

## INFRARED SPECTRA AND STRUCTURE OF CARBANIONS

### XVIII. A semiempirical study of carbanions of cyanoacetic acid derivatives\*

J. KANETI, A. FATTAH NAZIR,\*\* I. G. BINEV, V. B. RADOMIRSKA and  
I. N. JUCHNOVSKI

*Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia (Bulgaria)*

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#### ABSTRACT

The IR spectra of cyanoacetic acid, ethyl cyanoacetate and cyanoacetamide as well as those of related mono- and, whenever possible, dianions have been studied in dimethylsulphoxide (DMSO) and DMSO- $d_6$ . The observed nitrile and carbonyl absorption frequencies correlate linearly with the corresponding Wiberg bond indices given by CNDO/2 calculations with full geometry optimization. These calculations predict carbanionic structures throughout except in the case of the dinegative ion of cyanoacetamide, which could be considered as originating from the aminoacetylenic tautomer of  $\text{NCCH}_2\text{CONH}_2$ . Parallel MINDO/3 calculations, however, predict that the latter dianion is again a carbanion. This result is in reasonable agreement with normal coordinate calculations and the experimental isotopic shifts of vibrational frequencies of the dianion  $^{13}\text{CCH}^-\text{CONH}^-$ .

#### INTRODUCTION

Organometallic derivatives of cyanoacetic acid are the simplest models of the Ivanoff reagent [1]. An extensive study of the related carbanions would thus obviously be useful for a better understanding of the chemical reactivity of these polyfunctional reagents. The IR absorption of these compounds in the 1400–1800 and 2000–2300  $\text{cm}^{-1}$  frequency regions, because of carbonyl and nitrile vibrations, is a good source of structural information. A solvent convenient for the intended study is DMSO because nitrile frequencies of certain carbanions are practically independent of the counterion due probably to complete dissociation [2]. In addition, the use of DMSO is convenient for comparison of the experimental data with the results of semiempirical molecular orbital calculations; for example, it has been recently reported that the calculated CNDO/2 gas phase  $\text{pK}^{\text{a}}$ -values of substituted methanes correlate perfectly with the experimental values measured in the same solvent [3].

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\*\*Research student from the Afghanistan Academy of Sciences, Kabul, Afghanistan.

The presence of the studied carbanions in DMSO solutions is conveniently detected using the intense absorption at about  $2100\text{ cm}^{-1}$  in the IR spectra which is assigned to nitrile band shifted down because of the conjugation [4]. The carbonyl frequencies (DMSO- $d_6$ ) are shifted downwards too and, together with the nitrile frequencies are suitable indicators of the structure and, possibly, the ionic aggregation of the studied species.

#### EXPERIMENTAL

The 1 to 4% solutions of the studied anions were prepared by addition of DMSO solutions of neutral compounds to excess dry sodium methoxide in 1 ml glass ampoules under pure argon. Dianions were prepared by mixing a concentrated solution of  $\text{NaCH}_2\text{SOCH}_3$  with solutions of neutral  $\text{NCCH}_2\text{CONH}_2$  or  $\text{NCCCH}_2\text{COOH}$  under argon. The generated carbanion solutions remain unchanged for several hours i.e. long enough for spectral measurements. Infrared spectra were taken in  $\text{CaF}_2$  cells (0.03–0.24 mm path length) on a Carl Zeiss Jena UR-20 spectrophotometer.

$^{15}\text{NCCH}_2\text{CONH}_2$  was synthesized by alkylation of KCN (50%  $^{15}\text{N}$ ) with ethyl bromoacetate and followed by ammoniolysis by 25% aqueous ammonia.

#### RESULTS AND DISCUSSION

Nitrile and carbonyl frequencies of neutral cyanoacetic acid and its derivatives (Table 1) are distributed in relatively narrow frequency ranges and data discerning the different substituents to the carbonyl group are provided by the carbonyl frequencies only. The monoanion of cyanoacetic acid has a  $\nu_{\text{CN}}$  band at a slightly lower frequency as might have been expected from the inductive effect of the carboxylate anion. The carbanionic center in the remaining mono- and dianions gives rise to the possibility for conjugative interaction and consequently to a strong decrease in the vibrational frequencies: the shift of the nitrile frequencies for the studied molecules is between  $120$  and  $160\text{ cm}^{-1}$  and that of the carbonyl frequencies from  $130$  to  $300\text{ cm}^{-1}$ . These changes of the vibrational properties indicate considerable structural changes in the studied anions and deserve a detailed quantum chemical study. We started with CNDO/2 calculations [5] using a computer program for complete optimization of the molecular geometry [6]. As predicted by these calculations, bond lengths between the heavy atoms in the studied carbanions generally demonstrate a tendency to become closer to each other (Table 2) whereas the valence angles become close to  $120^\circ$ . Similar results have been reported for allyl carbanions [7, 8] where C—C bonds are nearly equal in length. The present results are consistent with the CNDO/2 data for the carbanion of acetonitrile [4] where a planar structure with strong conjugation between the nitrile group and the carbanionic center has been predicted.

