

IR spectral and structural changes, caused by the conversion of 4-cyanobenzamide into azanion: a combined experimental/computational approach

J. A. Tsenov*, S. S. Stoyanov, I. G. Binev

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

Received January 25, 2008; Revised March 20, 2008

A combined IR experimental/DFT computational approach has been applied to follow the spectral and structural changes, caused by the conversion of 4-cyanobenzamide into azanion. The conversion has shown a weak effect on the cyano stretching band $\nu(\text{C}\equiv\text{N})$ and strong effects on both amide $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{N})$ stretching bands. According to the computations, the two latter vibrational modes are strongly delocalized in the azanion and participate essentially in a few vibrations each. Again according to the computations, the strong structural changes, caused by the conversion, take place *at* and *next* to the azanionic center; the non-planar 4-cyanobenzamide molecule turns into a planar azanion.

Key words: IR spectra, *ab initio* HF; DFT B3LYP, structure, 4-cyanobenzamide, azanion.

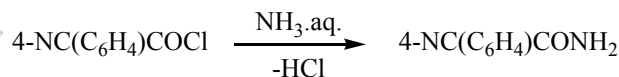
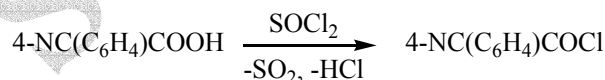
INTRODUCTION

4-cyanobenzamide **1** in Scheme 1 was first prepared by partial hydrolysis of 1,4-dicyanobenzene in 1912 [1]. This compound is mentioned nowadays mainly in relation with *Tetrahymena Pyriformis* [2, 3].

Ten years ago Ognianova *at al.* reported about a 76–180 cm^{-1} interval of decrease in the carbonyl stretching frequencies $\nu_{\text{C}=\text{O}}$ of 23 amides, accompanying their conversion into azanions (4-cyanobenzamide was not studied) [4]. It is known on the other hand that conversion of nitriles into anions results in very essential decrease in the cyano stretching frequency $\nu_{\text{C}\equiv\text{N}}$ and strong, in certain cases dramatic increase in the integrated intensity $A_{\text{C}\equiv\text{N}}$ of the corresponding IR bands [5–7] (and references therein). This rule is valid for anions where the cyano group is in resonance with the anionic center, even in cases they are quite distant. In the azanions (**2**, **3** in Scheme 1) of 4-cyanobenzamide, the cyano group and the azanionic center are distant and there is no formal resonance between them. So, the molecule/azanion pair of 4-cyanobenzamide is an interesting example of weakly interacting cyano group and anionic center, i.e. with a presumed weak effect of the molecule \rightarrow azanion conversion on the $\text{C}\equiv\text{N}$ group spectral and structural characteristics. Another indication to this presumption is the low (absolute) value of -0.23 for the σ^+ constant of the CONH^- group.

EXPERIMENTAL

We prepared 4-cyanobenzamide from 4-cyanobenzoic acid *via* 4-cyanobenzoyl chloride:



The first reaction was carried out (60 min at 80°C) in the presence of catalytic amounts of *N,N*-dimethylformamide, then the excess of SOCl_2 was evaporated *in vacuo*. The second reaction was accomplished by cold ammonia (20% by weight water solution) under cooling. The white residue of 4-cyanobenzamide was washed with 1% (by weight) cold aqueous NaOH solution and with cold water, then recrystallized from water in the presence of a few drops of ammonia. M.p. 225–226°C; lit. m.p. 225–228°C [9].

4-Cyanobenzamide azanion was prepared by adding dimethyl sulfoxide (DMSO/DMSO- d_6) solution of the parent compound to excess of dry $\text{CD}_3\text{O}^-\text{Na}^+$ under argon, stirring and collecting the clear azanion solution with a syringe-filter. We prepared the sample of dry $\text{CD}_3\text{O}^-\text{Na}^+$ itself by reacting CD_3OD (Fluka 99% at enrichment) with Na and evaporating the excess of methanol *in vacuo*. 4-Cyanobenzamide reacted with $\text{CD}_3\text{O}^-\text{Na}^+$ to form azanion in DMSO/DMSO- d_6 promptly (within 3–4 min) and practically completely: no bands of the parent compound were shown in the spectra after

* To whom all correspondence should be sent:
E-mail: soa@orgchm.bas.bg

metalation. The IR spectra were recorded on a Bruker IFS113v and Tensor 27 FTIR spectrometers in a CaF₂ cell of 0.129 mm path length, at a resolution of 1 cm⁻¹ and 64 scans.

