

INFRARED SPECTRA AND STRUCTURE OF CARBANIONS

V*. ASSIGNMENT OF THE NITRILE GROUP INFRARED BANDS OF THE PHENYL ACETONITRILE AND ACETONITRILE LITHIUM DERIVATIVES

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(Received May 12th, 1975)

Summary

The structure of the lithium derivatives of phenyl acetonitrile and acetonitrile is discussed in terms of their IR spectra. It has been found from new and already-published data that the IR spectra [$\nu(\text{CN})$ region] of the lithium, sodium, potassium and chlormagnesyl derivatives of phenyl acetonitrile in various solvents, and in the solid state, are similar. They are characterized by very strong $\nu(\text{CN})$ bands in the 2068–2102 cm^{-1} region, and correspond to the mesomeric phenyl acetonitrile carbanion.

The $\nu(\text{CN})$ bands, found in the 2050–2071 cm^{-1} region, suggest the structure $[\text{CH}_2\text{---C}\equiv\text{N}]^-\text{Li}^+$ for lithium acetonitrile, both in solution and in solid state. The influence of the counter ion and the solvent is discussed in terms of the concept of ion-pairs.

Some published data are reconsidered; it is shown that up to now, no reliable data on the presence of tautomeric forms of lithium acetonitrile either in solution or in solid state exist. Some odd bands in the spectra of samples of alkali-metal derivatives of phenyl acetonitrile and acetonitrile are assigned to the dimers of the nitriles mentioned above, and the metal derivatives of these dimers.

Data on the structure of ionic intermediate species are of great interest in the study of the kinetics and mechanisms of some important reactions. The phenyl acetonitrile and acetonitrile carbanions are no exception in this respect, the latter in particular being a model of the reaction centre in the acrylonitrile

* For Part III see ref. 6; for Part IV see ref. 9.

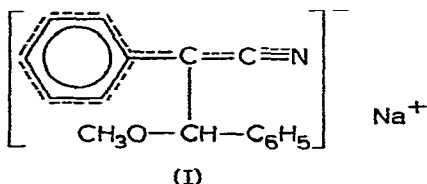
anion polymerization, etc. On the other hand, IR spectral data of carbanions are, in our opinion, by themselves of interest.

IR spectral data on phenyl acetonitrile and acetonitrile carbanions have been reported, and the band assignments have been discussed [1-5], but there is considerable dissension among authors. The purpose of the present study is to elucidate the chemical structure of the organolithium compounds mentioned, as well as the structure of some products resulting from further reactions.

Results and discussion

A. Lithium phenyl acetonitrile

The case of metalated phenyl acetonitrile is, in our view, the least disputable. According to Crüger [1], the sodium derivative of phenyl acetonitrile exists only in the form $\text{C}_6\text{H}_5\text{CH}(\text{Na})\text{CN}$, and it shows only one $\nu(\text{CN})$ band at 2080 cm^{-1} (in KBr pellet, pyridine or benzene solutions). At the same time, the band at 2102 cm^{-1} [in hexamethyl phosphoramide (HMPA), counter ion ClMg^+] was assigned as $\nu(\text{CN})$ of the mesomeric phenyl acetonitrile carbanion [2]. Quite recently [5] we reported the band at 2096 cm^{-1} (in HMPA, counter ions Li^+ and K^+), as well as the bands at $2079\text{--}2090\text{ cm}^{-1}$ and $2070\text{--}2078\text{ cm}^{-1}$ [doublets* in tetrahydrofuran (THF), counter ions Li^+ , Na^+ and K^+], with the same assignment [5]. This assignment was confirmed by NMR data [1], Hückel MO [2] and SCF MO [5] calculations, and it is confirmed by our present data (Table 1). On the other hand, the methoxide adduct of α -cyanostilbene (I) showed a very similar $\nu(\text{CN})$ band [6]. (The structure of adducts of type I was



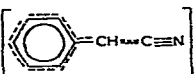
established on the basis of their UV [7], NMR [8] and IR [9] spectra.)