We attempted to find a quantitative relationship between the experimental vibrational frequencies and the calculated MO indices avoiding a CNDO-

TABLE 1

Carbonyl and nitrile frequencies ( $\text{cm}^{-1}$ ) of cyanoacetic acid derivatives and calculated Wiberg bond indices for the optimized molecular geometries

Compound			CNDO/2		MINDO/3	
	$\bar{\nu}_{\text{CO}}$	$\bar{\nu}_{\text{CN}}$	$W_{\text{CO}}$	$W_{\text{CN}}$	$W_{\text{CO}}$	$W_{\text{CN}}$
NCCH <sub>2</sub> COOH	1728	2259	1.8247	2.8640	1.6563	2.8732
NCCH <sub>2</sub> COO <sup>-</sup>	1634 as 1450 sym	2250	1.4679	2.8213	1.3760 1.3834	2.8177
NCCH <sup>-</sup> COO <sup>-</sup>	1475 as 1366 sym	2113	1.3349	2.5058	1.2447	2.4883
NCCH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	1747 <sup>a</sup>	2259 <sup>a</sup>	1.8189	2.8624	1.6543	2.8721
NCCD <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	1747 <sup>a</sup>	2260 <sup>a</sup>				
NCCH <sup>-</sup> CO <sub>2</sub> CH <sub>3</sub>	1615 <sup>a</sup>	2144 <sup>a</sup>	1.4406	2.6785	1.4324	2.6981
NCCD <sup>-</sup> CO <sub>2</sub> CH <sub>3</sub>	1615 <sup>a</sup>	2144 <sup>a</sup>				
NCCH <sub>2</sub> CONH <sub>2</sub>	1702	2259	1.7144	2.8647	1.5535	2.8697
NCCH <sub>2</sub> CO <sup>+</sup> NH <sub>2</sub>	1698	2259				
<sup>13</sup> NCCH <sub>2</sub> CONH <sub>2</sub>	1702	2238	1.4065	2.6650	1.3532	2.6726
NCCH <sup>-</sup> CONH <sub>2</sub>	1564	2129				
<sup>13</sup> NCCH <sup>-</sup> CONH <sub>2</sub>	1565	2110	1.3302	1.3231 <sup>b</sup>	1.2120	2.4645
NCCH <sup>-</sup> CONH <sup>-</sup>	1455	2093.5				
<sup>13</sup> NCCH <sup>-</sup> CONH <sup>-</sup>		2072				

<sup>a</sup> Experimental frequencies for ethyl esters. <sup>b</sup> Bond index for the acetylenic triple bond  $W_{\text{CC}(\text{N})} = 2.5263$ .

TABLE 2

Optimized CNDO/2 and MINDO/3 (second rows) bond lengths of cyanoacetic acid derivatives

Compound	N=C	(N)C-C	C-C(O)	C=O	C-O	C-N
NCCH <sub>2</sub> COOH	1.191	1.426	1.457	1.268	1.367	
	1.159	1.465	1.507	1.223	1.344	
NCCH <sub>2</sub> COO <sup>-</sup>	1.194	1.420	1.481	1.300	1.301	
	1.165	1.460	1.561	1.259	1.260	
NCCH <sup>-</sup> COO <sup>-</sup>	1.220	1.370	1.428	1.320	1.322	
	1.192	1.388	1.461	1.291	1.295	
NCCH <sub>2</sub> COOCH <sub>3</sub>	1.191	1.426	1.475	1.260	1.400	
	1.159	1.464	1.511	1.221	1.339	
NCCH <sup>-</sup> COOCH <sub>3</sub>	1.200	1.370	1.390	1.310	1.390	
	1.172	1.412	1.397	1.247	1.391	
NCCH <sub>2</sub> CONH <sub>2</sub>	1.191	1.426	1.460	1.277		1.373
	1.160	1.464	1.513	1.233		1.334
NCCH <sup>-</sup> CONH <sub>2</sub>	1.200	1.373	1.391	1.314		1.398
	1.175	1.410	1.414	1.260		1.368
NCCH <sup>-</sup> CONH <sup>-</sup>	1.342	1.239	1.422	1.320		1.343
	1.194	1.384	1.470	1.291		1.330

