

SYNTHESIS, CRYSTAL STRUCTURE AND INFRARED SPECTROSCOPIC PROPERTIES OF 4-METHYLBENZAMIDOMETHYL CYANIDE. A COMBINED EXPERIMENTAL AND QUANTUM THEORETICAL STUDY

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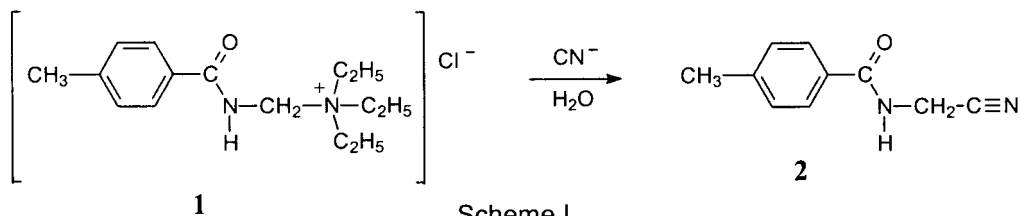
Abstract: The title compound (**1**) was synthesized in reaction of [4-methyl(benzamidomethyl)]triethylammonium chloride with cyanide anion in aqua solution.

Full geometry optimizations of the system were carried out at B3LYP, HF and MP2/6-31++G(d,p) levels of theory, employing Schlegel's gradient optimization algorithm. The located minima on the studied potential energy hypersurfaces were subsequently characterized by harmonic vibrational analysis, in order to test their character and to compute the harmonic vibrational frequencies and the corresponding IR intensities. Theoretical IR spectra of the studied system were used to make a more exact assignment of bands appearing in the experimental FT IR spectrum. Special emphasis was put on the explanations of reasons behind the very weak IR intensity of the fundamental CN stretching mode, which is quite unusual finding when this normal mode is in question.

Keywords: amidomethyl cyanide, IR spectra, ab initio method, Moller-Plesset perturbation theory, density functional theory, vibrational analysis

INTRODUCTION

In extension of our previous work of benzamidomethylation of different types of compounds [1,2], title compound **2** was obtained in a reaction of (4-methylbenzamidomethyl)triethylammonium chloride (**1**) with cyanide anion in aqua solution (Scheme I). Phenomena of absence of $\text{C}\equiv\text{N}$ bond in the infrared spectra of this compound is particularly interesting from a purely spectroscopic viewpoint, having in mind the rather characteristic features of this spectral area in nitrile compounds.



EXPERIMENTAL

(4-Methylbenzamidomethyl)triethylammonium chloride (**1**) was obtained in a similar manner as (benzamidomethyl)triethylammonium chloride described in our previous work [1].

4-Methylbenzamidomethyl cyanide (**2**). A solution of KCN (0,874 g; 13,43 mmol) in water (20 mL) in small portion was added to the water (30 mL) solution of **1** (3,826 g; 13,43 mmol). The mixture was stirred for 2-3 h at room temperature. White lumps formed, which were ground with a glass rod. Colourless crystals were collected by filtration.

The typical yield of colourless crystals Melting point of crude product was 125-130 °C. Purification was performed by dissolving the product in dioxane and precipitating with drops of cold water. The typical yield of colourless crystals with M.p 135 °C (uncorr) was 1,72 g (9,87 mmol, 73,49 %). Anal. Calcd for C₁₀H₁₀N₂O: C 68,94; H 5,78; N 16,09 %. Found: C 69,08; H 5,90; N 16,17 %. MS m/z (rel intensity) 174 (27), 119 (100), 90,9 (41) and 64,9 (17). ¹H-NMR/ppm: 9,10 (1H, t, NH); 7,79-7,29 (4H, m, Ar); 4,30 (2H, d, CH₂) and 2,35 (3H, s, CH₃); ¹³C-NMR/ppm: 166,50 C=O; 117,60 C≡N; 27,66 CH₂; 20,94 CH₃ and Aromatic: 141,97; 130,05; 129,01 and 127,35. FTIR/cm⁻¹: 3292 N-H, 1645 Amid I and 1530 Amid II.

Melting point was determined with Reichert hitting plate and was uncorrected. Carbon-hydrogen elemental analysis was carried out with Coleman Model 33. Nitrogen elemental analysis was carried out by Dumas method. The mass spectra was obtained using a Finnigan MAT8200 spectrometer. NMR spectra were recorded at Bruker 400 MHz using DMSO-*d*₆ as solvent and reference. FT-infrared spectra was measured on a Perkin-Elmer System 2000 FT IR, by the method of KBr pellets.

