

IR spectra and structure of 3,5,5-trimethyl(cyclohex-2-enylidene) malononitrile and its potassium cyanide and sodium methoxide carbanionic adducts: experimental and B3LYP studies

S. S. Stoyanov*, A. D. Popova, J. A. Tsenov

Department of Structural Organic Analysis, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G Bonchev St., Block 9, 1113 Sofia, Bulgaria

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

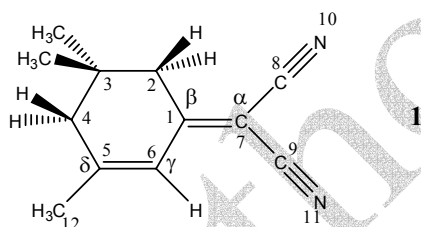
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A combined IR experimental/B3LYP computational approach has been applied to follow the formation and isomerization of potassium cyanide and sodium methoxide carbanionic adducts of 3,5,5-trimethyl(cyclohex-2-enylidene) malononitrile **1**. A good agreement has been found between theoretical and experimental IR data. In agreement between theory and experiment, **1** forms β - and δ -adducts with the above-mentioned nucleophiles. Structural changes, caused by conversion of **1** into β - and δ -adducts, have also been studied. According to the computations, the chemical motive force in the $\beta \rightarrow \delta$ isomerization is the much higher stability (by ca. 50 kJ·mol⁻¹) of the δ -adducts compared to β -ones.

Key words: IR, DFT B3LYP, 3,5,5-trimethyl(cyclohex-2-enylidene) malononitrile, adducts, carbanion, isomerization.

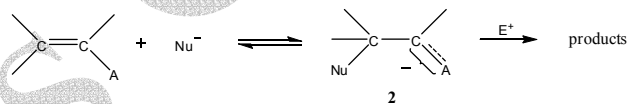
INTRODUCTION

3,5,5-trimethyl(cyclohex-2-enylidene) malononitrile (TMCHM, **1**) was prepared by Lemke in 1970 as a precursor in the Knoevenagel-type synthesis of a large series of its 12-ylidene derivatives [1–3].

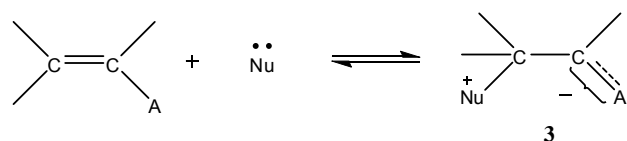


These derivatives are high-quality dyes for synthetic polymers [4] (and references there in); some of these dyes have solvatochromic properties [1–3]. Nowadays, 12-ylidene derivatives of **1** are of special interest as non-linear optical [4–15] and fluorescent [7] materials. We did not find in the literature detailed vibrational studies of **1** itself; some 12-ylidene derivatives of **1** have been studied thoroughly by IR [5–7], polarized IR [6] and Raman [5] spectra, B3LYP quantum-chemical calculations [5, 7] and single-crystal X-ray diffraction [8–15].

On the other hand, it is well-known [16] that nucleophilic attacks to C=C bonds are favoured by electron-accepting substituents, where A, Nu⁻ and E⁺ are the acceptor, nucleophile and electrophile, respectively.

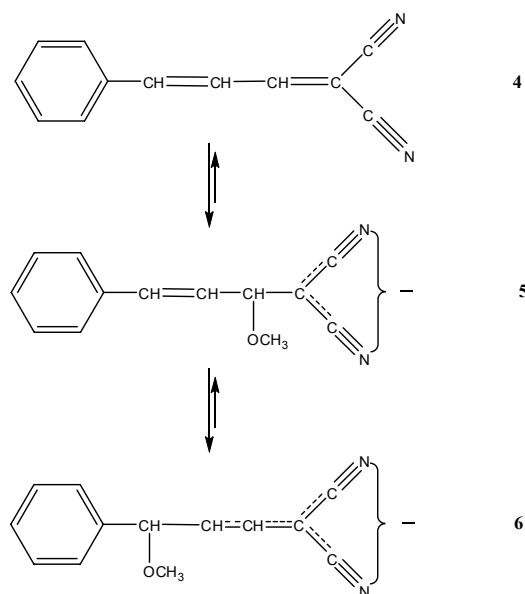


When the nucleophilic attacks take place in aprotic solvents (E⁺ is usually H⁺), the intermediate adducts **2** have been isolated in many cases [17–23]. Both sodium methoxide (Nu⁻≡CH₃O⁻) [22–23] and potassium cyanide (Nu⁻≡CN⁻) [24–27] carbanionic adducts of benzylidenemalononitrile [22] and other strongly polarized alkenes [21–28], butadienes and hexatrienes [22] have been studied. Nucleophilic attacks by uncharged Lewis bases Nu: result in the formation of zwitterions **3**.