FORCE calculation. This can be done, as recently shown [4], using the Wiberg bond indices [9]. The following correlation of the studied nitrile frequencies and the corresponding Wiberg indices (Table 1) was found

$$\bar{\nu}_{\text{CN}} = 473.7 W_{\text{CN}} + 898.5 \text{ cm}^{-1}$$

where correlation coefficient,  $r = 0.955$ , for 7 data points. Taking for the carboxylate ion the average value of the symmetric and antisymmetric frequencies, we obtained

$$\bar{\nu}_{\text{CO}} = 535 W_{\text{CO}} + 774.6 \text{ cm}^{-1}$$

where  $r = 0.931$  and  $n = 7$ . These two correlations are close enough to be considered as a general relationship between the Wiberg bond indices and the observed carbonyl and nitrile frequencies

$$\bar{\nu}_{\text{CX}} = 498 W_{\text{CX}} + 832 \text{ cm}^{-1}$$

where  $r = 0.995$  and  $n = 14$ .

It is known that semiempirical MO calculations predict stretching force constants systematically larger than the values obtained from normal coordinate calculations [10]. The latter correlation however gives hope that Wiberg indices could provide better estimates for these values. However, the required stretching force constant can be found semiempirically with the aid of a correlation between the bond indices and known experimental values for several simple molecules.

Going back to the structure of mono- and dianions, predicted by the present CNDO/2 calculations, one can see that among the normal carbanions, the dinegative ion of cyanoacetamide shows a quite unusual structure, viz. a doubly deprotonated aminoacetylene carboxamide (see the bond lengths in Table 2). This structure reminds us of the early suggestions of tautomeric forms of acetonitrile anion [11] and of anions of acetonitriles with conjugated substituents [12]. These concepts were criticized recently on the basis of extensive experimental and theoretical studies [4, 13]. This dianion shows an absorption band at  $2093 \text{ cm}^{-1}$  (in DMSO) that can be assigned either to a nitrile vibration or to a vibration of an acetylenic triple bond. The bond index of the acetylenic bond in this structure and the observed absorption frequency correspond to the correlation  $W_{\text{CX}} - \bar{\nu}_{\text{CX}}$  (see Fig. 1). It is, therefore, cumbersome to answer the questions concerning the actual structure of the dianion of cyanoacetamide and the assignment of its  $2093 \text{ cm}^{-1}$  absorption band on the basis of the present CNDO/2 calculations only. Additional data could result from a normal coordinate treatment of this subject as well as from more reliable, e.g. MINDO/3 calculations. The use of Wiberg bond indices in the intended GF calculations can certainly facilitate the choice of the required (stretching) force constants for the structure in question. The experimental result that is to be reproduced by these calculations is the observed  $^{15}\text{N}$ -isotopic shift of the  $2093 \text{ cm}^{-1}$  absorption band of the dinegative ion of cyanoacetamide. This value, as shown in Table 1, is a  $21 \text{ cm}^{-1}$  down-

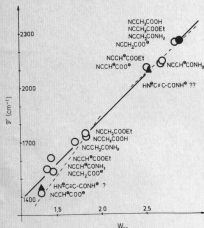


Fig. 1. Nitrile and carbonyl frequencies of cyanoacetic acid derivatives vs. CNDO/2 bond indices. Dark triangles correspond to the CNDO/2 (incorrect) structure of cyanoacetamide dianion.

ward shift. Qualitatively, this large isotopic shift indicates that the CNDO/2 structure of cyanoacetamide dianion is quite doubtful.