COMPUTATIONS

The *ab initio* force field computations (full optimization) of the species studied were performed using the GAMESS software [10] at the Hartree-Fock HF/6-31++G** level. The GAUSSIAN 98 program package [11] 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 [12]. We applied the B3LYP functional which combined the Becke's three-parameter non-local exchange with the correlation functional of Lee, Yang and Parr [13, 14], adopting a 6-31++G** basis set without any symmetry restrictions. For every structure, the stationary points found on the molecular potential energy surfaces (PEHS) were characterized using the standard harmonic vibrational analysis. The absence of 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 in both *ab initio* and DFT computations has recently resulted in better or equally good structural predictions, compared to other basis sets for both molecules and anions [7, 15, 16] (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

Energy analysis

The molecule of 4-cyanobenzamide can exist as one conformation **1** only; two conformations are in principle possible for its azanion, **2** and **3** (Fig. 1, Scheme 1). The energies of the species studied are compared in Table 1. It is seen there that the energy difference between the two anionic conformers of 31.01 kJ·mol⁻¹ is quite essential, so we can *a priori* assume that the isolated conformer **2** should be strongly predominant over **3**.

Table 1. B3LYP/6-31++G** zero-point vibrational energy (ZPVE) corrected total energies ($E^{\text{corr.}}$ in hartree) of the 4-cyanobenzamide molecule **1** and of its azanions **2** and **3**, as well as their differences (ΔE in kJ·mol⁻¹).

Species	Conformers ^a	$E^{\text{corr.}}$	ΔE^b
molecule	1	-493.102417	0.00
azanion	2	-492.558760	1427.37
azanion	3	-492.546949	1458.38

a See in Scheme 1; b - $\Delta E = E_n - E_1$.

The deprotonation energy of a given Brønsted acid can be defined [7, 16] (and references therein) as $E^D = E^{\text{corr.}}(\text{anion}) - E^{\text{corr.}}(\text{molecule})$ (for the most stable conformers of these species). Georgieva and Velcheva have recently found that E^D 's correlate fairly well with pKa's of Brønsted acids, containing cyano or carbonyl groups, in DMSO solvent, according to Eqn. 1 [7].

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

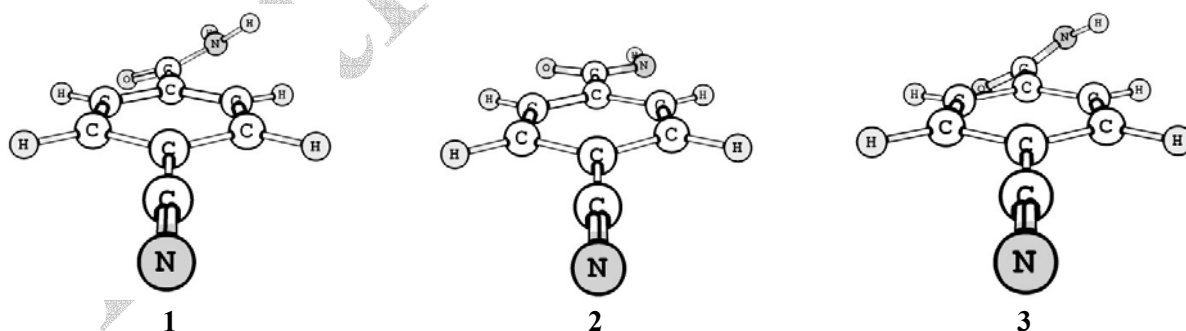
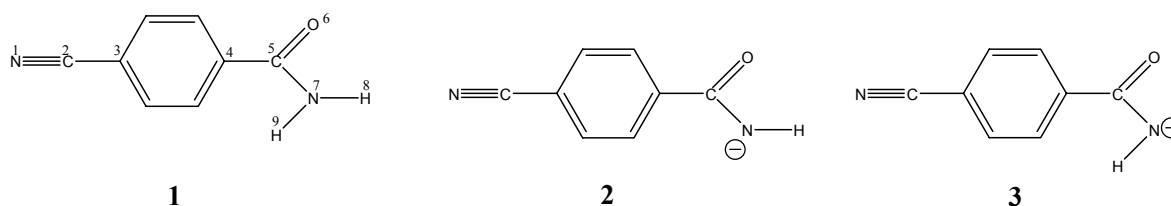


