# INFRARED SPECTRA AND STRUCTURE OF CARBANIONS—XIII\*

## A STUDY OF THE CARBANIONS GENERATED FROM ACETONITRILE, ACETONITRILE-D<sub>3</sub> AND ACETONITRILE-<sup>13</sup>N

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Abstract—The study of the IR spectral data for metallated acetonitrile (counter ions Li<sup>\*</sup>, Na<sup>\*</sup>, K<sup>\*</sup> in solvents tetrahydrofuran, THF, and hexamethylphosphotriamide, HMPT) and its D<sub>3</sub>- and <sup>13</sup>N- derivatives together with CNDO/2 and normal coordinate calculations showed that the mesomeric ion H<sub>2</sub>C=C=N has a favoured planar structure and the carbon-metal bond has a pronounced ionic character.

Metallation of acetonitrile gives a highly reactive intermediate with a carbanionic structure capable of undergoing miscellaneous chemical transformations.<sup>1</sup> This carbanion being one of the smallest cyano containing has incited a number of papers dealing mainly with its spectral properties and aiming at the elucidation of the electronic structure of metallated MeCN and the nature of its bonding with the counter ion.<sup>2-5</sup>

Some of these studies have promoted the concept of the simultaneous presence of a number of prototropic and metallotropic forms in the solutions of alkali metal derivatives of acetonitrile,<sup>2-4</sup> and others assume a polymer associated nature of lithium-acetonitrile.<sup>4</sup> The hypothesis of Krüger<sup>2</sup> on the existence of tautomeric species of acetonitrile-lithium is currently accepted in the literature<sup>3-3</sup> (Scheme 1).

$$\begin{array}{ll} M-CH_{2}-C = N \neq \pm M-CH = C = NH \neq \pm M-C=C-NH_{2} \\ (1) & (2) & (3) \\ (4) H-C = C-NH-M \neq \pm H_{2}C = C = N-M (5) \\ & Scheme 1. (M = Li, Na) \end{array}$$

We have demonstrated<sup>4</sup> that, most probably, the mesomeric carbanion species of lithium-acetonitrile exist as ion pair structures and that a considerable amount of the infrared data used to confirm the existence of metallotropic and prototropic species are in fact pertinent to products of further transformations of metallated acetonitrile.

The high reactivity of metallated acetontrile and its tendency to dimerize cause serious difficulties in the investigation of its spectra.<sup>4</sup> We were restricted to study the frequency region between 1900 and 2600 cm<sup>-1</sup> because of the necessity to use metallating agents and solvents themselves showing intense and complex IR absorption outside this region. It is useful therefore to consider the available IR data concerning the effects of counter ions and isotope substitutions together with the results obtained by quantum chemical and normal coordinate calculations for a confident interpretation.

#### RESULTS AND DESCUSSION

The IR spectra of metallated acetonitrile and its Dyand <sup>13</sup>N- isotopic derivatives were recorded in the region 1900-2600 cm<sup>-1</sup> in solvents THF and HMPT with counterions Li\*, Na\* and K\* (see Experimental). The stretching absorption band of metallated acetonitrile, as given in Table 1, appears in the rather narrow region 2050-2072 cm<sup>-1</sup> and is practically independent of the substantial differences between the solvating ability of the two solvents and the nature of the counter ions. These small frequency shifts indicate that we deal with practically the same anionic structure in all cases and the stretching vibrational frequency is influenced by the solvents and counterions to the extent usual for carbanions.<sup>4-8,12</sup> It has been recently demonstrated<sup>4-9</sup> that the replacement of K\* for Li\* causes an enhancement of PCN in carbanions of substituted aryl- and alkyl-acetontriles by about 10 cm<sup>-1</sup>. The replacement of the solvent THF for HMPT also causes an enhancement of the same frequencies of the order of 10 cm<sup>-1</sup>. These data, as well as the extremely high intensity of the nitrile absorption band ( $A \sim 6 \times 10^4$  1. g-ion<sup>-1</sup>. cm<sup>-2</sup>, observed for the strongly conjugated carbanions of substituted benzylcyanides too<sup>9-12</sup> support the assumption of an ionic character of the bond formed between the alkali metal cation and the acetonitrile carbanion. One should, therefore, consider as possible the mesomeric anions 6-8 below instead of the metallotropic species in Scheme 1.