This result has been established in cases of tertiary phosphine adducts (**3**, Nu⁻≡R₃P:) of benzylidenemalononitrile by IR [29–31], NMR [32] and confirmed by X-ray diffraction [33]. The heptylamine zwitterionic adduct (Nu⁻≡C₇H₁₅NH₂) of the same compound has also been studied by IR spectra [24]. Juchnovski *at al.* [22] found 30 years ago that 1,1-dicyano-4-phenylbutadiene **4** and other strongly polarized conjugated butadienes react with CH₃O⁻Na⁺ to form the β -adduct **5**. Within 24 hours, however, **5** isomerizes spontaneously and practically completely into the corresponding δ -adduct **6**.

* To whom all correspondence should be sent:
E-mail: cacafuego@abv.bg



The authors [22] supposed that the 5→6 isomerization was provoked by the higher stability of **6**, due to larger delocalization of the carbanionic charge in **6** compared to **5**. This supposition was confirmed by *ab initio* HF calculations: The δ -adduct **6** is by 28.2 kJ·mol⁻¹ more stable than the β -adduct **5**. The title compound **1** is an analogue of **4**, so it was of interest to check whether and what kind of adducts would be formed by the reaction of **4** with potassium cyanide and sodium methoxide.

EXPERIMENTAL

Compound **1** was prepared by the classical Gelmo's method [1] and a sample of it was given to us by Kolev *et al.* [5]. The cyanide and methoxide were prepared by adding DMSO/DMSO-*d*₆ solutions of **1** to excess of dry KCN and NaOCH₃, respectively, under argon. After 1 min intense stirring, the reaction mixtures were separated by syringe-filter and the clear adduct solutions were put immediately into a CaF₂ cell of 0.129 mm path length. The IR spectra were recorded on Bruker IFS 113v and Tensor 27 FT spectrometers at a resolution of 1 cm⁻¹ and 64 scans.

COMPUTATIONS

The Gaussian 98 program package [34] was used for Density Functional Theory (DFT, full optimization) computations of energies, structures and IR spectra of the species studied. This theory is the groundwork of a series of cost-effective methods to approximate electron correlation effects [35]. We have employed the B3LYP functional, which combines Becke's three-parameter non-local exchange with the correlation functional of Lee, Yang and

Parr [36, 37], adopting a 6-31++G** basis set with any symmetry restrictions. For each structure, the stationary points found on the molecular potential energy hypersurfaces were characterized using the standard analytical harmonic procedure. The absence of irrational frequencies or negative eigenvalues of the second-derivative matrix confirmed that the stationary points corresponded to global minima on the potential energy surfaces [35]. A standard least-square program was used for calculating the single-parameter linear regression indices.

RESULTS AND DISCUSSION

Correlation analysis

Comparison of the native B3LYP/6-31++G** vibrational frequencies of TMCHM **1** with those measured in DMSO solvent (see *Spectral analysis* below) resulted in the formation of an excellent (0.99 < R < 1) correlation (Eqn. 1):

$$\nu(\text{exp.}) = 0.93373 \nu(\text{theor.}) + 55.75 \text{ (cm}^{-1}\text{)} \quad (1)$$

Correlation coefficient R = 0.99994; Standard deviation S.D. = 8.94 cm⁻¹; Number of data points n = 34.

Eqn. (1) was used for correlational scaling [38] of the theoretical frequencies. As stated in Alcolea's review article [39] (and references therein), the use of scaling equations instead of scaling factors gave better results, especially in the low-frequency region. For more recent works see [40–49] (and references therein).

Spectral analysis

Our theoretical and experimental IR data for **1** are compared in Table 1 together with the approximate description of the corresponding vibrations.