Fig. 1. B3LYP/6-31++G** optimized structures of the studied species.



Scheme 1. Possible conformers of the molecule (**1**) and azanion (**2**, **3**) of 4-cyanobenzamide.

So, having in mind $E^{\text{corr.}}$ of **1** and **2** in Table 1, we can estimate pKa (DMSO) of 4-cyanobenzamide near 14.2. Hence, 4-cyanobenzamide should be a moderately weak N–H acid, like e.g. 1,2,3-triazole, uracil or succinimide; their pKa's (DMSO) are 13.9, 14.1 and 14.6, respectively [17].

Correlation analysis

We compared B3LYP/6-31++G** vibrational frequencies for the parent molecule **1** with those measured experimentally in DMSO/DMSO- d_6 solvent. Thus, we obtained the following linear correlation (Eqn. 2):

$$v(\text{exp.}) = 0.92757v(\text{theor.}) + 74.7 \text{ (cm}^{-1}\text{)} \quad (2)$$

Correlation coefficient $R = 0.99968$; Standard deviation S. D. = 23.4 cm^{-1} ; Number of data points $n = 12$.

According to the Jaffe's classification [18], this correlation is *excellent*, with $0.99 < R < 1.00$. Eqn. 2 can be used for correlational scaling of theoretical vibrational frequencies of species studied in this work. It is known [19] (and references therein) that use of scaling equations instead of scale factors gives better results, especially in the low-frequency region. Correlational scaling is still used nowadays [15, 16, 20–24] (and references therein).

We tested Eqn. 2 in the following way:

- i) We scaled the B3LYP/6-31++G** frequencies of the anionic conformers **2** and **3**, and compared them with the experimental frequencies of the azanion, measured in DMSO/DMSO- d_6 .
- ii) We calculated the mean absolute deviations,

$$\text{m.a.d.} = n \sum_{i=1}^n |v_{\text{theor.}}^i - v_{\text{exp.}}^i| \text{ and obtained}$$

values of 9.6 and 11.8 cm^{-1} for **2** and **3**, respectively. Thus, we can say that, like the isolated azanion (Table 1), the DMSO solvated **2** predominates over the DMSO solvated **3**.

Spectral analysis

Theoretical and experimental IR data for 4-cyanobenzamide molecule (**1** in Scheme 1) are compared in Table 2. We can see there a good agreement between experimental and scaled theoretical frequencies. M.a.d. between them is 17.8 cm^{-1} , which value lies within the interval of $9\text{--}20 \text{ cm}^{-1}$, typical for the DFT calculations for molecules containing cyano or carbonyl groups [5, 16, 24–27] (and references therein). We preferred to include in Table 2 the frequencies $\nu^{\text{as}}(\text{NH}_2)$, $\nu^{\text{s}}(\text{NH}_2)$ and $\delta^{\text{sciss}}(\text{NH}_2)$, measured in CDCl_3 , as the stretching frequencies of $-\text{XH}_n$ groups ($X = \text{O, N}$ at al.), measured in DMSO, are strongly underestimated, and the bending ones