So the IR spectra ($1800\text{--}2300\text{ cm}^{-1}$) of the phenyl acetonitrile carbanion (counter ions Li^+ , Na^+ , K^+ and ClMg^+), measured in various solvents, as well as in the solid state, are similar in showing $\nu(\text{CN})$ bands at $2068\text{--}2102\text{ cm}^{-1}$. The fact that these bands occur in a relatively broad region is due to the influence of the counter ions, the aggregate state and the solvents. Increase in $\nu(\text{CN})$ in the order $\text{K}^+ < \text{Na}^+ < \text{Li}^+$ takes place in the cases of some other carbanion salts [5] and also anion radicals [10,11] in ethereal solvents, and this phenomenon may be ascribed to the electrostatic anion-counter ion interactions in the contact and solvent-separated ion pairs [5,10,11].

It can be pointed out that the $\nu(\text{CN})$ bands of the metalated phenyl acetonitrile are very intense: $A(\text{CN}) \approx 10^5\text{ l mol}^{-1}\text{ cm}^{-2}$, while for neutral phenyl acetonitrile $A(\text{CN}) \approx 10^3\text{ l mol}^{-1}\text{ cm}^{-2}$. A strong increase in $A(\text{CN})$ (ca. 1-2 or-

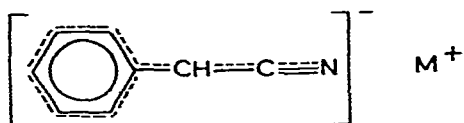
* The doublet character of the bands was ascribed to the presence of "free" ions and ion pairs in the solutions [5].

TABLE 1
INFRARED DATA

Lithium derivative of:	Solvent	Bands in the 1800-2300 cm ⁻¹ region	Assignment
C ₆ H ₅ CH ₂ CN	THF	2089 ≈2070 (sh)	ν(CN) of  Li ⁺
	HMPA	2096 [5] ≈2092 (sh)	the same [5] the same
	solid	2070	
CH ₃ CN	THF	2062 2051	ν(CN) of [CH ₂ ---C≡N] ⁻ Li ⁺
	HMPA	2071 2050	the same
	solid	2067 (br)	the same
CD ₃ CN	THF	2054 2046	ν(CN) of [CD ₂ ---C≡N] ⁻ Li ⁺
	HMPA	2071 2049	the same
	solid	2055 (br)	the same

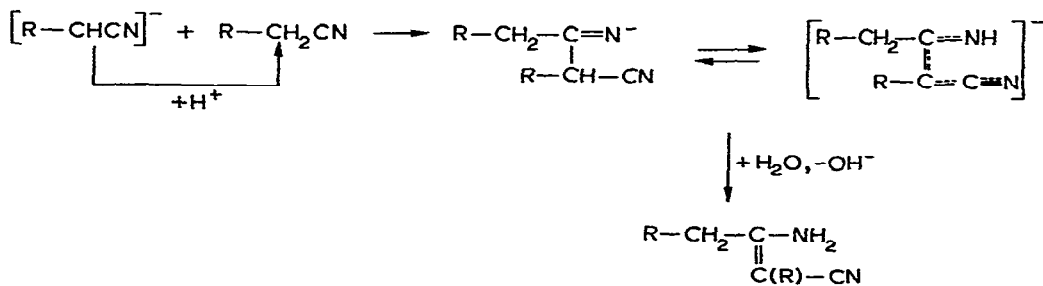
ders) is characteristic of carbanions [5,6,9] and anion radicals [10,11] containing nitrile groups, and it may be explained qualitatively by the strong migration of either the carbanion charge (in carbanions) or the odd electron (in anion radicals) over the conjugated system in the course of the ν(CN) vibration.

All data mentioned above conform with structure II only.



(II): M = Li, Na, K, ClMg

The datum 2180 cm⁻¹ (in nujol), reported in ref. 4 for lithium phenyl acetonitrile, must be considered unreliable (cf. Table 1). We would assign the band at 2180 cm⁻¹ as ν(CN) of 2-amino-1,3-diphenylcrotonitrile (III, R = C₆H₅), generated in the course of the phenyl acetonitrile dimerization (Scheme 1).