All X-ray crystallographic measurements were made with graphite monochromatic Mo-K α radiation at temperature of 213 K. The structure was solved by direct methods and expanded using Fourier techniques. After refinement of all non-hydrogen atoms including anisotropic displacement parameters against all reflections, the positions of hydrogen atoms were localised in a Fourier difference map and finally refined with isotropic temperature factor. Absolute configurations of the models were checked with Flack parameter, which for both present models converged to zero.

COMPUTATIONAL DETAILS

Full geometry optimizations of the title compound were carried out at HF/6-31++G(*d,p*), B3LYP/6-31++G(*d,p*) and MP2/6-31++G(*d,p*) levels of theory, employing Schlegel's gradient optimization algorithm. The second and third theoretical levels are based on methodologies that explicitly include the dynamical electron correlation effects. The second method is a density functional theory (DFT) based, and employs a combination of Becke's three-parameter adiabatic connection exchange functional (B3) with the Lee-Yang-Parr (LYP) correlation functional. Subsequently to locating the stationary points on the studied potential energy hypersurfaces (PESs), harmonic vibrational analyses were carried out in order to check the character of these stationary points and to compute the harmonic vibrational frequencies. The absence of negative eigenvalues of the second derivative matrix (Hessian matrix) indicated that the located stationary point on the PES was a true minimum (instead of, e.g. a saddle point). The standard Pople-style basis set used for orbital expansion includes diffuse functions on all atoms, polarization *p* functions on hydrogen atoms and polarization *d* functions on all non-hydrogen atoms. Within the density functional B3-LYP approach, the Kohn-Sham equations were solved iteratively for all purposes of the present study, using the "ultrafine" (99, 590) grid for numerical integration (99 radial and 590 angular integration points). The employed DFT methodology computational is in fact a hybrid HF-DFT one (*i.e.* it includes an admixture of HF exchange energy), in contrast to the "pure" DFT methods.

RESULTS AND DISCUSSION

The title compound crystallizes in orthorhombic crystal system (space group *P*2₁2₁2₁), with 8 formula units in the unit cell. The unit cell parameters are *a* = 800.68 pm, *b* = 1188.2 pm and *c* = 1949.8 pm.

The optimized geometry parameters for the title compound corresponding to the located minima on the MP2/6-31++G(*d,p*) PES are compared to the experimental crystallographic data in Table 1. In Fig. 1, the geometry of the title compound

corresponding to the minimum on MP2/6-31++G(*d,p*) PES is shown. In Fig. 2, the atomic numbering scheme is given.

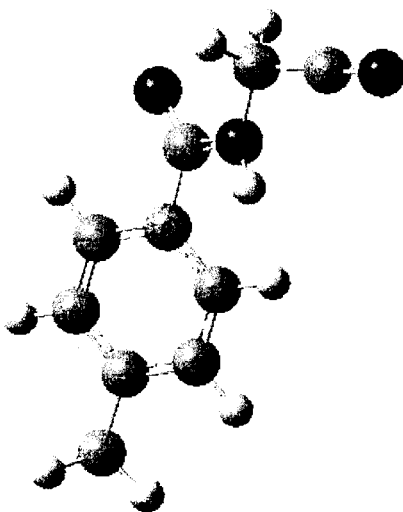


Figure 1. The optimized geometry of 4-methylbenzamidomethyl cyanide at MP2/6-31++G(*d,p*) level of theory

As can be seen from Table 1 and Figure 1, the basic structural parameters of the title compound calculated at both levels of theory are in good agreement with the crystallographic data obtained in the present study. It is worth mentioning that quantitative agreement between theory and experiment is not expected in such cases, since theoretical results refer to isolated species in gas phase, at temperature of absolute zero. The crystallographic data, on the other hand, refer to species included in a molecular crystal at room temperature, within which they certainly experience some environmental perturbation, due to both electrostatic (long-range) and exchange (short-range) forces.

In Table 2, the computed harmonic vibrational frequencies for the minimum located on MP2 hypersurface is presented. The presented values in this table were obtained by scaling the as-computed (raw) frequencies by single scaling factors of 0.9681. Such scaling is usually performed in order to account for systematical errors inherent to essentially all quantum chemical methods. The experimental spectrum is given in Fig. 3. Perhaps the most prominent feature in the appearance of the infrared spectrum of this compound is the extremely small infrared intensity of the C-N stretching band. This band is a typical feature of the IR spectra of a cyanide-group containing molecular species. The non existence of a prominent high intensity band in the corresponding spectral region was therefore quite unexpected, and even in the first phase of this research introduces certain doubts on the nature of the synthesized products. The molecular structure of the product was, however, further on verified by both NMR investigations and by crystal structure solution. One of the first reasons to which we supposed that this effect may be attributed was the crystal symmetry effect. However, both the crystal structure refinement and theoretical studies strongly support the molecular nature of this phenomenon. It seems that the non-appearance of the C-N stretching band in the infrared spectra of molecular compounds containing a -COHN(CH₂)CN fragment is more a rule than exclusion. We will demonstrate this statement in much more details in our following publications devoted to this subject.