are moderately overestimated [28], obviously due to strong $-\text{XH}_n \cdots \text{O}=\text{S}(\text{CH}_3)_2$ hydrogen bonds, which effects can be estimated only qualitatively within the Onzeger's approach [29]. There are no peculiarities of the cyano stretching band: moderately high frequency $\nu(\text{C}\equiv\text{N})$ and intensity $A(\text{C}\equiv\text{N})$, as the cyano and phenylene groups are in resonance. As it can be expected [28] the carbonyl stretching band $\nu(\text{C}=\text{O})$ is very strong, the strongest one in the spectrum. A strong band corresponds to the $\nu(\text{C}-\text{N})$ vibration (No 14 in Table 2). Its frequency of 1385 cm^{-1} is very close to $\nu(\text{C}-\text{N})$ of pyridine-3-carboxamide, 1381 cm^{-1} (solvent DMSO- d_6) [26].

We compare in Table 3 theoretical and experimental IR data for the azanion of 4-cyanobenzamide (**2** in Scheme 1). The agreement between experimental and scaled theoretical frequencies is essentially better than above. M.a.d. between them is 9.6 cm^{-1} only, close to the lower limit of the corresponding integral of $9\text{--}25 \text{ cm}^{-1}$, typical for DFT calculations of vibrational frequencies for anions containing cyano or carbonyl groups [5, 16, 24–27] (and references therein). The following spectral changes take place as a result of the conversion of 4-cyanobenzamide into azanion:

- i) The computational method used predicts only qualitatively the changes in the cyano stretching band characteristics, *viz.*: $\nu(\text{C}\equiv\text{N})$ decrease, predicted 33 cm^{-1} , measured 5 cm^{-1} only; $A(\text{C}\equiv\text{N})$ increase, predicted 7.1 fold, measured 1.7 fold only.
- ii) According to the computations, the $\nu(\text{C}=\text{O})$ vibrational mode in the azanion is delocalized, taking essential parts in vibrations Nos. 7–9 in Table 3. If we take into account the average frequency values of $\nu(\text{C}=\text{O})^{\text{theor.}} = 1569 \text{ cm}^{-1}$ and $\nu(\text{C}=\text{O})^{\text{exp.}} = 1572 \text{ cm}^{-1}$ we could estimate $\nu(\text{C}=\text{O})$ decrease of: predicted 135 cm^{-1} , measured 114 cm^{-1} . Further, if we assume the total integrated intensities of the corresponding IR bands $\sum_{i=1}^3 \text{theor. } A_i(\text{C}=\text{O}) = 538.8$ and $\sum_{i=1}^3 \text{exp. } A_i(\text{C}=\text{O}) = 188.7 \text{ km}\cdot\text{mol}^{-1}$ as a measure of the azanionic $A(\text{C}=\text{O})$, we should estimate the $A(\text{C}=\text{O})$ increase as: predicted 1.6 fold, measured 1.8 fold. For comparison we calculated as above the changes in the $\nu(\text{C}=\text{O})$ IR band, accompanying the molecule \rightarrow azanion conversion in the case of pyridine-3-carboxamide (data from ref. 26). We obtained in this manner $\nu(\text{C}=\text{O})$ decrease: calculated 132 cm^{-1} , measured 122 cm^{-1} and $A(\text{C}=\text{O})$ increase: calculated 1.4 fold, measured 1.4 fold.
- iii) The $\nu(\text{C}-\text{N})$ mode is strongly delocalized in the azanion: it participates to vibrations Nos. 8, 9, 16 and 17 (Table 3).

iv) Again, according to the calculations, some statement is valid for the new $\delta(\text{CNH}^-)$ mode: it takes essential parts in vibrations Nos. 12, 16, 17 and 18 (Table 3).

Table 2. Theoretical (B3LYP/6-31++G**) and experimental (DMSO/DMSO- d_6) frequencies (ν in cm^{-1}) and integrated intensities (A in $\text{km}\cdot\text{mol}^{-1}$) of 4-cyanobenzamide molecule.

