; v, very; sh, shoulder. <sup>e</sup>Followed by 11 lower-frequency vibrations. <sup>f</sup>Mean absolute deviation.

**Table 2.** B3LYP/6-31++G\*\* theoretical and experimental ( $\nu$  in  $\text{cm}^{-1}$  DMSO solutions) nitrile frequencies and relative intensities for methylene-bis-malononitrile molecule **1** and their anions **2-4**.

No.	Theoretical data			Experimental data <sup>a</sup>	
	$\nu^b$	A <sup>c</sup>	Approximate description <sup>d</sup>	$\nu$	A <sup>e</sup>
1	2266	0.7	$\nu_{af}^s(\text{C}\equiv\text{N})$	2264	sh
	2265	0.0	$\nu_{sf}^s(\text{C}\equiv\text{N})$	2264	sh
	2259	0.1	$\nu_{sf}^{as}(\text{C}\equiv\text{N})$	2258	vw
	2259	0.2	$\nu_{af}^{as}(\text{C}\equiv\text{N})$	2258	vw
2	2269	7.2	$\nu^s(\text{C}\equiv\text{N})$	2268	w
	2253	14.4	$\nu^s(\text{C}\equiv\text{N})$	2251	w
	2168	73.9	$\nu^{as}(\text{C}\equiv\text{N})$	2161	m
	2120	261.2	$\nu^{as}(\text{C}\equiv\text{N})$	2113	s
3	2141	16.9	$\nu_{sf}^s(\text{C}\equiv\text{N})$	2142	m
	2128	157.8	$\nu_{af}^s(\text{C}\equiv\text{N})$	2115	vw
	2074	679.9	$\nu_{sf}^{as}(\text{C}\equiv\text{N})$	2091	s
	2068	114.0	$\nu_{af}^{as}(\text{C}\equiv\text{N})$	2078	s
4	2061	21.7	$\nu_{sf}^s(\text{C}\equiv\text{N})$	2111 <sup>f</sup>	m
	2056	266.1	$\nu_{af}^s(\text{C}\equiv\text{N})$	2071 <sup>f</sup>	m
	1975	764.3	$\nu_{sf}^{as}(\text{C}\equiv\text{N})$	1975 <sup>f</sup>	s
	1969	3.2	$\nu_{af}^{as}(\text{C}\equiv\text{N})$	1969 <sup>f</sup>	m
<b>MAD<sup>f</sup></b>	<b>8.0</b>	-	-	-	-

<sup>a</sup>Measured after having decomposed the complex bands into components. <sup>b</sup>Scaled with 0.9552 for  $\nu_{\text{C}\equiv\text{N}}$  for molecule of **1** and 0.9642 for anions **2-4** [19]. <sup>c</sup>Scaled theoretical intensities with 0.4010 [19] <sup>d</sup>Vibrational modes:  $\nu$ , stretching; s-symmetrical, as-asymmetrical, sf-sinphase, af-antiphase. <sup>e</sup>Relative intensities: m, moderate; w, weak; v, very; sh, shoulder. <sup>f</sup>Measured in THF solution, counter-ion  $\text{Na}^+$ .

**Fig. 4.** Experimental (a) and theoretical (b) IR spectra of anions **2-4** in nitrile stretch region  $2300\text{-}1800\text{ cm}^{-1}$ .

solvent is significantly lower than DMSO and we have no doubts in the existence of ion aggregation. The position of nitrile bands varies within  $10\text{ cm}^{-1}$  depending on counterion ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ). Nevertheless, the nitrile frequencies of trianion **4** are predicted satisfactorily by the computations performed for the free trianion.

As we can see in Table 2, the theory predicts very well the frequencies of the bands observed in

the nitrile stretch region. By analogy with other studied anionic dicyanometanides we believe that the same can be said about the intensity. The theoretical values of intensities of carbanion **2** lies in the interval  $50\text{-}100\text{ km.mol}^{-1}$  for  $\nu^s(\text{C}\equiv\text{N})$  and  $200\text{-}300\text{ km.mol}^{-1}$  for  $\nu^{as}(\text{C}\equiv\text{N})$  typical for other dicyanometanides [14-19]. The mean absolute deviation (MAD) for nitrile frequencies is only 8

cm<sup>-1</sup> and it is smaller than those observed in a wide variety of nitriles, and their anions [18,19].