There is nothing special in the data for the CH stretching vibrations, (Nos. 1–14 in Table 1). As it could be expected [50], the $\nu(\text{=C-H})$ vibration was the most high-frequency one among them. We found in the experimental spectra a single moderate band in the $\nu(\text{C}\equiv\text{N})$ region, without shoulders or satellites, at 2223 cm⁻¹. The calculations predict a small splitting $\Delta\nu(\text{C}\equiv\text{N})_2 = \nu^s(\text{C}\equiv\text{N})_2 - \nu^{\text{as}}(\text{C}\equiv\text{N})_2$ of 13 cm⁻¹ (Table 1, vibrations 15 and 16). The real splitting is probably even smaller, so we assign the band at 2223 cm⁻¹ as a superposition of the $\nu^s(\text{C}\equiv\text{N})$ and $\nu^{\text{as}}(\text{C}\equiv\text{N})$ bands like in the cases of dozens of ylidene malonitriles [22–24, 51] (and references therein). The strongest bands in the spectrum of TMCHM at 1614 and 1545 cm⁻¹ correspond to the endo- and exocyclic $\nu(\text{C=C})$ vibrations (Table 1, vibrations 17 and 18).

Table 1. Theoretical (B3LYP 6-31++G**) and experimental (solvent DMSO / DMSO-d₆) frequencies (ν in cm⁻¹) and integrated intensities (A in km·mol⁻¹) of TMCHM molecule **1**.

No.	B3LYP6-31++G**			Experimental data ^a		
	ν	ν^b	A	Approximate description ^c	ν	A^d
1	3189	3034	3.7	$\nu(\text{C-H})$	3030	vw
2	3131	2979	14.8	$\nu^a(\text{CH}_3)$	- ^e	-
3	3116	2966	25.8	$\nu^{\text{as}}(\text{CH}_3)$	2962	m
4	3108	2958	40.4	$\nu^{\text{as}}(\text{CH}_3)$	2962	m
5	3103	2953	11.8	$\nu^{\text{as}}(\text{CH}_3)$	2962	m
6	3101	2951	21.1	$\nu^{\text{as}}(\text{CH}_3)$	2962	m
7	3099	2949	3.4	$\nu^{\text{as}}(\text{CH}_2)$	2962	m
8	3073	2925	11.1	$\nu^{\text{as}}(\text{CH}_3)$	2936	vw
9	3047	2900	30.7	$\nu^{\text{as}}(\text{CH}_2)$	2902	w
10	3039	2894	13.8	$\nu^s(\text{CH}_3)$	2902	w
11	3031	2886	33.0	$\nu^s(\text{CH}_3)$	2871	w
12	3025	2880	23.0	$\nu^s(\text{CH}_3)$	2871	w
13	3011	2867	9.9	$\nu^s(\text{CH}_2)$	- ^e	-
14	2995	2852	18.1	$\nu^s(\text{CH}_2)$	2828	vw
15	2330	2232	73.3	$\nu^s(\text{C}\equiv\text{N})_2$	2223	47.5
16	2317	2219	30.1	$\nu^{\text{as}}(\text{C}\equiv\text{N})_2$	2223	47.5
17	1668	1613	187.5	$\nu(\text{C}=\text{C})^{\text{endo}}$	1614	78.9
18	1579	1530	148.3	$\nu(\text{C}=\text{C})^{\text{exo}}$	1545	70.1
19	1517	1473	8.5	$\delta^{\text{as}}(\text{CH}_3)$	1470	2.1
20	1512	1467	5.4	$\delta^{\text{as}}(\text{CH}_3)$	- ^e	-
21	1500	1456	5.5	$\delta^{\text{as}}(\text{CH}_3)$	1450	sh
22	1492	1449	1.8	$\delta^{\text{as}}(\text{CH}_3)$	- ^e	-
23	1486	1444	15.6	$\delta^{\text{as}}(\text{CH}_3)$	1439	w
24	1481	1439	11.1	$\delta^{\text{as}}(\text{CH}_3)$	1439	w
25	1475	1433	2.6	$\delta^{\text{sciss}}(\text{CH}_2)$	- ^e	-
26	1464	1422	11.2	$\delta^{\text{sciss}}(\text{CH}_2)$	1416	w
27	1432	1393	5.8	$\delta^s(\text{CH}_3)$	- ^e	-
28	1419	1381	12.2	$\delta^s(\text{CH}_3)$	1386	m
29	1411	1373	10.8	$\delta^s(\text{CH}_3)$	1370	w
30	1404	1367	9.2	$\delta(\text{CH})$	1350	vw
31	1373	1337	7.6	(delocalized)	- ^e	-
32	1352	1318	25.1	$\nu(\text{C}-\text{C})(\text{ring})$	1326	m
33	1320	1288	3.5	$\gamma^{\text{wag}}(\text{CH}_2)$	1286	w
34	1317	1285	3.2	$\gamma^{\text{wag}}(\text{CH}_2)$	1286	w
35	1285	1256	0.2	$\nu(\text{C}-\text{C})(\text{ring})$	- ^e	-
36	1223	1197	2.9	$\nu(\text{C}-\text{CH}_3)$, $\delta(\text{C}-\text{C})(\text{ring})$	1201	vw
37	1199	1175	6.8	$\nu(\text{C}-\text{C}\equiv\text{N})$	1183	vw
38	1188	1165	4.0	$\nu(\text{C}-\text{C})(\text{ring})$, $\gamma(\text{CH}_2)$	1163	vw
39	1166	1144	5.1	$\nu(\text{C}-\text{CH}_3)$, $\delta(\text{CC})(\text{ring})$	1149	vw
40 ^f	1156	1135	8.1	$\nu(\text{C}-\text{CH}_3)$	1135	vw