No	B3LYP/6-31++G**			Approximate description ^c	Experimental data ^a	
	ν	ν^b	A		ν	A
1	3728	3533	43.3	$\nu^{\text{as}}(\text{NH}_2)$	3528 ^d	m
2	3594	3408	54.4	$\nu^{\text{s}}(\text{NH}_2)$	3413 ^d	m
3	3228	3069	1.5	$\nu(\text{PhH})$	3095	8.1
4	3218	3060	2.1	$\nu(\text{PhH})$	3081	5.1
5	3212	3054	1.0	$\nu(\text{PhH})$	^e	-
6	3197	3040	4.7	$\nu(\text{PhH})$	3001	vw
7	2337	2242	32.4	$\nu(\text{C}\equiv\text{N})$	2230	13.4
8	1756	1704	340.5	$\nu(\text{C}=\text{O}) + \delta^{\text{sciss}}(\text{NH}_2)$	1686	106.3
9	1657	1612	5.6	$\nu(\text{Ph}) + \delta(\text{Ph}) + \delta(\text{Ph}-\text{H})$	^e	-
10	1625	1582	158.8	$\delta^{\text{sc}}(\text{NH}_2)$	1602 ^d	m
11	1601	1560	5.8	$\nu(\text{Ph}) + \delta(\text{Ph}) + \nu(\text{Ph}-\text{H})$	1561	5.7
12	1540	1503	0.7	$\delta(\text{PhH}) + \nu(\text{Ph}-\text{CO}) + \nu(\text{Ph}-\text{CN})$	^e	-
13	1437	1408	15.1	$\delta(\text{PhH}) + \delta(\text{Ph})$	1407	0.81
14	1370	1345	253.4	$\nu(\text{C}-\text{N}) + \nu(\text{Ph}-\text{CO}) + \nu(\text{Ph}-\text{CN})$	1385	76.3
15	1339	1317	29.0	$\delta(\text{PhH}) + \delta(\text{Ph})$	1291	7.6
16	1332	1310	4.8	$\delta(\text{PhH}) + \delta(\text{Ph})$	^e	-
17	1223	1209	1.4	$\delta(\text{PhH}) + \nu(\text{Ph}-\text{CN})$	^e	-
18	1206	1193	1.7	$\delta(\text{PhH})$	^e	-
19	1141	1133	8.6	$\delta(\text{PhH}) + \delta(\text{NH}_2)$	^e	-
20 ^f	1138	1130	0.6	$\delta(\text{PhH}) + \nu(\text{CO})$	^e	-

a - Measured after having decomposed the complex bands into components. Relative intensities: m, moderate; w, weak; v, very; b - Scaled, according to correlation Eqn. (1); c - Vibrational modes: ν , stretching; δ , in-plane bendings; superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; d - Solvent CDCl_3 ; e - These bands, expected as weak ones, were not detected in the experimental spectrum; f - Followed by 25 lower-frequency vibrations.

Table 3. Theoretical (B3LYP/6-31++G**) and experimental (DMSO/DMSO- d_6 , counter ion Na^+) frequencies (ν in cm^{-1}) and integrated intensities (A in $\text{km}\cdot\text{mol}^{-1}$) of 4-cyanobenzamide azanion.

