

INFRARED SPECTRA AND STRUCTURE OF CARBANIONS—XIII*

A STUDY OF THE CARBANIONS GENERATED FROM ACETONITRILE, ACETONITRILE-D₃ AND ACETONITRILE-¹⁵N

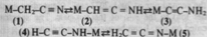
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Abstract—The study of the IR spectral data for metallated acetonitrile (counter ions Li⁺, Na⁺, K⁺ in solvents tetrahydrofuran, THF, and hexamethylphosphotriamide, HMPT) and its D₃- and ¹⁵N- derivatives together with CNDO/2 and normal coordinate calculations showed that the mesomeric ion H₂C=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.¹ 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.²⁻⁵

Some of these studies have promoted the concept of the simultaneous presence of a number of prototropic and metalotropic forms in the solutions of alkali metal derivatives of acetonitrile,²⁻⁴ and others assume a polymer associated nature of lithium-acetonitrile.⁴ The hypothesis of Krüger² on the existence of tautomeric species of acetonitrile-lithium is currently accepted in the literature²⁻⁵ (Scheme 1).



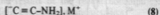
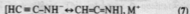
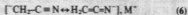
Scheme 1. (M = Li, Na)

We have demonstrated⁶ 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 metalotropic and prototropic species are in fact pertinent to products of further transformations of metallated acetonitrile.

The high reactivity of metallated acetonitrile and its tendency to dimerize cause serious difficulties in the investigation of its spectra.⁶ We were restricted to study the frequency region between 1900 and 2600 cm⁻¹ 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 DISCUSSION

The IR spectra of metallated acetonitrile and its D₃- and ¹⁵N- isotopic derivatives were recorded in the region 1900–2600 cm⁻¹ 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⁻¹ 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.^{6,8,12} It has been recently demonstrated⁶⁻⁹ that the replacement of K⁺ for Li⁺ causes an enhancement of ν_{CN} in carbanions of substituted aryl- and alkyl-acetonitriles by about 10 cm⁻¹. The replacement of the solvent THF for HMPT also causes an enhancement of the same frequencies of the order of 10 cm⁻¹. These data, as well as the extremely high intensity of the nitrile absorption band (A ~ 6 × 10⁴ l. g-ion⁻¹. cm⁻², observed for the strongly conjugated carbanions of substituted benzyliocyanides too^{9,12} 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 metalotropic species in Scheme 1.



Scheme 2. (M = Li, Na)

The isotopic shift of the observed intense absorption band due to the replacement of ¹⁴N by ¹⁵N (Table 1) is 22 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-C≡C gives a value smaller than 5 cm⁻¹ (general valence force field, force constants taken from Ref. 13). On the other hand, the amino acetylenide species should be

*Part XI: *Tetrahedron* 33, 2993 (1977).

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Table 1.

Compound	Solvent	ν_{CN} of neutral molecules & isotopic shifts (cm^{-1})		Carbanions with different counter ions ^b		
				Li^+	Na^+	K^+
CH_3CN	HMPT	2249	—	2050	— 2051	— 2051
		2295w	—	2072	— 2061	— 2061
	THF	2252	—	2051	— 2050	— 2049
		2293w	—	2062	— 2065sh	—
CD_3CN	HMPT	2257	-8	2050	0 2051	1 2050
	THF	2261	-9	2045	2043	2041
$\text{CH}_3\text{C}^{15}\text{N}$	HMPT	2222	27	2028	22 2029	22 2029
		2288w	7	2050	22 2041	20

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 1¹⁴) and is close to that of anion radicals of aromatic nitriles.¹⁴ This indicates the prevailing participation of the $\text{C}\equiv\text{N}$ bond in the observed normal mode. The metallation, therefore, does not give rise to drastic changes of bond multiplicities in the indicator group $\text{C}\equiv\text{N}$.

We measured isotopic shifts of $0\text{--}1\text{ cm}^{-1}$ in HMPT and $0\text{--}8\text{ cm}^{-1}$ 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 C=C bonds and consequently a large H-D isotopic shift of the order of the reported 168 cm^{-1} for HCN-DCN^{15} or $133\text{--}135\text{ cm}^{-1}$ for $\text{CH}_2\text{C}\equiv\text{CH-CH}_2\text{C}\equiv\text{CD}$.¹⁵ 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

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 $^{13}\text{CH}_3\text{C}^{15}\text{N}$ (Fig. 1). The ^{14}N - ^{15}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 ν_{CN} frequencies for metallated acetonitriles is probably the different environment of the carbonionic particles. Thus, the doublet character of the ν_{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 $2050\text{--}2051\text{ cm}^{-1}$ to the ν_{CN} of "free" carbanions and the second one at $2061\text{--}2072\text{ cm}^{-1}$ (depending on the counter ion) to the ν_{CN} of the ion pair. The spectrum presented on Fig. 1 can be assigned as follows:

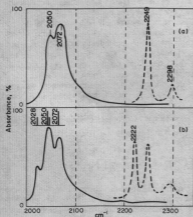


Fig. 1. IR spectra of HMPT solutions of: (a) (.....) acetonitrile, $1\text{ g}\cdot\text{mole}^{-1}$; (—) acetonitrile-lithium, $5 \times 10^{-2}\text{ g}\cdot\text{ion}\cdot\text{l}^{-1}$; (b) (.....) acetonitrile (52% at ^{15}N), $1\text{ g}\cdot\text{mole}^{-1}$; (—) acetonitrile-lithium (52% at ^{15}N), $5 \times 10^{-2}\text{ g}\cdot\text{ion}\cdot\text{l}^{-1}$.