(III) (cis or trans)

Indeed, when we treated the samples of lithium phenyl acetonitrile with

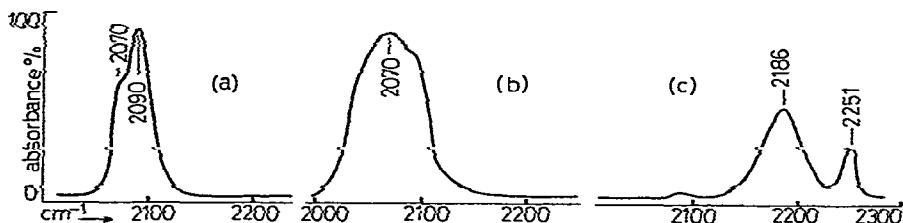


Fig. 1. IR spectra of lithium phenyl acetonitrile. (a) Solution in THF. (b) Solid, in nujol; assignment: Table 1. (c) Spectrum of the sample (b), after protonation. The spectrum of the sample (a) after protonation is very similar. Assignment: 2186 cm^{-1} , $\nu(\text{CN})$ of the enamino-nitrile (III, $\text{R} = \text{C}_6\text{H}_5$); 2250 cm^{-1} , $\nu(\text{CN})$ of partially regenerated phenyl acetonitrile.

humid air, the bands reported in Table 1 faded away, and bands at 2178 cm^{-1} (in THF) and 2186 cm^{-1} (in nujol) appeared (Fig. 1).

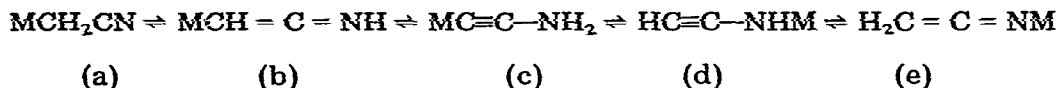
$\nu(\text{CN})$ frequencies in this region are characteristic of the enamionitriles [13,14] (see also Section C). A strong $\nu(\text{CN})$ band at 2186 cm^{-1} (neat) is present also in the spectrum of the phenyl acetonitrile dimerization product, which we obtained under the conditions described in ref. 12.

The assignment given above finds direct support in ref. 4, where it was established that the product showing $\nu(\text{CN})$ at 2180 cm^{-1} (nujol) had a dimeric molecular weight (in comparison with phenyl acetonitrile) (cryoscopic data in DMSO).

B. Lithium acetonitrile

A sample of the acetonitrile sodium derivative has shown bands at 2050, 2240, 2160 and 2115 cm^{-1} (in KBr) [1]. The last band was assigned to $\nu(\text{CN})$ of the sodium derivative of the acetonitrile dimer (see Scheme 1, $\text{R} = \text{H}$), this impurity being difficult to avoid. The detection of a sharp band at 3260 cm^{-1} (assigned as $\nu(\equiv\text{C}-\text{H})$) and a wide band at 3130 cm^{-1} [$\nu(\text{N}-\text{H})$] has lead the authors to the assumption that all possible tautomeric forms of $\text{NaC}_2\text{H}_2\text{N}$ (Scheme 2) are present in the solid mixture [1]. But according to NMR data, the form NaCH_2CN is strongly predominant in pyridine solution [1].

SCHEME 2



According to Gornowicz and West [3], a sample of monolithiated acetonitrile (suspension in THF-hexane) gives only two bands in the $1600\text{--}2400\text{ cm}^{-1}$ region, viz. 2040 and 2130 cm^{-1} . By analogy to the spectra of $\text{R}_2\text{C}(\text{Li})\text{CN}$ (only one band near 2000 cm^{-1}), the authors [3] have assigned the band at 2040 cm^{-1} to $\nu(\text{CN})$ of LiCH_2CN , and having in mind the previous assignment [1], they suppose that the band at 2130 cm^{-1} corresponds to another tautomeric form (Scheme 2, b-e).