$$[^{C}CH_{2}-C = N \leftrightarrow H_{2}C = C = N^{-}], M^{*}$$
(6)

$$[HC = C - NH^{-} \leftrightarrow CH = C = NH], M^{*}$$
(7)

$$[^{-}C = C - NH_2], M^*$$
 (8)

Scheme 2. (M = Li, Na)

The isotopic shift of the observed intense absorption band due to the replacement of <sup>14</sup>N by <sup>15</sup>N (Table 1) is  $22 \text{ cm}^{-1}$ . Thus, an assignment of this absorption to the amino-acetylenide anion 8 would be erroneous because the normal coordinate treatment of the triatomic fragment N-CmC gives a value smaller than 5 cm<sup>-1</sup> (general valence force field, force constants taken from Ref. 13). On the other hand, the amino acetylenide species should be

<sup>\*</sup>Part XI: Tetrahedron 33, 2993 (1977).

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		P <sub>CN</sub> of neutral molecules & isotopic		Carbanions with different counter ions PCN(Cm <sup>-1</sup> )				r ions	
Compound	Solvent	Shifts(	cm'')	LI'		Na*		Κ.	
CH CN	111.650	2249		2050		2051		2051	
CH <sub>3</sub> CN	HMPI	2295w		2072	_	2061		2061	
	THE	2252		2051	_	2050		2049	
	1111	2293w		2062		2065sh			
	HMPT	2257	- 8	2050	0	2051	I	2050	1
CD <sub>2</sub> CN				2045		2043		2041	
	THF	2261	- 9	2054		2065sh			
CH.C <sup>B</sup> N	UMPT	2222	27	2028	22	2029	22	2029	22
unge a	net i	2288w	7	2050	22	2041	20		-

Table 1.

regarded as less probable because of the lower electronegativity of C as compared to N and because of the localization of the negative charge since no possibilities for conjugation exist. The measured  $^{14}N-^{15}N$  isotopic shift for metallated acetonitrile is only slightly smaller than the values for neutral nitriles (Table 1<sup>14</sup>) and is close to that of anion radicals of aromatic nitriles.<sup>14</sup> This indicates the prevailing participation of the C=N bond in the observed normal mode. The metallation, therefore, does not give rise to drastic changes of bond multiplicities in the indictor group C-C=N.

We measured isotopic shifts of  $0-1 \text{ cm}^{-1}$  in HMPT and  $0-8 \text{ cm}^{-1}$  in THF for the band discussed (Table 1) on perdeuteration of acetonitrile. The ynamide species 7 however supposes strong mechanical coupling of D-C and CmC bonds and consequently a large H-D isotopic shift of the order of the reported  $168 \text{ cm}^{-1}$  for HCN-DCN<sup>15</sup> or  $133-135 \text{ cm}^{-1}$  for CH<sub>2</sub>CmCH-CH<sub>3</sub>CmCD.<sup>15</sup> The small value of the H-D shift indicates that the participation of C-H coordinates in the observed normal mode is insignificant and contradicts to the assignment to the ynamide 7. Thus, the above considerations clearly



Fig. 1. IR spectra of HMPT solutions of: (a) (....) acetonitrile, 1 g-mole.1<sup>-1</sup>; (-----) acetonitrile-lithium,  $5 \times 10^{-2}$  g-ion.1<sup>-1</sup>; (b) (.....) acetonitrile (52% at. <sup>15</sup>N), 1 g-mole.1<sup>-1</sup>; (------) acetonitrilelithium (52% at. <sup>15</sup>N),  $5 \times 10^{-2}$  g-ion.1<sup>-1</sup>.

indicate that the species showing the observed IR spectra is the carbanion 6.