2072 cm^{-1} $\nu_{\text{C}14\text{N}}$ of solvent separated ion pairs;

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

2050 cm^{-1} $\nu_{\text{C}15\text{N}}$ of solvent separated ion pairs;

2028 cm^{-1} $\nu_{\text{C}15\text{N}}$ of "free" carbanions.

It is difficult to suggest a reliable assignment of the components of the ν_{CN} doublets observed in THF. These are clearly registered for counter ion Li^+ but the shoulder at higher frequency disappears entirely for counter ion K^+ . 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^+ , Na^+ , Li^+ as observed previously⁶⁻⁹ for carbanions of secondary nitriles and benzyli cyanides.

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 $\text{H}_2\text{C}=\text{C}\equiv\text{N}$, in complete agreement with our results of CNDO/2 calculations¹⁶ for this ion.

The total energy of the carbanion of acetonitrile was

minimized with respect to all geometric parameters of the molecule. The following optimum values were found: $R_{C-N} = 1.255$ Å; $R_{C-C} = 1.355$ Å; $R_{C-H} = 1.116$ Å; angle $HCH = 118^\circ$. The favoured structure of the ion is planar C_{2v} . The charge distributions (optimized geometries) for ${}^-\text{CH}_2\text{CN}$ and CH_3CN are compared below:

	Q_M	Q_C	Q_C	Q_N
${}^-\text{CH}_2\text{CH}$	-0.0722	-0.4122	0.0640	-0.5073
CH_3CN	0.0318	-0.0163	0.0905	-0.1693

It is well known that CNDO/2 calculations predict bond lengths for multiple bonds 0.02–0.03 Å longer than the experimental ones,¹⁶ whereas the lengths of the single bonds C–C are predicted 0.01–0.06 Å too short. Therefore, we can assume the following bond lengths as more realistic: $R_{C-N} = 1.20$ Å and $R_{C-C} = 1.38$ Å. This value for R_{C-N} agrees fairly with the correlation $\rho_{CN} = R_{CN}$ suggested by Ritschl¹⁷ which gives for $\rho_{CN} = 2050 \text{ cm}^{-1}$ a value of $R_{CN} = 1.19$ – 1.21 Å. This implies that the multiplicity of the $C \equiv N$ bond in the carbanion is substantially reduced as compared with the parent nitrile. The Wiberg bond indices¹⁸ also agree with this conclusion, as can be seen below:

	W_{CN}	W_{CC}	W_{CH}
CH_3CN	2.8550	1.1160	0.9534
${}^-\text{CH}_2\text{CN}$	2.4950	1.4898	0.9470
$\text{CH}_2=\text{NH}^\ddagger$	2.0617	—	0.9567

‡ Completely optimized geometry;
 $R_{C-N} = 1.279$ Å, nonempirical calculations
give 1.257 Å.¹⁹

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: $K_{CH} = 5.46 \text{ mdyn.Å}^{-1}$, $K_{CC} = 6.64 \text{ mdyn.Å}^{-1}$ and $K_{CC,CN} = 0.283 \text{ mdyn.Å}^{-1}$.²⁰ A fair agreement between the experimental and calculated frequencies (see below) was found for $K_{CN} = 15.19 \text{ mdyn.Å}^{-1}$.

	$\rho_{CN} \text{ exp., HMP}^\ddagger$	$\rho_{CN} \text{ calc.}$
${}^-\text{CH}_2\text{CN}$	2050–2051	2051
${}^-\text{CH}_2\text{C}^{13}\text{N}$	2028–2029	2029
CD_2CN	2050	2055