a - Measured after having decomposed the complex bands into components; b - Scaled, according to correlation Eqn. (1); c - Vibrational modes: ν , stretching; δ , in-plane bending; γ , out-of-plane bending; superscripts: s, symmetrical; as, asymmetrical; sciss, scissoring; wag, wagging; endo, endocyclic; exo, exocyclic; d - Relative intensities: m, moderate; w, weak; v, very; sh, shoulder; e - These bands were not detected in the experimental spectrum; f - Followed by 38 lower-frequency vibrations.

TMCHM **1** reacts rapidly with KCN and NaOCH₃. The bands of the starting compound **1** disappear and a few new bands appear in the IR spectra. So, let us consider the data in Table 2. The new bands are like the bands in the spectra of

adducts of cinnamylidenemalononitrile [22–24]. Immediately after reacting **1** with KCN, we can see in the spectrum four very strong and two weak bands in the $\nu(\text{C}\equiv\text{N})$ region (See also Fig. 1). Having in mind that the adduct **A** shows lower-frequency bands than **B** (as predicted by computations) as well as that the bands of **A** fade away on account of these of **B**, we assume that **A** and **B** (Table 2) are β - and δ -cyanide adducts of **1** respectively. The spectra show practically a full conversion of the β -cyanide adduct into the δ -one within 60 min. (Fig. 1). The weak bands above 2200 cm⁻¹ of **A** and **B** (Table 2) correspond to the new (added) non-conjugated cyano group.

Table 2. Theoretical (B3LYP 6-31++G**) and experimental (solvent DMSO) cyano stretching IR frequencies (ν in cm⁻¹) and integrated intensities (A in km·mol⁻¹) of cyanide and methoxide carbanionic adducts of TMCHM.

No.	B3LYP 6-31++G **			Experimental data ^a		
	ν	ν^b	A	Approximate description ^c	ν	A^d
β-cyanide adduct						
15 ^e	2298	2202	43.3	$\nu(\text{C}\equiv\text{N})^f$	2210	w ^g
16	2242	2149	157.0	$\nu^s(\text{C}\equiv\text{N})_2$	2163	vs ^g
17 ^h	2192	2103	613.6	$\nu^{\text{as}}(\text{C}\equiv\text{N})_2$	2101	vs ^g
δ-cyanide adduct						
15 ^e	2307	2210	44.2	$\nu(\text{C}\equiv\text{N})_2$	2219	9.7
16	2259	2165	334.4	$\nu^s(\text{C}\equiv\text{N})_2$	2163	115.7
17 ^h	2217	2126	493.4	$\nu^{\text{as}}(\text{C}\equiv\text{N})_2$	2119	193.6
δ-methoxide adduct						
18 ⁱ	2241	2148	229.8	$\nu^s(\text{C}\equiv\text{N})_2$	- ^j	-
19 ^k	2194	2104	603.8	$\nu^{\text{as}}(\text{C}\equiv\text{N})_2$	- ^j	-
δ-methoxide adduct						
18 ⁱ	2256	2162	321.1	$\nu^s(\text{C}\equiv\text{N})_2$	2163	151.0
19 ^k	2214	2123	503.3	$\nu^{\text{as}}(\text{C}\equiv\text{N})_2$	2120	212.9
6. δ-methoxide adduct of cinnamethylidene-malononitrile [24]						
12 ^l	2445 ^m	2183 ^m		$\nu^s(\text{C}\equiv\text{N})_2$	2164	110.1
13 ⁿ	2398 ^m	2141 ^m		$\nu^{\text{as}}(\text{C}\equiv\text{N})_2$	2123	220.4