№	B3LYP/6-31++G**			Approximate description ^c	Experimental data ^a	
	ν	ν^b	A		ν	A
1	3447	3272	24.0	$\nu^{\text{s}}(\text{NH}^-)$	^e	-
2	3219	3060	5.2	$\nu(\text{PhH})$	3084	vw
3	3210	3052	7.8	$\nu(\text{PhH})$	^e	-
4	3183	3027	12.9	$\nu(\text{PhH})$	3050	0.4
5	3182	3026	15.9	$\nu(\text{PhH})$	3039	5.2
6	2301	2209	227.4	$\nu(\text{C}\equiv\text{N})$	2225	22.4
7	1634	1590	87.0	$\nu(\text{Ph}) + \delta(\text{PhH}) + \nu(\text{C}=\text{O})$	1602	3.3
8	1623	1580	323.3	$\nu(\text{C}=\text{O}) + \delta(\text{PhH}) + \nu(\text{C}-\text{N})$	1581	77.5
9	1576	1537	128.5	$\nu(\text{Ph}) + \nu(\text{C}=\text{O}) + \nu(\text{C}-\text{N})$	1533	107.9
10	1518	1483	8.5	$\delta(\text{PhH}) + \nu(\text{Ph}) + \nu(\text{Ph}-\text{CO})$	1497	10.5
11	1429	1400	0.6	$\delta(\text{PhH}) + \nu(\text{Ph}) + \nu(\text{Ph}-\text{CN})$	1400	16.7
12	1389	1363	94.2	$\delta(\text{CNH}^-) + \nu(\text{Ph}-\text{CO}) + \delta(\text{OCN})$	1358	42.5
13 ^d	1343	1321	10.2	$\nu(\text{Ph})$	^e	-
14	1310	1290	0.7	$\delta(\text{PhH})$	1291	1.0
15	1211	1198	18.3	$\nu(\text{Ph}-\text{CN}) + \nu(\text{Ph}) + \delta(\text{PhH})$	1206	vw
16	1197	1185	44.8	$\delta(\text{CNH}^-) + \delta(\text{PhH}) + \nu(\text{C}-\text{N})$	1180	vw
17	1180	1169	41.3	$\delta(\text{PhH}) + \delta(\text{CNH}^-) + \nu(\text{C}-\text{N})$	^e	-
18	1127	1120	1.2	$\nu(\text{Ph}-\text{CO}) + \delta(\text{PhH}) + \delta(\text{CNH}^-)$	1128	41.0
19 ^e	1107	1102	8.9	$\delta(\text{PhH}) + \nu(\text{Ph})$	^e	-

a - Measured after having decomposed the complex bands into components. Relative intensities: w, weak; v, very; b - Scaled, according to correlation Eqn. (1); c - Vibrational modes: ν , stretching; δ , in-plane bendings; superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; d - These bands, expected as weak ones, were not detected in the experimental spectrum; e - Followed by 23 lower-frequency vibrations.

Structural analysis

There are no experimental data on the *steric structure* of either 4-cyanobenzamide or its azanion in literature. According to our computations, the conversion of the molecule into azanion causes certain essential steric structure variations (Table 4). It is seen in Table 4 that the largest R changes are the shortening of R(5, 6) with 0.044 Å lengthening of R(5, 7) with 0.048 Å. The A changes correspond to A(6, 5, 7) (8.2°) and A(5, 7, 8) (-9.8°). So, the largest changes both in bond lengths and bond angles take place *at* and *next* to the anionic center. The effects of the molecule → azanion conversion on the R(C≡N), R(C–C(N)) and A(CCN) are by 1–2 orders weaker. The analysis of dihedral angles in Table 4 shows that the non-planar 4-cyanobenzamide molecule turns into a planar azanion.

The changes in the *electronic structure* of 4-cyanobenzamide, caused by its conversion into azanion, can be demonstrated 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 (higher orders correspond to shorter bonds, under equal other conditions cf. Table 4).

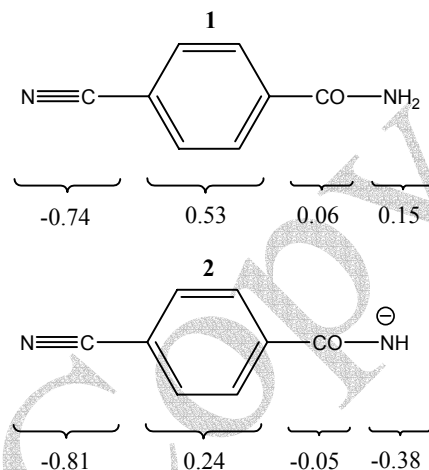
Table 4. Selected B3LYP/6-31++G** bond lengths R (Å), bond angles A (degrees) and dihedral angle D (degrees) of 4-cyanobenzamide molecule 1 and its azanion 2.