Das and Wilkie [4] described the following bands in the $1800\text{--}2400\text{ cm}^{-1}$ region of the spectrum of lithiated acetonitrile: two bands near 2000 cm^{-1} (in

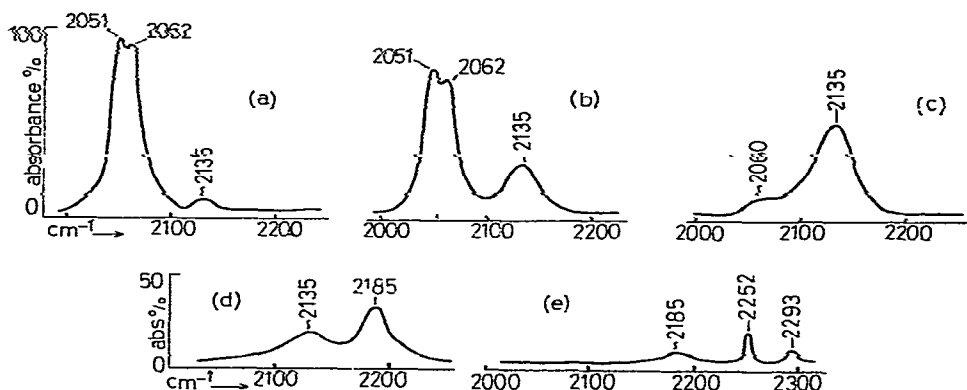


Fig. 2. IR spectra of: (a) Acetonitrile, metalated by excess of naphthalene-dilithium, in THF. (b) Acetonitrile (ca. 10% excess), metalated by naphthalene dilithium, in THF. The spectrum of the sample (a), at the beginning of the protonation, is practically the same. (c) Acetonitrile, metalated by ca. 0.5 M naphthalene-dilithium, in THF. The spectrum of the sample (a), after partial protonation, is very similar. (d) Samples (a), (b), (c), after almost complete protonation. (e) Sample (a), rapidly protonated (excess H₂O or EtOH). Assignment: 2051, 2062 cm⁻¹, $\nu(\text{CN})$ of $[\text{CH}_2\text{---C}\equiv\text{N}]^-\text{Li}^+$; 2130-2140 cm⁻¹, $\nu(\text{CN})$ of lithium diacetonitrile (V, counter ion Li⁺); ≈ 2185 cm⁻¹, $\nu(\text{CN})$ of diacetonitrile (III, R = H); 2252, 2293 cm⁻¹, bands of the partially regenerated acetonitrile.

ether), ascribed to the dilithium derivative*; a band at 2200 cm⁻¹ (in DMSO), without assignment; a band at 2160 cm⁻¹ (in nujol), assigned as $\nu(\text{CN})$ of LiC₂H₂N.

Our data (Table 1 and Figs. 2a, 3a and 5a) show that the spectra of lithium acetonitrile are similar in solution and solid state in showing very strong bands in the 2050-2071 cm⁻¹ region. By analogy to the case of secondary saturated nitrile carbanions [5], we ascribe the presence of a doublet at 2051, 2062 cm⁻¹ (Fig. 1a) to the formation of two ion-pair types. The bands in the 2050-2071 cm⁻¹ region (Table 1, Figs. 2a, 3a and 5a) are close to the band at 2050 cm⁻¹, described [1] for sodium acetonitrile, and the one at 2040 cm⁻¹, reported [3] for lithium acetonitrile.

The IR spectral data of some related systems confirm the present assignment: The only bands found near 2000 cm⁻¹ [3] were ascribed to structures of the kind R₂C(Li)CN (R = CH₃ and (CH₃)₃Si) [3]. The bands at 2018-2063 cm⁻¹ (in THF) were assigned to the anions $[\text{>C}\text{---C}\equiv\text{N}]^-$ (counter ions Li⁺, Na⁺ and K⁺) in the cases of the alkali-metal derivatives of propionitrile, isobutyronitrile, cyclopentane- and cyclohexane-carbonitriles [5].