The absorption bands observed for carbanions with Li\* and Na\* counterions are split in doublets (Table 1). This property cannot be due to such intramolecular reasons as, e.g. Fermi resonance since similar intense doublets are found in the IR spectrum of "CH<sub>2</sub>C"N, (Fig. 1). The "N-"N isotopic shift for the two components of the last compound is equal, therefore the two species giving rise to these bands should be very similar and the reason for the appearance of two PCN frequencies for metallated acetonitriles is probably the different environment of the carbonionic particles. Thus, the doublet character of the  $\nu_{CN}$  bands could be related to the presence of "free" carbanions and solvent separated ion pairs. This assignment is supported by the fact that the shape of the observed doublets is different with different counter ions Li\*, Na\*, K\* and at different concentrations of the counter ions (Figs. 2 and 3). This enables us to attribute the first of the two observed bands at 2050-2051 cm<sup>-1</sup> to the PCN of "free" carbanions and the second one at 2061-2072 cm<sup>-1</sup> (depending on the counter ion) to the  $\nu_{CN}$  of the ion pair. The spectrum presented on Fig. 1 can be assigned as follows:

2072 cm<sup>-1</sup>  $\nu_{\rm C}$  14<sub>N</sub> of solvent separated ion pairs;

 $2050 \text{ cm}^{-1}\nu_{\rm C}14_{\rm N}$  of "free" carbanions;

2050 cm<sup>-1</sup>  $\nu_{\rm C} 15_{\rm N}$  of solvent separated ion pairs;

2028 cm<sup>-+</sup>v<sub>C</sub>15<sub>N</sub> of "free" carbanions.

It is difficult to suggest a reliable assignment of the components of the  $\nu_{CN}$  doublets observed in THF. These are clearly registered for counter ion Li<sup>\*</sup> but the shoulder at higher frequency disappears entirely for counter ion K<sup>\*</sup>. In this case the dependence of the shape of the observed absorption bands on the type of the counterions is weak, but in general the frequencies go higher in the sequence K<sup>\*</sup>, Na<sup>\*</sup>, Li<sup>\*</sup> as observed previously<sup>4\*</sup> for carbanions of secondary nitriles and benzylcyanides.

The above qualitative interpretation of isotope effects and the comparison of the data obtained by measurements in the two different solvents indicate that the structure of the anion of acetonitrile is  $H_2C=C=N$ , in complete agreement with our results of CNDO/2 calculations<sup>16</sup> for this ion.

The total energy of the carbanion of acetonitrile was

minimized with respect to all geometric parmeters of the molecule. The following optimum values were found:  $R_{C=N} = 1.255 \text{ A}$ ;  $R_{C=C} = 1.355 \text{ A}$ ;  $R_{C=H} = 1.116 \text{ A}$ ; angle HCH-118°. The favoured structure of the ion is planar C<sub>2v</sub>. The charge distributions (optimized geometries) for  $^{-}CH_2CN$  and  $CH_3CN$  are compared below:

	Qu	Qr	Qc	Qw
CH,CH	- 0.0722	- 0.4122	0.0640	- 0.5073
CH,CN	0.0318	- 0.0163		- 0.1693

It is well known that CNDO/2 calculations predict bond lengths for multiple bonds 0.02–0.03 A longer than the experimental ones,<sup>16</sup> whereas the lengths of the single bonds C-C are predicted 0.01–0.06 A too short. Therefore, we can assume the following bond lengths as more realistic:  $R_{CN}$ -1.20 A and  $R_{CC}$ -1.38 A. This value for  $R_{CN}$  agrees fairly with the correlation  $\nu_{CN}$ - $R_{CN}$ suggested by Ritsch1<sup>17</sup> which gives for  $\nu_{CN}$  = 2050 cm<sup>-1</sup> a value of  $R_{CN}$  1.19–1.21 A. This implies that the multiplicity of the Ci=N bond in the carbanion is substantially reduced as compared with the parent nitrile. The Wiberg bond indices<sup>18</sup> also agree with this conclusion, as can be seen below:

	W <sub>CN</sub>	Wcc	W <sub>CH</sub>	
CHICN	2,8550	1.1160	0.9534	
CH-CN	2.4950	1,4898	0.9470	
CH <sub>2</sub> =NH <sup>+</sup>	2.0617		0.9567	
+Completely	optim	ized g	eometry	
$R_{C=N} = 1.279 A.$	nonemp	irical cal	culations	
give 1.257 A.1*				

The calculations made for the optimization of molecular geometries provide the possibility to obtain the harmonic force constants and, consequently, to attempt to reproduce the vibrational spectra. In fact we used an iterative procedure to find the  $K_{CN}$  stretching force constant keeping the remaining constants fixed as follows:  $K_{CH} = 5.46 \text{ mdyn.A}^{-1}$ ,  $K_{CC} = 6.64 \text{ mdyn.A}^{-1}$  and  $K_{CC,CN} = 0.283 \text{ mdyn.A}^{-1.20}$  A fair agreement between the experimental and calculated frequencies (see below) was found for  $K_{CN} = 15.19 \text{ mdyn.A}^{-1}$ .

	≠ <sub>CN</sub> exp., HMPt	VCN calc
CH <sub>2</sub> CN	2050 - 2051	2051
CH2C"N	2028 - 2029	2029
CD <sub>2</sub> CN	2050	2055

The value taken for the  $K_{CC}$  stretching force constant was calculated as the second derivative of the total i energy at the optimum bond length and scaled by the factor 2.8.<sup>21</sup> It is obviously larger than the corresponding value for MeCN (6.18 mdyn.A<sup>-120</sup>) whereas the value

found for  $K_{CN}$  is smaller than that for CH<sub>3</sub>CN (18.87 mdyn.A<sup>-1</sup>).<sup>20</sup> These results support once more the suggested carbanionic structure 6 for metallated acetonitrile.

We are aware that the vibrational problem considered here has no unique solution.22 The normal coordinate treatment of the tricyanomethide anion, for example, furnished three sets of "most probable" force constants differing mainly in the values for the C-C≡N fragment.<sup>23</sup> A similar result can be obtained in our case too. A proper choice of the most probable set of force constants, in our opinion, should be made on the basis of MO calculations. We found that the calculated  $\nu_{CN}$  stretching frequency is very sensitive to the magnitude of the interaction force constant K<sub>CC,CN</sub> and, vice versa, small changes of the diagonal constants K<sub>CC</sub> and K<sub>CN</sub> require considerable change of KCC.CN in order to reproduce the experimental frequencies (Table 2). The semiempirical MO calculations however provide a criterion to choose the most reliable value of K<sub>CC,CN</sub> in spite of the fact that the (stretching) force constants calculated with the aid of, e.g. CNDO/2 are 2-3 times too large as compared to the values given by normal coordinate treatments. A reasonable assumption giving the possibility to make a unique choice of the force field F is that the scaling factors for the off-diagonal elements calculated by a MO method should be close to the scaling factors for the respective diagonal elements of the F-matrix (that is, the stretching force constants, bending force constants, etc.). Thus, assuming the scaling factor  $\alpha_{CC,CN}$  equal to the mean<sup>24</sup> geometrical  $\sqrt{(a_{CC}a_{CN})}$ or acc.cn =  $(\alpha_{\rm CC} + \alpha_{\rm CN})/2$ , we can regard the first of the three sets of force constants in Table 2 as most probable. This choice is in good agreement with the recently reported<sup>23</sup> correlation of Wiberg bond indices with the "experimental" K<sub>CN</sub> and K<sub>CC</sub> force constants in a series of molecules containing amino-, imino- and nitrile groups.