a - Measured after having decomposed the complex bands into components; b - Scaled, according to correlation Eqn. (1); c - Vibrational modes: ν , stretching; superscripts: s, symmetrical; as, asymmetrical; d - Relative intensities: w, weak; vs, very strong; e - Preceded by 14 $\nu(\text{C}-\text{H})$ vibrations; f - Bands of the new (additionally introduced) cyano group; g - We have not measured spectra of this adduct with the absence of bands of corresponding δ -cyanide adduct; h - Followed by 67 lower-frequency vibrations; i - Preceded by 17 $\nu(\text{C}-\text{H})$ vibrations; j - We did not find measurable amounts of this adduct; k - Followed by 74 lower-frequency vibrations; l - Preceded by 11 $\nu(\text{C}-\text{H})$ vibrations; m - HF/6-31G [24]; n Followed by 63 lower-frequency vibrations.

The formation of **D** or the **C**→**D** isomerization was so rapid, that we were not able to detect other bands in the spectrum measured immediately after the reaction. In agreement between theory and experiment, the only adduct, registered in this case, was **D** (Table 2). This statement could be confirmed by experimental data for the δ -methoxide adduct of cinnamylidenemalononitrile [24] (**6** in Table 2): **D** and **6** show very close cyano stretching frequencies and close intensities.