The assignment of the bands 2050-2071 cm⁻¹ in the spectra of the metalated acetonitrile as $\nu(\text{CN})$ of the corresponding carbanion $[\text{CH}_2\text{---C}\equiv\text{N}]^-$ is in agreement also with the quantum chemical data on carbanions and some other related systems. The correlation between $\nu(\text{CN})$ of the lithium derivatives of acetonitrile, phenyl acetonitrile, some other carbanions with counter ion Li⁺, as well as $\nu(\text{CN})$ of some neutral aromatic nitriles, and the C≡N bond order calculated by SCF MO, is presented in Fig. 4. The calculations were carried out by the

* This assignment is incorrect: a band near 1800 cm⁻¹ was described [3] for the dilithium derivative. In fact, only these bands could correspond to $\nu(\text{CN})$ of lithium acetonitrile (cf. ref. 3 and Table 1).

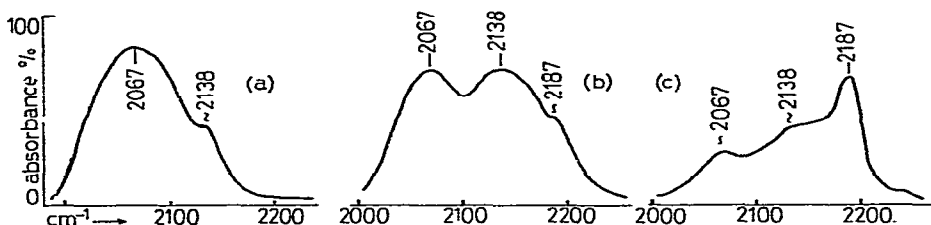


Fig. 3. IR spectra of: (a) Lithium acetonitrile, solid in nujol. (b) Sample (a), partially protonated. (c) Sample (a), almost completely protonated.

LCAO MO method (according to P.P.P.*) for planar carbanion models; the parameters suggested by Bloor [15] having been used; the repulsion integrals were calculated by the Mataga—Nishimoto formula [16]. An inductive model (I_c decreasing by 0.4 eV for one alkyl group) was used to account for the alkyl group influence.

It can be seen in Fig. 4 that there exists a general non-linear correlation between $\nu(\text{CN})$ and $\text{SCF P}^{\pi'}_{\text{CN}}$, which includes the neutral aromatic nitriles, aryl-aliphatic and aliphatic nitrile carbanions, as well as the acetonitrile carbanion.

Very strong bands in the 2046-2071 cm^{-1} region are characteristic** of the

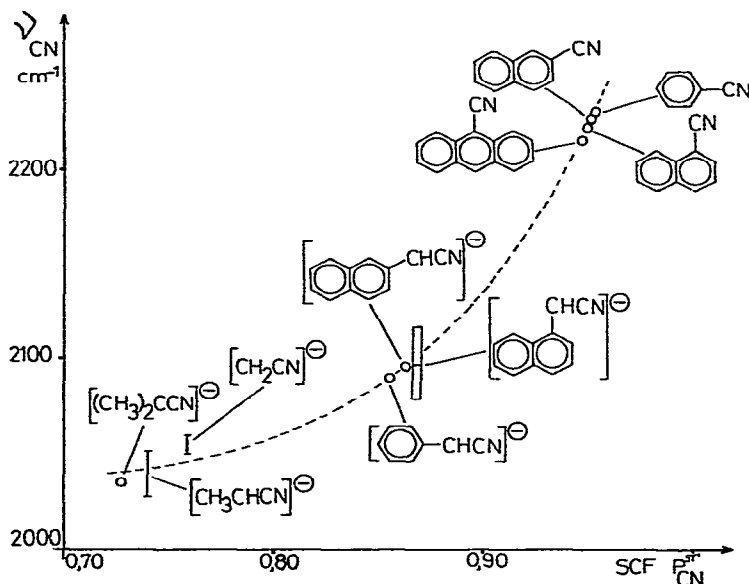


Fig. 4. Plot of $\nu(\text{CN})$ (in THF) vs. SCF P_{CN}^{H} . A frequency region is shown for some compounds, due to the doublet character of the corresponding $\nu(\text{CN})$ bands. The two values of P_{CN}^{H} for lithium α -naphthylacetonitrile correspond to the two planar conformers of the carbanion.