Indices ^a	Molecule	Azanion	Δ ^b
R(4, 5)	1.507	1.530	0.023
R(5, 6)	1.227	1.271	0.044
R(5, 7)	1.370	1.322	-0.048
R(7, 8)	1.010	1.024	0.014
R(2, 3)	1.436	1.432	-0.004
R(1, 2)	1.163	1.167	0.004
A(4, 5, 7)	116.6	113.7	-2.9
A(6, 5, 7)	121.9	130.1	8.2
A(5, 7, 8)	116.3	106.5	-9.8
A(10, 3, 2)	120.1	120.3	0.2
A(3, 2, 1)	179.9	180.0	0.1
D(11, 4, 5, 7)	-21.7	0.0	21.7
D(12, 4, 5, 6)	-21.5	0.0	21.5
D(6, 5, 7, 8)	6.3	0.0	-6.3

a - Atom numbering according to Scheme 1; b - Δ = Index (anion) – Index (molecule) (Å or degrees). The largest $|\Delta|$ values are given in bold.

Scheme 2 contains values of net electric charges q_i over fragments of molecule 1 and azanion 2. The electric 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, azanionic, etc.) charge between individual fragments of anions [22, 30] (and references therein). According to our calculations, the anionic charge in 4-cyanobenzamide azanion is distributed, as follows: 0.07, 0.29

and 0.11 e⁻ are delocalized over the cyano, phenylene and carbonyl groups, respectively, and 0.53 e⁻ of it remain localized in the azanionic center. The Δq_i value of the cyano group is the least one within all Δq_i to confirm the weak effect of the molecule → azanion conversion on the C≡N group of 4-cyanobenzamide (cf. above).



Scheme 2. Natural Bond Orbital (NBO) net electric charges q_i over fragments of molecule 1 and azanion 2 of 4-cyanobenzamide.

Table 5. *Ab initio* HF/6-31G** bond orders P of 4-cyanobenzamide and its azanion

Bonds ^a	Molecule	Azanion	ΔP ^b
C ² ≡N ¹	2.901	2.926	0.025
C ² -C ³	0.992	0.998	0.006
C ⁵ =O ⁶	1.812	1.547	-0.265
C ⁴ -C ⁵	0.973	0.926	-0.047
C ⁵ -N ⁷	1.048	1.647	0.599
N ⁷ -H ⁸	0.884	0.937	0.053

a - Atom numbering according to Scheme 1; b - $\Delta P = P_{\text{anion}} - P_{\text{molecule}}$. The largest $|\Delta P|$ values are given in bold.

CONCLUSIONS

We found on the basis of both experimental and computational IR data that the effect of the conversion of 4-cyanobenzamide into azanion on the cyano group was weak. This statement was confirmed by the analysis both of steric and electronic structures, computed for the species studied.

Acknowledgements: The financial support by the Bulgarian Council of Scientific Research for Project Chem. – 1510 is gratefully acknowledged.

REFERENCES

1. M. Pfannl, O. Dafert, *Monat. Chem.*, **33**, 485 (1912).
2. M. T. D. Crolin, T. W. Schultz, *Chem. Res. Toxicol.*, **14**, 1284 (2001).
3. M. T. D. Crolin, N. Manda, J. R. Steward, G. D. Sinks, T. W. Schultz, *Chem. Res. Toxicol.*, **14**, 1498 (2001).