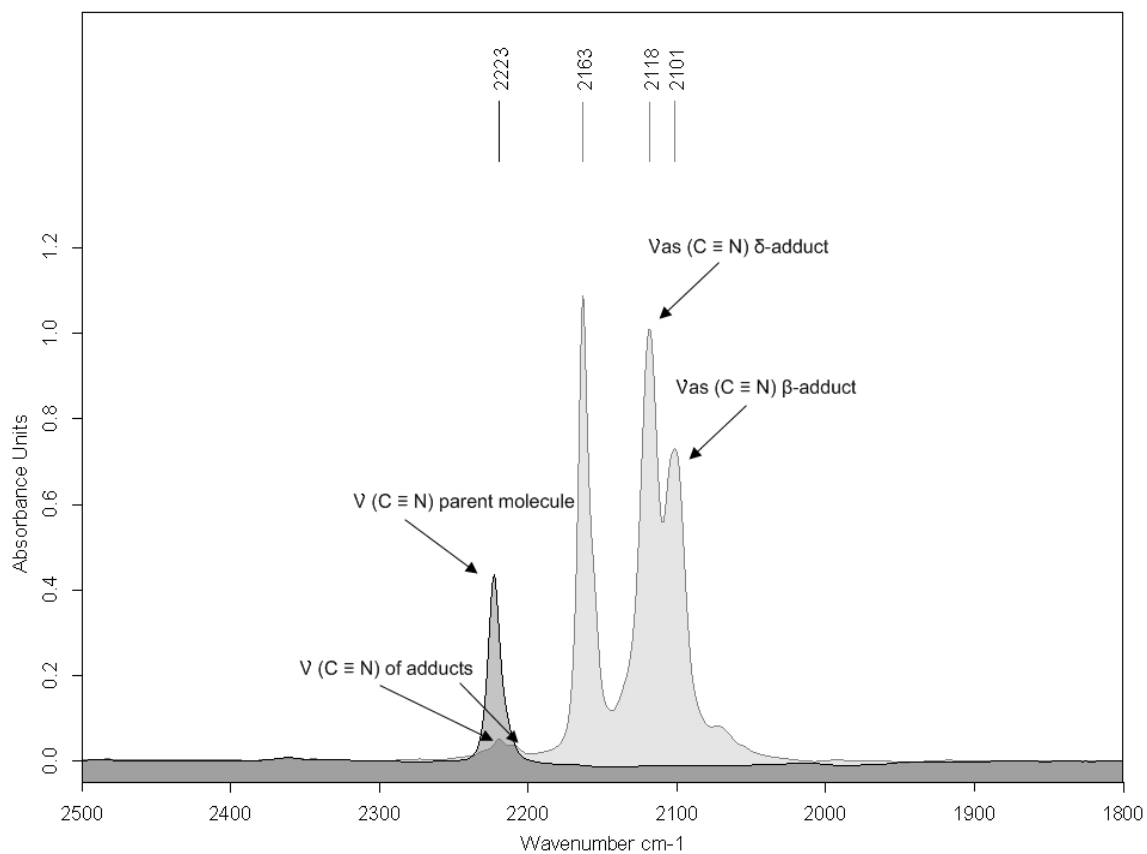


Fig. 1. IR spectra of TMCHM **1** (doubly shaded) and of its β- and δ-cyanide adducts.

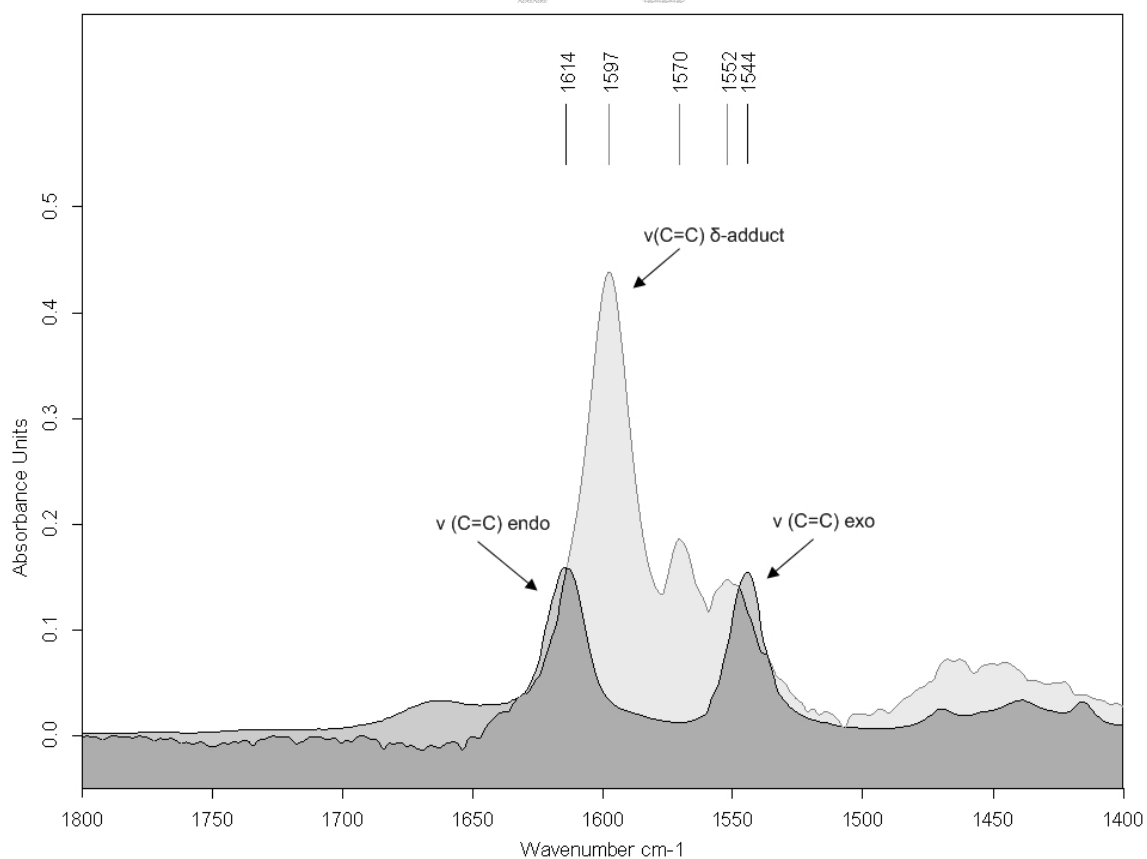


Fig. 2. IR spectra of TMCHM **1** (doubly shaded) and of its δ- methoxide adduct.