* P.P.P. = Pariser—Parr—Popie.

****** The $\nu(\text{CN})$ bands of the carbanions are 10 to 100 times more intense than the ones of the corresponding neutral compounds [5,6,9]. It seems that no similar rule exists in the case of $\nu(\text{C-H})$ bands [17], and the $\nu(\text{C-D})$ bands are usually even weaker. The bands $\nu(\text{C-D})$ of the deuterioacetonitrile carbanion are also to be expected in the 1800-2300 cm^{-1} region. It is difficult, however, to detect and identify these bands in the presence of the very strong $\nu(\text{CN})$ bands.

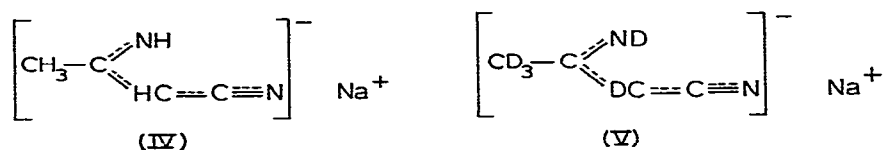
spectra of the lithiated deuterioacetonitrile (Table 1). These bands are completely analogous to the bands $2050\text{--}2071\text{ cm}^{-1}$ of the monolithium acetonitrile (isotopic shift up to -8 cm^{-1}). The small H—D isotopic shift and the similar appearance of the bands prove the weak participation of the hydrogen atoms in the corresponding vibration, this being the $\nu(\text{CN})$ vibration of the acetonitrile (or deuterioacetonitrile) carbanions in the present case.

It was noted in Section A that an unusually high intensity is characteristic of $\nu(\text{CN})$ of carbanions, in which the nitrile group is conjugated with the carbanionic center. Indeed, the bands in the regions $2051\text{--}2071\text{ cm}^{-1}$ (lithiated acetonitrile) and $2046\text{--}2071\text{ cm}^{-1}$ (lithiated deuterioacetonitrile) are very intense: $A \approx 6 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-2}$.

Hence the IR spectra ($1800\text{--}2300\text{ cm}^{-1}$) of the acetonitrile lithium derivative are very similar in solution and in solid state; very strong $\nu(\text{CN})$ bands in the $2071\text{--}2050\text{ cm}^{-1}$ region are characteristic of this organometallic compound. These, and all other data discussed above correspond to the structure $[\text{CH}_2\text{---C}\equiv\text{N}]^-\text{Li}^+$.

C. Assignment of some odd bands in the $1800\text{--}2300\text{ cm}^{-1}$ region which appear in the spectra of some metalated acetonitrile samples

Krüger [1] has assigned the band at 2115 cm^{-1} in the spectrum of a sample of sodium acetonitrile as $\nu(\text{CN})$ of the sodium derivative IV of 2-aminocrotonitrile ("diacetonitrile"). We obtained IV by the method of Meyer et al. [12]; its IR spectrum showed a strong band at 2120 cm^{-1} (solid, in nujol). The frequency of this band is close to the one reported in ref. 1, i.e. the assignment given by Krüger was confirmed.



A band at 2130 cm^{-1} was reported [3] as corresponding to some of the $\text{LiC}_2\text{H}_2\text{N}$ tautomeric forms (Scheme 2, b-e). Indeed, a band appeared at nearly the same frequency (2138 cm^{-1} in nujol, 2135 cm^{-1} in THF; Figs. 2 and 3) in the spectra of samples obtained after incomplete lithiation of acetonitrile, or after partial protonation of lithium acetonitrile. We almost succeeded in avoiding the presence of this band in the spectra of the lithium acetonitrile samples in solution and in solid state (Figs. 2a and 3a) by rapid metalation and use of metalation agent excess (see Experimental). In contrast, this band is dominant in the presence of considerable excess of acetonitrile (Fig. 2c).