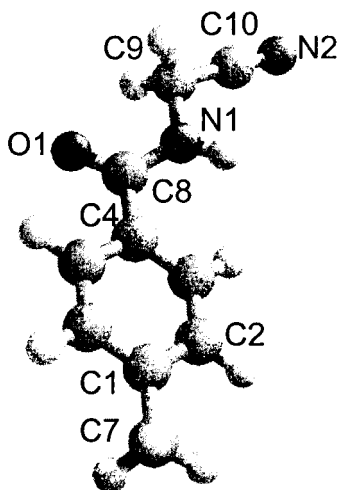


Figure 2. The atomic numbering scheme of 4-methylbenzamidomethyl cyanide

Table 1. The relevant structural parameters for the minimum located on MP2/6-31++G(*d,p*) PES of the title compound together with the experimental crystallographic data (the two sets of data refer to the two crystallographically distinct molecular species)

Parameter	MP2	Experimental
$R(O1-C8) / \text{pm}$	120.2	123.9; 123.7
$R(N1-C8) / \text{pm}$	136.5	134.5; 134.7
$R(N1-C9) / \text{pm}$	144.4	145.6; 145.7
$R(N2-C10) / \text{pm}$	113.5	114.6; 114.1
$R(C1-C6) / \text{pm}$	139.5	138.9; 138.9
$R(C1-C2) / \text{pm}$	138.9	139.5; 139.8
$R(C1-C7) / \text{pm}$	150.9	152.0; 152.3
$R(C2-C3) / \text{pm}$	138.8	138.9; 138.4
$R(C3-C4) / \text{pm}$	138.8	139.2; 139.8
$R(C4-C5) / \text{pm}$	139.3	139.6; 138.7
$R(C4-C8) / \text{pm}$	149.5	148.8; 149.7
$R(C5-C6) / \text{pm}$	138.1	138.5; 139.3
$R(C9-C10) / \text{pm}$	147.5	146.3; 146.5
$\angle C8-N1-C9 / ^\circ$	119.0	120.6; 119.6
$\angle C6-C1-C2 / ^\circ$	118.2	117.8; 117.9
$\angle C6-C1-C7 / ^\circ$	120.4	122.0; 121.1
$\angle C2-C1-C7 / ^\circ$	121.4	120.2; 121.1
$\angle C3-C2-C1 / ^\circ$	121.0	121.4; 121.8
$\angle C2-C3-C4 / ^\circ$	120.4	120.3; 119.9
$\angle C3-C4-C5 / ^\circ$	119.0	118.7; 118.8
$\angle C3-C4-C8 / ^\circ$	123.2	122.2; 123.9
$\angle C5-C4-C8 / ^\circ$	117.8	119.1; 117.3
$\angle C6-C5-C4 / ^\circ$	120.4	120.4; 120.9
$\angle C5-C6-C1 / ^\circ$	121.0	121.5; 120.8
$\angle O1-C8-N1 / ^\circ$	121.1	120.9; 120.2
$\angle O1-C8-C4 / ^\circ$	122.3	122.2; 121.4
$\angle N1-C8-C4 / ^\circ$	116.6	116.9; 118.5
$\angle N1-C9-C10 / ^\circ$	109.9	111.0; 112.2
$\angle N2-C10-C9 / ^\circ$	179.0	179.6; 179.5

Table 2. The calculated harmonic vibrational frequencies and infrared intensities for the minimum located on MP2/6-31++G(d,p) PES of the title compound (only the highest-frequency 40 modes are given)