### Structural analysis

The experimental [8] and theoretical data on the structure of the molecule **1** are compared in Table 3. It is interesting, to note that according to the experimental data the comparison of methylene-bis-malononitrile with malononitrile shows a significant lengthening of the triple bond of the cyano group: 1.157 Å [25] (Table 3), malononitrile 1.132 Å [8]. The theory does not provide similar effect and the differences are in the fourth digit. However bond angles, are predicted good by the theory, as the average absolute deviation is in the first digit.

According to the computations, the conversion of the molecule **1** into monoanion **2** and the monoanion **2** into dianion **3** (Scheme 1, Fig 2, 3) leads to change of the configuration of the carbanionic centres from sp<sup>3</sup> to sp<sup>2</sup> (atom C(2) and atom C(3)). Only the formation of third anionic center (atom C(1)) leads to preservation of the tetragonal configuration. According to the data listed in Table 3 the largest structural changes are at and near to the carbanionic centers. On every step of deprotonation C≡N bonds are lengthened, and C-CN bonds are

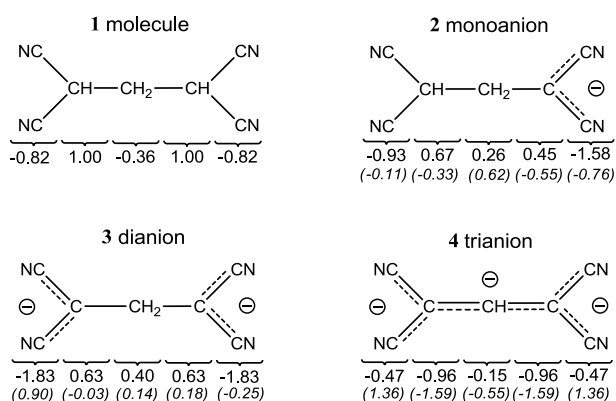
shortened. The changes in bond lengths and bond angles remote from the carbanionic center are smaller.

The electronic structure of the molecule and the anions of methylene-bis-malononitrile is presented in Scheme 4. The electronic charge changes  $\Delta q_i = q_i(\text{anion}) - q_i(\text{molecule})$  are usually quite informative to demonstrate the distribution of the new carbanionic charge over individual fragments of anions. These charge changes of the fragments at each step of deprotonation are given in parentheses. According to the theory, the changes in electron density are greatest in and near to the newly created carbanion centers, and yet they are distributed in all fragments. Upon conversion of the molecule **1** to carbanion **2** and the carbanion **2** to dianion **3** the electron density of cyano groups situated far from the new carbanionic centers increases by 0.08 e<sup>-</sup> and 0.14 e<sup>-</sup> respectively. The electronic density of the newly created charge in **2** and **3** is distributed almost uniformly between the carbanion center and the cyano groups (0.42 to 0.49 e<sup>-</sup>) attached to it. 0.56 e<sup>-</sup> of the third carbanionic charge remains localized in the middle fragment and the remaining electron density is distributed over the four cyano groups.

**Table 3.** B3LYP/6-31++G\*\* theoretical and experimental (Roentgen diffraction) bond lengths (Å) and bond angles (degree) of methylene-bis-malononitrile **1** and its anions **2-4**. The largest changes in the values are given in bold.