- V. Ognianova, J. Petrov, G. N. Andreev, *J. Mol. Struct.*, **598**, 27 (1997).
- M. K. Georgieva, N. B. Nedelchev, I. N. Juchnovski, *Bulg. Chem. Commun.*, **37**, 235 (2005).
- B. A. Stamboliyska, *Bulg. Chem. Commun.*, **37**, 289 (2005).
- M. K. Georgieva, E. A. Velcheva, *Int. J. Quant. Chem.*, **106**, 1316 (2006).
- I. G. Binev, E. A. Velcheva, V. B. Radomirska, I. N. Juchnovski, *Compt. Rend. Acad. Bulg. Sci.*, **47**, 33 (1994).
- C. Crisostomo, M. G. Crestani, J. J. Garcia, *J. Mol. Catal. A*, **266**, 139 (2007).
- M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.*, **14**, 1347 (1993).
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.
- T. M. Kolev, E. A. Velcheva, B. A. Stamboliyska, *Int. J. Quant. Chem.*, **102**, 1069 (2005).
- A. D. Becke, *J. Chem., Phys.*, **98**, 5648 (1993).
- C. Lee, W. Yang, G. R. Parr, *Phys. Rev. B*, **37**, 785 (1988).
- E. A. Velcheva, G. I. Nikolova, O. I. Petrov, *Bulg. Chem. Commun.*, **38**, 263 (2006).
- L. I. Daskalova, *J. Mol. Struct. (THEOCHEM)*, **848**, 9 (2008).
- F. A. Bordwell, *Acc. Chem. Res.*, **21**, 456 (1988).
- H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
- M. Alcolea Palafox, *Recent Res. Develop. Phys. Chem.*, **2**, 213 (1996).
- I. D. Reva, S. V. Ilieva, R. Fausto, *Phys. Chem. Chem. Phys.*, **2**, 4235 (2001).
- E. A. Velcheva, P. J. Vassileva-Boyadjieva, I. G. Binev, *Bulg. Chem. Commun.*, **40**, 423 (2008).
- A. D. Popova, M. K. Georgieva, O. I. Petrov, K. V. Petrova, E. A. Velcheva, *Int. J. Quant. Chem.*, **107**, 1752 (2007).
- A. D. Popova, Y. I. Binev, P. J. Vassileva-Boyadjieva, I. G. Binev, *Bulg. Chem. Commun.*, **40**, 502 (2008).
- S. S. Stoyanov, A. D. Popova, J. A. Tsenov, *Bulg. Chem. Commun.*, **40** (2008), in press.
- M. K. Georgieva, P. J. Vassileva-Boyadjieva, P. N. Angelova, *Bulg. Chem. Commun.*, **37**, 66 (2005).
- L. I. Daskalova, E. A. Velcheva, I. G. Binev, *J. Mol. Struct.*, **826**, 1987 (2007).
- P. J. Vassileva-Boyadjieva, E. A. Velcheva, Y. I. Binev, *Bulg. Chem. Commun.*, **37**, 313 (2005).
- G. N. Andreev, *Molecular Spectroscopy*, Plovdiv University Press, 1999 (in Bulgarian).
- E. A. Velcheva, L. I. Daskalova, I. G. Binev, *Bulg. Chem. Commun.*, **36**, 230 (2004).
- E. A. Velcheva, B. A. Stamboliyska, *J. Mol. Struct.*, (2007), in press.

ИЧ-СПЕКТРАЛНИ И СТРУКТУРНИ ПРОМЕНИ, ПОРОДЕНИ ОТ ПРЕВРЪЩАНЕТО НА 4-ЦИАНОБЕНЗАМИД В АЗАНИОН. КОМБИНИРАН ЕКСПЕРИМЕНТАЛНО-ТЕОРЕТИЧЕН ПОДХОД

Й. Ан. Ценов*, С. С. Стоянов, Ив. Г. Бинев

Лаборатория „Структурен органичен анализ“, Институт по органична химия с център по фитохимия, Българска академия на науките, ул. „Акад. Г. Бончев“ бл. 9, 1113 София

Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

Постъпила на 25 януари 2008 г.; Преработена на 20 март 2008 г.

(Резюме)

Приложен е комбиниран ИЧ експериментален/DFT теоретичен подход за проследяване на спектралните и структурни промени, породени от превръщането на 4-цианобензамид в азанион. Ефектът на превръщането се проявява слабо върху валентното трептене на $\nu(\text{C}\equiv\text{N})$ и силно върху двете amidни $\nu(\text{C}=\text{O})$ и $\nu(\text{C}-\text{N})$ валентни трептения. Според изчисленията последните две форми на трептения са силно делокализирани в азаниона и по същество всяко от тях участва в няколко трептения. Отново според изчисленията, превръщането в азанион поражда значителни промени в структурата при и непосредствено до азанионния център; непланарната молекула на 4-цианобензамида преминава в планарен азанион.