No.	MP2		Mode description
	ν / cm^{-1}	$I / \text{km mol}^{-1}$	
1	3465.4	43.5	$\nu(\text{NH})$
2	3017.1	1.9	$\nu(\text{CH})_{\text{ring}}$
3	2996.5	12.3	$\nu(\text{CH})_{\text{ring}}$
4	2979.0	11.0	$\nu(\text{CH})_{\text{ring}}$
5	2977.1	14.9	$\nu(\text{CH})_{\text{ring}}$
6	2941.9	2.2	$\nu(\text{CH})_{\text{CH}_2}$
7	2909.3	22.6	$\nu(\text{CH})_{\text{CH}_3}$
8	2886.6	19.8	$\nu(\text{CH})_{\text{CH}_3}$
9	2868.2	17.6	$\nu(\text{CH})_{\text{CH}_2}$
10	2836.2	34.3	$\nu(\text{CH})_{\text{CH}_3}$
11	2322.1	9.4	$\nu(\text{CN})_{\text{nitrile}}$
12	1708.2	404.2	$\nu(\text{CO}) + \delta(\text{NH})$
13	1610.0	61.4	$\nu(\text{CC})_{\text{ring}}$
14	1562.5	13.2	$\nu(\text{CC})_{\text{ring}}$
15	1511.2	272.8	$\nu(\text{CO}) + \delta(\text{NH}) + \delta(\text{CH})_{\text{ring}}$
16	1486.5	196.5	$\nu(\text{CO}) + \delta(\text{NH}) + \delta(\text{CH})_{\text{ring}}$
17	1447.2	5.9	$\delta(\text{CH}_2)_{\text{scissoring}}$
18	1439.0	7.6	$\delta(\text{CH}_3)$
19	1431.4	6.6	$\delta(\text{CH}_3)$
20	1382.5	1.7	$\delta(\text{CH}_3) + \delta(\text{CH})_{\text{ring}}$
21	1376.4	0.3	$\delta(\text{CH}_3) + \delta(\text{CH})_{\text{ring}}$
22	1345.1	16.5	$\delta(\text{CH}_2)$
23	1293.1	0.4	$\delta(\text{CH})_{\text{ring}}$
24	1244.8	250.3	$\nu(\text{CN}) + \delta(\text{NH}) + \delta(\text{CH})$
25	1207.1	2.8	$\delta(\text{NH}) + \delta(\text{CH}_2)$
26	1180.2	27.7	$\nu(\text{CC})_{\text{ring-Kekule-mode}}$
27	1170.3	2.4	$\nu(\text{CC})_{\text{ring-Kekule-mode}}$
28	1158.2	33.0	$\delta(\text{CH})_{\text{ring}}$
29	1123.2	24.7	$\nu(\text{CC})_{\text{ring-breathing}} + \nu(\text{CC})$
30	1067.0	1.8	$\delta(\text{CH})_{\text{ring}} + \nu(\text{CC})_{\text{ring}}$
31	1044.1	4.5	$\nu(\text{NC}_2)$
32	1037.1	3.8	$\delta(\text{CH}_3)$
33	994.6	0.4	$\delta(\text{CH})_{\text{ring}}$
34	991.4	3.1	$\delta(\text{CH})_{\text{ring}} + \delta(\text{CC})_{\text{ring}}$
35	977.1	8.5	$\delta(\text{CH}_3) + \delta(\text{CH}_2)$
36	969.6	0.4	$\delta(\text{CH})_{\text{ring}}$
37	963.0	4.5	$\delta(\text{CH}_3) + \delta(\text{CH})_{\text{ring}}$
38	923.4	4.7	$\nu(\text{CC}(\text{N}))$
39	849.3	4.7	$\delta(\text{CH})_{\text{ring}}$
40	834.8	19.1	$\delta(\text{CH})_{\text{ring}}$

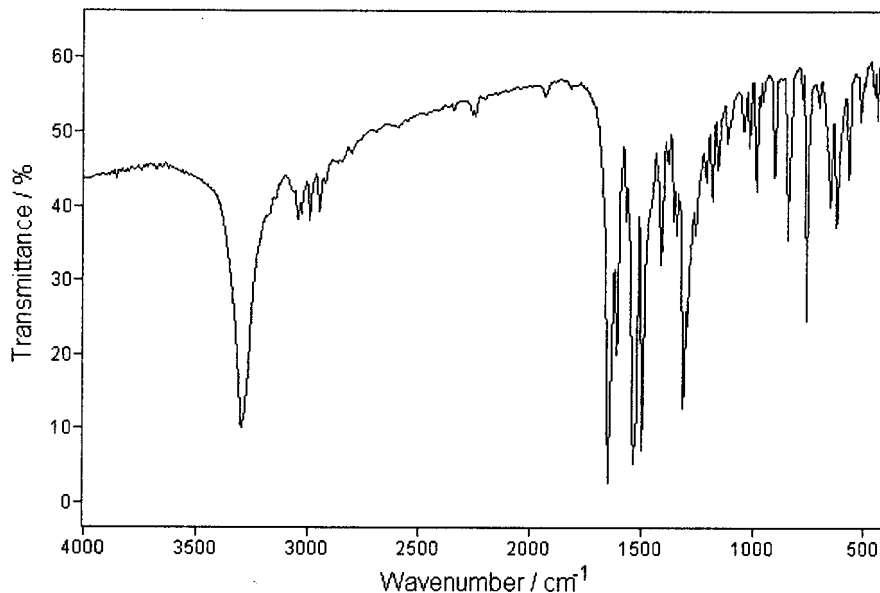


FIGURE 3. THE EXPERIMENTAL FT IR SPECTRUM OF THE STUDIED COMPOUND

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