The value taken for the K_{CC} stretching force constant was calculated as the second derivative of the total energy at the optimum bond length and scaled by the factor 2.8.²¹ It is obviously larger than the corresponding value for MeCN (6.18 mdyn.Å^{-1})²⁰ whereas the value

found for K_{CN} is smaller than that for CH_3CN ($18.87 \text{ mdyn.Å}^{-1}$).²⁰ 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–CN fragment.²³ 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 ρ_{CN} stretching frequency is very sensitive to the magnitude of the interaction force constant $K_{CC,CN}$ and, vice versa, small changes of the diagonal constants K_{CC} and K_{CN} require considerable change of $K_{CC,CN}$ in order to reproduce the experimental frequencies (Table 2). The semiempirical MO calculations however provide a criterion to choose the most reliable value of $K_{CC,CN}$ 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 geometrical mean²⁴ $\sqrt{(\alpha_{CC,CN})}$ or $\alpha_{CC,CN} = (\alpha_{CC} + \alpha_{CN})/2$, 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 reported²⁵ correlation of Wiberg bond indices with the "experimental" K_{CN} and K_{CC} 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 metaloacetonitriles (sp^3 -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_{CN} and W_{CC} 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^3 -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_2CN and NaCH_2CN 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	$K_{CC,CN} : \alpha_{CC,CN}$ 0.770	$K_{CC} : \alpha_{CC}$ 18.575	$K_{CN} : \alpha_{CN}$ 32.265	ρ_{CC}	ρ_{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

Table 3.

	CH ₂ CN	LiCH ₂ CN	NaCH ₂ CN	^o CH ₂ CN
R _{C-N} I(sp ³)	—	1.893	2.401	—
R _{C-N} II(sp ³)	—	1.944	2.440	—
W _{C-N} I	2.8550	2.7409	2.7011	—
W _{C-N} II	—	2.5246	2.4532	2.4950
W _{C-CN} I	1.1160	1.1186	1.1185	—
W _{C-CN} II	—	1.2124	1.3002	.4896
Charge on I	—	+0.3051	+0.4242	—
the metal II	—	+0.3143	+0.4404	—
ν _{CN} (cm ⁻¹) I	2251*	ca. 2195*	ca. 2170*	—
ν _{CN} (cm ⁻¹) II	—	ca. 2055 ^b	ca. 2025 ^b	2051*

*Measured experimentally.

^bData obtained by using CNDO optimized distances R_{CN} = 1.190 Å and R_{C-CN} = 1.429 Å for acetonitrile.^cData obtained by using CNDO optimized distances R_{CN} = 1.225 Å and R_{C-CN} = 1.355 Å for the acetonitrile carbanion.

(according to our CNDO/2 calculations) forms of metalated acetonitrile is the one actually observed in our IR measurements we employed the fact that the changes of ν_{CN} are dependent primarily on the changes of K_{CN} and K_{CC}²⁷ since K_{CCN} is practically the same for both models of MCH₂CN. Thus, we have

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

and may estimate ν_{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, sp³ and sp², predict enhancement of ν_{CN} for lithium as compared to the sodium derivatives. This result is in qualitative agreement with the experimental finding. Further, we found that ν_{CN} for

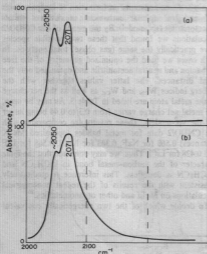


Fig. 2. IR spectra of HMPT solutions of [CD₂CN]²⁻ Li⁺. (a) concentrations of both the carbanions and counter ions 5 × 10⁻³ g-ion.l⁻¹; (b) the same carbanion concentration, concentration of the counter ion 1.5 × 10⁻¹ g-ion.l⁻¹ (threefold excess of naphthalene-dilithium, cf. Experimental).

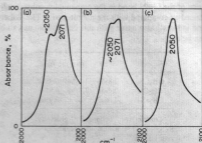


Fig. 3. IR spectra of [CD₂CN]²⁻, 5 × 10⁻² g-ion.l⁻¹ in HMPT. (a) counter ion Li⁺; (b) counter ion Na⁺; (c) counter ion K⁺.

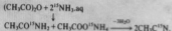
the sp³-model of MCH₂CN should be about 2170–2195 cm⁻¹, that is, too high as compared to the experiment. The same manipulation for the planar model gives 2025–2055 cm⁻¹ which coincides with the experimental result. The calculations for a model with the metal atom situated closely to nitrogen atom predict a drastic redistribution of bond electron densities (ketene imide structure, H₂C=C=N⁻M⁺) and ¹⁴N–¹⁵N isotopic shifts of ν_{CN} which are inconsistent with the experiment.

The strong enhancement of the integrated intensity of the nitrile absorption on metallation of acetonitrile (~60 × 10³ vs 1.3 × 10³ l.mol⁻¹.cm⁻²) can be satisfactorily reproduced by means of MO calculations of ∂μ/∂Q. We used an approximate scheme,²⁸ considering the C–CN fragment as the only part of the molecule participating in the ν_{CN} normal mode. Our results 1.43 D.A.⁻¹ for CH₂CN, 3.32 for the sp³-model of LiCH₂CN 4.05 for ^oCH₂CN and 4.42 D.A.⁻¹ for the sp²-model of LiCH₂CN 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 mono-alkali 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-¹³N was prepared according to the following scheme; 20% aqueous solution of ¹³NH₃ (52% enrichment) was used:



The distillation over P₂O₅ gave MeC¹³N containing small amounts of AcOH and Ac₂O. The further purification was carried out by another distillation over octylamine. 1.4 g purified MeC¹³N was obtained from 1 g ¹³NH₃.

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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