Table 3. Theoretical (B3LYP 6-31++G**) and experimental (solvent DMSO/DMSO-d₆) frequencies (ν in cm⁻¹) and integrated intensities (A in km·mol⁻¹) of δ -methoxide adduct of TMCHM.

No	B3LYP/6-31++G**				Experimental data ^a	
	ν	N ^b	A	Approximate description	ν	A^d
1	3153	3000	15.5	$\nu(\text{CH})$	3009	w
2	3133	2981	15.8	$\nu^{\text{as}}(\text{CH}_3)$	- ^e	-
3	3125	2974	33.5	$\nu^{\text{as}}(\text{CH}_3)$	- ^e	-
4	3103	2953	46.6	$\nu^{\text{as}}(\text{CH}_3)$	2952	m, br
5	3097	2948	46.4	$\nu^{\text{as}}(\text{OCH}_3)$	2952	m, br
6	3087	2938	62.7	$\nu^{\text{as}}(\text{CH}_3)$	- ^e	-
7	3081	2933	76.4	$\nu^{\text{as}}(\text{CH}_3)$	- ^e	-
8	3076	2928	9.9	$\nu^{\text{as}}(\text{CH}_3)$	- ^e	-
9	3071	2923	5.3	$\nu^{\text{as}}(\text{CH}_3)$	- ^e	-
10	3062	2915	19.9	$\nu^{\text{as}}(\text{CH}_3)$	2910	w, br
11	3053	2906	60.0	$\nu^{\text{as}}(\text{CH}_3)$	2910	w, br
12	3033	2888	91.9	$\nu^{\text{s}}(\text{CH}_3)$	- ^e	-
13	3025	2880	66.5	$\nu^{\text{s}}(\text{CH}_3)$	2865	w
14	3017	2872	46.7	$\nu^{\text{s}}(\text{CH}_3)$	2865	w
15	3012	2868	29.3	$\nu^{\text{s}}(\text{CH}_3)$	2865	w
16	3000	2857	30.9	$\nu^{\text{s}}(\text{CH}_3)$	- ^e	-
17	2972	2831	70.4	$\nu^{\text{s}}(\text{OCH}_3)$	2823	w
18	2256	2162	321.1	$\nu^{\text{s}}(\text{C}\equiv\text{N})$	2163	151.0
19	2214	2123	503.3	$\nu^{\text{as}}(\text{C}\equiv\text{N})$	2118	212.9
20	1634	1582	394.7	$\nu(\text{C}=\text{C})$	1598	386.5
				1571 ^f	w	
				1552 ^f	w	
21	1523	1478	7.2	$\delta^{\text{as}}(\text{CH}_3)$	- ^e	vw
22	1515	1471	12.0	$\delta^{\text{as}}(\text{OCH}_3)$	1467	vw
23	1506	1462	4.5	$\delta^{\text{as}}(\text{CH}_3)$	1463	w
24	1503	1459	6.9	$\delta^{\text{as}}(\text{CH}_3)$	1463	w
25	1496	1452	1.6	$\delta^{\text{as}}(\text{CH}_3)$	1451	w
26	1493	1449	2.9	$\delta^{\text{as}}(\text{CH}_3)$	1451	w
27	1488	1445	5.1	$\delta^{\text{as}}(\text{CH}_3)$	1451	vw
28	1486	1443	3.2	$\delta^{\text{as}}(\text{OCH}_3)$	1451	vw
29	1478	1436	1.5	$\delta^{\text{sciss}}(\text{CH}_2)$	1425	vw
30	1474	1432	2.8	$\delta^{\text{sciss}}(\text{CH}_2)$	1425	-
31	1459	1418	3.1	$\delta^{\text{s}}(\text{OCH}_3)$	1425	m
32	1420	1382	2.8	$\delta^{\text{s}}(\text{CH}_3)$	- ^e	m
33	1401	1364	17.4	$\delta^{\text{s}}(\text{CH}_3)$	1365	m
34	1397	1361	44.1		1365	w
35	1396	1359	5.3	$\delta^{\text{s}}(\text{CH}_3)$	1365	vw
36	1375	1340	5.3	$\delta(\text{CH})$	1345	vw
37	1347	1313	5.3	$\nu(\text{C}-\text{C})$	1320	vw
38	1315	1283	5.3	$\nu(\text{C}-\text{C}(\text{CN})_2)$	1302	vw
39	1312	1280	5.3	$\nu(\text{C}-\text{C})$	1302	m
40	1294	1264	2.3	$\nu(\text{C}-\text{C})$	1270	w
41	1282	1253	115.8	$\nu(\text{C}-\text{C})$	1266	vw
42	1255	1228	17.7	$\nu(\text{C}-\text{C}(\text{CN})_2)$	1226	vw
43	1218	1193	4.7	$\nu(\text{C}-\text{C})$	1206	vw
44	1198	1174	30.2	$\nu(\text{C}-\text{C})$	1185	vw
45	1193	1170	13.0	$\nu(\text{C}-\text{C})$	1148	vw
46	1172	1150	1.4	$\tau(\text{OCH}_3)$	1138	vw
47 ^g	1165	1144	10.0	$\nu(\text{C}-\text{C})$	1138	vw