We used the latter correlation to estimate the changes of nitrile force constants on formation of ion pairs with Li" and Na" (planar carbanion) or covalent metalloacetonitriles (sp<sup>3</sup>-model). By the means of our CNDO/2 calculations we found that these two possible species have practically the same (gas phase) total energies. In both cases we used the optimized geometry of the free carbanion and neutral acetonitrile and optimized only the C-M distances. The latter values together with the Wiberg indices W<sub>CN</sub> and W<sub>CC</sub> as well as the net charge of the metal atom are listed in Table 3. As may be seen. the metal net charge varies from 0.3 to 0.44 being larger for the sp<sup>2</sup>-models. These results are comparable with the CNDO/2 data for metal halides (optimized Me-X distances) 0.568 for NaF, 0.303 for NaCl, 0.568 for LiF and 0.428 for LiCl. Thus, we may conclude that the ionic character of the carbon-metal bond in LiCH<sub>2</sub>CN and NaCH<sub>2</sub>CN is doubtless. This inference is qualitatively consistent with the results of the recent nonempirical calculations on MeLi and other organometallics.26

To decide which of the two energetically equivalent

Table 2.								
CNDO/2	К <sub>СС.СН</sub> ; асс.сн 0.770		Kcc: acc 18.575		K <sub>CN</sub> ; a <sub>CN</sub> 32.265		Vec	*CN
First set	0.275	(2.80)	6.501	(2.86)	14.758	(2.19)	1117	2051
Second set	0.127	(6.05)	6.69	(2.78)	14.51	(2.22)	1117	2051
Third set	0.064	(12.03)	6.77	(2.74)	14.41	(2.24)	1117	2051

	CH3CN	LICH <sub>2</sub> CN	NaCH <sub>2</sub> CN	<sup>⊕</sup> CH <sub>2</sub> CN
l(sp <sup>3</sup> )		1.893	2.401	
RC-H II(sp <sup>2</sup> )		1.944	2.440	-
	2.8550	2.7409	2.7011	_
WC=N II		2.5246	2.4532	2.4950
1	1.1160	1.1186	1.1185	_
MC-CN II	_	1.2124	1.3002	.4896
Charge on 1	_	+ 0.3051	+ 0.4242	
the metal II	-	+ 0.3143	+ 0.4404	
1	2251*	ca. 2195*	ca. 2170°	
<i>⊮</i> C=N(cm <sup>-1</sup> ) II		ca. 2055°	ca. 2025*	2051*

Table 3.

\*Measured experimentally.

<sup>\*</sup>Data obtained by using CNDO optimized distances  $R_{CN} = 1.190$  Å and  $R_{C-C(N)} = 1.429$  Å for acetonitrile. <sup>\*</sup>Data obtained by using CNDO optimized distances  $R_{CN} = 1.225$  Å and

<sup>b</sup>Data obtained by using CNDO optimized distances  $R_{CN} = 1.225$  A and  $R_{C-C(N)} = 1.355$  Å for the acetonitrile carbanion.

(according to our CNDO/2 calculations) forms of metallated acetonitrile is the one actually observed in our IR measurements we employed the fact that the changes of  $\nu_{\rm CN}$  are dependent primarily on the changes of K<sub>CN</sub> and K<sub>CC</sub><sup>27</sup> since K<sub>CC,CN</sub> is practically the same for both models of MCH<sub>2</sub>CN. Thus, we have

$$\Delta \nu_{\rm CN} = \frac{\partial \nu_{\rm CN}}{\partial K_{\rm CN}} \Delta K_{\rm CN} + \frac{\partial \nu_{\rm CN}}{\partial K_{\rm CC}} \Delta K_{\rm CC}$$

and may estimate  $\nu_{CN}$  on the basis of the correlations of  $K_{CN}$  and  $K_{CC}$  with the Wiberg indices. The data in Table 3 show that both models, sp<sup>2</sup> and sp<sup>3</sup>, predict enhancement of  $\nu_{CN}$  for lithium as compared to the sodium derivatives. This result is in qualitative agreement with the experimental finding. Further, we found that  $\nu_{CN}$  for



Fig. 2. IR spectra of HMPT solutions of  $[CD_2CN]^{\Theta} Li^{\Theta}$ . (a) concentrations of both the carbanions and counter ions  $5 \times 10^{-2}$  g-ion.1<sup>-1</sup>; (b) the same carbanion concentration, concentration of the counter ion  $1.5 \times 10^{-1}$  g-ion.1<sup>-1</sup> (threefold excess of naphthalene-dilitium, cf. Experimental).