A band at 2125 cm^{-1} (in THF) was found in the spectra of the deuterioacetonitrile lithiation products under similar conditions. Strong bands at 2110 cm^{-1} (nujol) and 2126 cm^{-1} (in HMPA) were present in the spectra of the sodium derivative of the deuterioacetonitrile dimer (V).

The data mentioned above lead to the conclusion that the obviously identical bands: 2130 cm^{-1} [3], 2135 and 2138 cm^{-1} (this work) are due to the presence of the lithium derivative of the acetonitrile dimer (Scheme 1, R = H) in the samples studied. When the metalation was carried out in the presence of a

considerable excess of the parent acetonitrile, or after carrying out a slow protonation of the lithium acetonitrile samples, this product was dominant (Fig. 2c). On the other hand, regeneration of a good half of the parent acetonitrile took place after rapid protonation (excess of water or ethanol) of lithium acetonitrile (Fig. 2e). Similar processes took place in the solid samples (Fig. 3), but their course (Scheme 1) is not easy to observe in this case, because of the considerable width of the corresponding bands. The simultaneous presence of lithium acetonitrile and neutral diacetonitrile in the solid samples (see Figs. 3b and c, and the text below) is due to the fact that the reactions take place under heterogeneous conditions.

It follows from Scheme 1 that 2-aminocrotononitrile should be obtained after protonation of the metalated acetonitrile dimer. Indeed, the band at 2136 cm^{-1} [$\nu(\text{CN})$ of the lithium diacetonitrile] disappeared and a new band at 2136 cm^{-1} appeared, upon adding small amounts of water or ethanol to the sample of the metalated acetonitrile dimer (Fig. 2c). We assign the band at 2185 cm^{-1} as $\nu(\text{CN})$ of 2-aminocrotononitrile, taking into account that similar spectral changes took place when IV underwent protonation and 2-amino-crotonitrile was obtained [$\nu(\text{CN})\ 2185\text{ cm}^{-1}$].

The band at 2160 cm^{-1} , reported [4] as $\nu(\text{CN})$ of lithium acetonitrile (solid) does not agree with the data in ref. 3, or with the present data. Obviously, this band does not correspond to the species mentioned [difference in $\nu(\text{CN})$ of ca. 100 cm^{-1}]. On the other hand, the wave number of this band does not coincide with the data on $\nu(\text{CN})$ of the acetonitrile dimerization products (Figs. 2 and 3), although these products have certainly been present in the samples studied [4], since the metalating agent had been used in deficient amounts. One can note that in all wave-numbers above 1100 cm^{-1} reported in ref. 4 the last significant digit is zero; this fact suggests that they have been measured with an error of $\pm 5\text{ cm}^{-1}$ or even more. This is not surprising taking into account the considerable width of the corresponding absorption bands in the solid state (Fig. 3). We cannot be sure that the band at 2160 cm^{-1} [4] is identical with one of the bands above 2100 cm^{-1} in Fig. 1, but it is possible that such an affirmation should prove true. The bands at 2170 and 2140 cm^{-1} , reported [4] as of lithium deuteroacetonitrile, may be looked upon in an analogous way (cf. the data for compound V).

We consider the band at 2200 cm^{-1} (in DMSO), assigned [4] to $\nu(\text{CN})$ of lithium acetonitrile as unreliable. Having in mind the $\text{pK}'\text{s}$ of acetonitrile (29.1 [18]) and of DMSO (33.1 [19]), both in DMSO, one should expect that the acetonitrile carbanion could be obtained in DMSO. Indeed, on addition of