a - Measured after having decomposed the complex bands into components; b - Scaled, according to correlation Eqn. (1); c - Vibrational modes: ν , stretching; δ , in-plane bending; γ , out-of-plane bending; τ , torsion; superscripts: s, symmetrical; as, asymmetrical; sciss, scissoring; wag, wagging; d - Relative intensities: m, moderate; w, weak; v, very; sh, shoulder; br, broad; e - These bands were not detected in the experimental spectrum; f - The origin of these bands is not known; g - Followed by 46 lower-frequency vibrations.

Table 3 contains detailed IR data for the δ -methoxide adduct of **1**. We shall put special emphasis on the band at 1598 cm⁻¹. It is the strongest one in the spectrum with A of 386.5 km·mol⁻¹ (see also Fig. 2), and corresponds to the vibration of the newly formed quasi-double C¹---C⁶ bond, which is strongly polarized by the C(CN)₂⁻ group.

Structural analysis

The shapes of TMCHM **1** and of its β - and δ -cyanide adducts are shown on Figure 3.

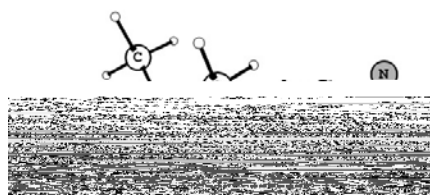


Fig. 3. B3LYP/6-31++G** optimized structures of TMCHM **1** and of its β - and δ -cyanide adducts (**A** and **B** in Table 2).

It is seen there that the conversion of **1** into adducts is not accompanied by essential changes in the general form of the parent molecule. However, the structural elements in the fragment, where the reactions take place, undergo essential variations (Table 4). Big changes in the bond length take place in cases when double or quasi-double bonds become single ones and *vice versa*, e.g. R(5,6) and R(1,7).

Table 6. Total energies (E in hartree) of TMCHM molecule, its cyanide and methoxide adducts and energy differences (ΔE in $\text{kJ}\cdot\text{mol}^{-1}$) between the corresponding β - and δ -adducts.

Species	E	$\Delta E^a = E_\delta - E_\beta$
TMCHM (1)	-575.213306	-
TMCHM – β -CN ⁻ adduct	-668.119159	49.69
TMCHM – δ -CN ⁻ adduct	-668.137592	-
TMCHM – β -CH ₃ O ⁻ adduct	-690.395773	53.61
TMCHM – δ -CH ₃ O ⁻ adduct	-690.415380	-

a - Corrected with zero-point vibrational energies (ZPVE).

CONCLUSIONS

The combined IR experimental/B3LYP computational approach, applied in the present work, made it possible both to prove the conversion of 3,3,5-trimethyl(cyclohex-2-enylidene)malononitrile into potassium cyanide and sodium methoxide adducts, as well as the chemical motive force which is the main groundwork of the β -adduct \rightarrow δ -adduct isomerizations: the much higher stability (i.e. lower total energy) of the δ -adducts, compared to the β -ones.

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