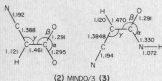
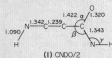
The MINDO/3 [14] calculations carried out predict that deprotonation gives rise to smooth changes of bond lengths of cyanoacetamide and retention of its functional groups (see Table 2). The only difference between the mono- and dianion of this compound is that in the latter case the conjugation between the nitrile group and the carbanion site is stronger as indicated by the calculated bond lengths. The conjugation between the carboxamide group and the carbanion site in the dianion, however, should be weaker than in the monoanion. Qualitatively this result seems to be in better agreement with the recent concepts on the structure of metalloacetonitriles and related carbanions [4, 13] than the CNDO/2. The final solution of this problem could be obtained, in our opinion, with the aid of vibrational analysis. We decided to choose the stretching force constants according to the corresponding bond indices and looked for a correlation of these indices with known force constants of HCN, CH<sub>3</sub>CN [15], CH<sub>2</sub>O [16] and <sup>-</sup>CH<sub>2</sub>CN [4]. Taking the Wiberg indices for all bonds in the optimized structures of these molecules we obtained

$$F = 6.73 W(\text{CNDO}/2) - 0.25 \text{ N} \cdot \text{m}^{-1} \cdot 10^{-2}$$

and

$$F = 6.17 W(\text{MINDO}/3) + 0.35 \text{ N} \cdot \text{m}^{-1} \cdot 10^{-2}$$

These two correlations were used for the choice of the stretching force constants for the structures given below.



$$1 \alpha = 120^\circ; \beta = 113.5^\circ; \gamma = 117.3^\circ$$

$$2 \alpha = 126.6^\circ; \beta = 117^\circ; \gamma = 134.4^\circ$$

$$3 \alpha = 115.1^\circ; \beta = 128.6^\circ; \gamma = 135^\circ$$

Diagonal force constants for bending and other vibrations as well as interaction force constants cannot be selected in this manner and were taken from the reported experimental values for similar molecular fragments [15-17]. The calculation for the CNDO/2 structure of cyanoacetamide dianion (1) gave  $2389 \text{ cm}^{-1}$  for the vibration of the acetylenic bond and  $2387 \text{ cm}^{-1}$  for the same in the  $^{15}\text{N}$ -labelled species. This result obviously does not correspond to the available experimental data, that is, the structure of the dinegative ion of cyanoacetamide predicted by the present CNDO/2 calculations can be certainly regarded as a failure.

The GF calculation for the MINDO/3 structure (2) with stretching force constants from the second of the above relationships between bond indices and force constants and remaining elements of the force constant matrix as in the previous case yielded a nitrile frequency for the  $^{14}\text{N}$ -species of  $2221 \text{ cm}^{-1}$  and  $2206 \text{ cm}^{-1}$  for the  $^{15}\text{N}$  dianion. This result corresponds fairly well with the experimental frequencies and reproduces satisfactorily the observed  $^{15}\text{N}$  isotopic shift. We can thus regard it as evidence that the actual structure of cyanoacetamide dianion is correctly predicted by the present MINDO/3 calculations. The difference between calculated and experimental frequencies is well within the reported average error of nitrile frequencies obtained with the aid of MINDO/3 [18].

The structures of the second dianion, that of cyanoacetic acid itself, predicted by CNDO/2 and MINDO/3 are quite similar (Table 2). For confidence we made an additional GF calculation for the MINDO/3 geometry (3). Stretching force constants were calculated as mentioned above; the remaining elements of the force constant matrix were taken from a calculation of

the propiolate anion  $\text{HC}\equiv\text{C}-\text{COO}^-$  [17]. This calculation predicted a nitrile frequency of  $2188\text{ cm}^{-1}$  and two "carbonyl" (that is, merely  $\text{C}-\text{C}-\text{O}$ ) frequencies of  $1596$  and  $1478\text{ cm}^{-1}$ . These values again reproduce the experimental data within the reported MINDO/3 corrections [18]. The observed splitting of carboxylate frequencies,  $109\text{ cm}^{-1}$ , is well reproduced by the predicted value of  $118\text{ cm}^{-1}$ . Thus, one can conclude that the structure of this important dianion, the free carbanion of the Ivanoff reagent, is predicted qualitatively correctly by both CNDO/2 and MINDO/3 methods. This structure, however, does not correspond to the dienolate structure



The potential surfaces of the studied carbanions obtained with the aid of the present semiempirical MO calculations possess single minima, that is, no tautomerism of nitrile anions as supposed earlier [11, 12] is predicted. This result is consistent with the experimental and theoretical studies of acetonitrile carbanion [4] and carbanions of acetonitriles with conjugated substituents [13]. We can conclude once more that one and only one conjugated base corresponds to the possible stable tautomeric forms of neutral  $\text{C}-\text{H}$  acidic molecules [19].

#### CONCLUSIONS

Semiempirical MO calculations reproduce the structures of carbanions with conjugated substituents reasonably well. Caution should be exercised, however, in the cases of dinegative ions of polyfunctional molecules where CNDO/2 could fail to predict the correct geometry. In such cases MINDO/3 predictions appear more reliable.

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