bond lengths and bond angles <sup>a</sup>	Molecule 1		Monoanion 2	Dianion 3	Trianion 4
	Theoretical data	Experimental data [8]	Theoretical data <sup>b</sup>	Theoretical data <sup>b</sup>	Theoretical data <sup>b</sup>
C(4)≡N(5)	1.160	1.132(3)	<b>1.178</b>	<b>1.183</b>	<b>1.195</b>
C(6)≡N(7)	1.160	1.132(3)	<b>1.179</b>	<b>1.185</b>	<b>1.191</b>
C(8)≡N(11)	1.160	1.132(3)	1.161	<b>1.183</b>	<b>1.195</b>
C(9)≡N(10)	1.160	1.132(3)	1.162	<b>1.185</b>	<b>1.191</b>
C(1)–C(2)	1.556	1.546(3)	1.501	1.153	1.527
C(2)–C(4)	1.475	1.486(3)	<b>1.402</b>	1.400	1.408
C(2)–C(6)	1.473	1.478(3)	<b>1.402</b>	1.398	1.402
C(1)–H(14)	1.092	1.03(2)	1.099	1.100	1.099
C(2)–H(8)	1.099	1.04(2)	-	-	-
<b>MAD</b>	<b>0.029</b>	-	-	-	-
<C(2)C(4)N(5)	178.0	177.9(3)	175.5	179.2	175.4
<C(2)C(6)N(7)	176.6	176.6(3)	178.2	178.5	178.1
<C(1)C(2)C(4)	110.1	108.8(2)	<b>117.9</b>	<b>121.7</b>	<b>121.1</b>
<C(4)C(2)C(6)	111.0	110.3(2)	<b>120.8</b>	<b>119.9</b>	<b>113.7</b>
<C(2)C(1)C(3)	112.6	112.5(2)	113.0	<b>120.1</b>	<b>121.2</b>
<C(1)C(2)C(6)	111.4	111.7(2)	<b>120.8</b>	<b>120.6</b>	<b>124.4</b>
<C(2)C(1)H(14)	108.4	109(1)	112.5	109.4	107.3
<C(2)C(1)H(15)	109.6	109(1)	110.7	105.7	-
<C(1)C(2)H(8)	109.3	111(1)	-	-	-
<C(6)C(2)H(8)	107.6	107(1)	-	-	-
<H(14)C(1)H(15)	108.2	109(2)	107.	105.7	-
<b>MAD</b>	<b>0.6</b>	-	-	-	-

<sup>a</sup>Atom numbering according to Figure 1. <sup>b</sup>The largest changes towards values of molecule **1** are given in bold.



**Scheme 4.** NBO electronic charges of methylene-bis-malononitrile **1** and its anions.

## CONCLUSION

We found on the basis of both experimental and computational IR data that the effect of conversion of 1,1,3,3-tetracyanopropane into anions is strong. The cyano stretching frequencies at the first step of deprotonation decreases by maximum  $140\text{ cm}^{-1}$  upon deprotonation and further to 200 and  $300\text{ cm}^{-1}$  upon the next steps of deprotonation. At every step a large change in the geometry occurs and significant part of the electronic charge generated by the formation of carbanionic centers is distributed over the cyanogroups.  $0.42\text{ e}^-$ ,  $0.49\text{ e}^-$  and  $0.56\text{ e}^-$  from the newly generated anionic charge remains localized over the first, second and third carbanionic center respectively. This findings are in agreement with the observed spectral change.

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## ИЧ-СПЕКТРИ И СТРУКТУРА НА 1,1,3,3-ТЕТРАЦИАНОПРОПАН И НЕГОВИТЕ КАРБАНИОНИ: ЕКСПЕРИМЕНТАЛНО И КВАНТОВОХИМИЧНО ИЗСЛЕДВАНЕ

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(Резюме)

Приложен е комбиниран ИЧ експериментален/DFT теоретичен подход за проследяване на спектралните и структурни промени, породени от превръщането на 1,1,3,3-тетрацианопропан в моно-, ди- и трианион. Превръщането на молекулата в моноион се отразява слабо върху валентното трептене на  $\nu(\text{C}\equiv\text{N})$  на отдалечените от карбанионния център цианогрупи ( $13\text{ cm}^{-1}$ ) и силно върху близкоразположените цианогрупи ( $140\text{ cm}^{-1}$ ). Карбанионният заряд е разпределен главно в анионния център и цианогрупите директно свързани с него (общо  $0,85\text{ e}^-$ ). Превръщането на молекулата в ди- и трианион е съпроводено с по-силно понижение на  $\nu(\text{C}\equiv\text{N})$ , достигащо до  $300\text{ cm}^{-1}$ . Установено е много добро съответствие между експерименталните и теоретичните данни. Според изчисленията разпределението на карбанионния заряд, получен при второто и третото депротониране се разпределя почти равномерно във всички фрагменти.