Fig. 3. IR spectra of [CD<sub>2</sub>CN]<sup>©</sup>, 5×10<sup>-2</sup> g-ion.l<sup>-1</sup> in HMPT. (a) counter ion Li<sup>+</sup>; (b) counter ion Na<sup>+</sup>; (c) counter ion K<sup>+</sup>.

the sp<sup>3</sup>-model of MCH<sub>2</sub>CN should be about 2170-2195 cm<sup>-1</sup>, that is, too high as compared to the experiment. The same manipulation for the planar model gives 2025-2055 cm<sup>-1</sup> which coincides with the experimental result. The calculations for a model with the metal atom situated closely to nitrogen atom predict a drastic redistribution of bond electron densities (ketene imide structure, H<sub>2</sub>C=C\*N<sup>-</sup>M<sup>-</sup>) and <sup>14</sup>N-<sup>15</sup>N isotopic shifts of  $\nu_{CN}$ which are inconsistent with the experiment.

The strong enhancement of the integrated intensity of the nitrile absorption on metallation of acetonitrile (~  $60 \times 10^3$  vs  $1.3 \times 10^3$  l.mol<sup>-1</sup>.cm<sup>-2</sup>) can be satisfactorily reproduced by means of MO calculations of  $\partial \mu/\partial Q$ . We used an approximate scheme,<sup>28</sup> considering the C-CEN fragment as the only part of the molecule participating in the  $\nu_{\rm CN}$  normal mode. Our results 1.43 D.A<sup>-1</sup> for CH<sub>3</sub>CN, 3.32 for the sp<sup>3</sup>-model of LiCH<sub>2</sub>CN 4.05 for 'CH<sub>2</sub>CN and 4.42D. A<sup>-1</sup> for the sp<sup>2</sup>-model of LiCH<sub>2</sub>CN are qualitatively consistent with the experimental enhancement of the integrated intensity of the observed nitrile absorption of metalloacetonitriles.

The combined consideration of the IR spectra and the results of CNDO/2 and normal coordinate calculations demonstrates that the carbon-metal bonding in monoalkali metal derivatives of acetonitrile is clearly of ionic type. The structure of the carbanion is preferably planar and the alkali counter ion in the contacting ion pair is situated close to the carbon atom of the methylene group.

#### EXPERIMENTAL

Acetonitrile- $^{15}$ N was prepared according to the following scheme; 20% aqueous solution of  $^{15}$ NH<sub>3</sub> (52% enrichment) was used:

$$(CH_{3}CO)_{2}O + 2^{13}NH_{3-30}$$
  
 $\downarrow$   
 $CH_{3}CO^{13}NH_{2} + CH_{3}COO^{13}NH_{4} \xrightarrow{3H_{1}O} 2CH_{3}C^{13}N.$ 

The distillation over  $P_2O_3$  gave MeC<sup>13</sup>N containing small amounts of AcOH and Ac<sub>2</sub>O. The further purification was carried out by another distillation over octylamine. 1.4 g purified MeC<sup>13</sup>N was obtained from 1 g<sup>13</sup>NH<sub>3</sub>.

The metallation of acetonitrile was carried out by adding the substrate solns to solns of 10% excess of the dialkali derivative of naphthalene in the corresponding solvents under pure argon. The spectra were recorded on an UR-20 (C. Zeiss, Jena) spectrophotometer in calcium fluoride cells.

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