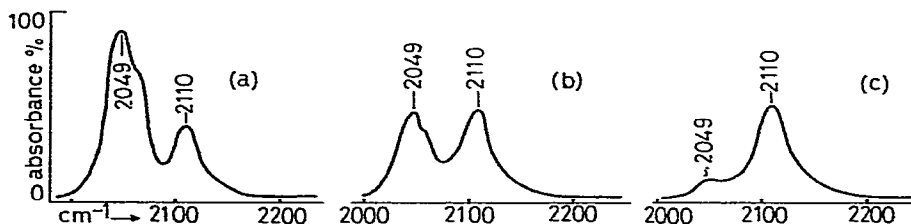


Fig. 5. IR spectra of acetonitrile, metalated by dimethylsodium, in DMSO. The spectra were run at 5 min intervals.

dimethylsodium to a DMSO solution of acetonitrile, and with immediate running of the spectrum, the $\nu(\text{CN})$ band of the acetonitrile carbanion at 2049 cm^{-1} can be observed (Fig. 5; cf. Table 1, data on HMPA). The acetonitrile carbanion is not stable under these conditions: sodium diacetonitrile (IV) is formed rapidly [$\nu(\text{CN})$ at 2109 cm^{-1} , see Fig. 5]. This datum is in full agreement with Scheme 1, the role of proton donor in this case being played by DMSO.

Conductometric, voltammetric, and also molecular weight, UV and NMR spectral data of the products of lithiation of acetonitrile, as well as data for the preparation of derivatives, are reported in ref. 4. Unfortunately, all the experiments have been carried out in DMSO. We do not think the data in ref. 4 should be ignored, but we do think that they characterize other species and not lithium acetonitrile, as postulated by the authors, and therefore those data should be reconsidered.

Krüger [1] mentioned the sharp band of medium intensity at 3260 cm^{-1} as evidence for the presence of tautomeric forms (Scheme 2) in the samples of metalated acetonitrile, and assigned it to $\nu(\equiv\text{C}-\text{H})$ of the "acetylene" form of sodium acetonitrile (Scheme 2, e). By examining the spectra of sodium diacetonitrile (IV) we detected such a band at 3258 cm^{-1} . We assign this band, however, to $\nu(\text{N}-\text{H})$ of IV; this assignment was confirmed by the presence of a similar band at 2412 cm^{-1} [solid, $\nu(\text{N}-\text{D})$] in the spectrum of the corresponding deuterated compound V. The frequency ratio in this case, $\nu(\text{H})/\nu(\text{D})$, is 1.35, close to the norm [20]*.

The fact that the $\nu(\text{N}-\text{H})$ band of IV, and the $\nu(\text{N}-\text{D})$ bands of V are sharp for the solid state spectrum should not be considered as surprising: one should expect that, due to the partial negative charge on the imino group of the anions IV and V, its tendency to act as proton donor in the hydrogen bond-formation should be strongly diminished.

Thus, some odd bands in the IR spectra of the alkali-metal derivatives of phenyl acetonitrile and acetonitrile may be assigned as bands of the products of their further conversions. Things being so, the hypothesis of the existence of tautomeric forms in these cases [1] should be considered, at present, as unsubstantiated. It is possible that such an explanation could also be given in other cases of highly reactive organometallic compounds.

Experimental

The metalation of the nitriles studied was carried out by adding the substrate solution to a small excess of the naphthalene dianion solution (counter ion Li^+) in the corresponding solvent, under pure argon. The solid state samples were prepared by adding nujol to the carbanion solution and subsequent evaporation of the solvent in vacuo.

The spectra were recorded on a Zeiss UR-10 spectrophotometer; the spectra in solution were measured in CaF_2 cells.

* The ratio $\nu(\equiv\text{C}-\text{H})/\nu(\equiv\text{C}-\text{D})$ is always considerably smaller, due to the strong vibrational coupling of the $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ bonds [20].

References

- 1 C. Krüger, *J. Organometal. Chem.*, **9** (1967) 125.
- 2 I.N. Juchnovski, *Teor. Eksp. Khim.*, **3** (1967) 410.
- 3 G.A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **93** (1971) 1714.
- 4 R. Das and C.A. Wilkie, *J. Amer. Chem. Soc.*, **94** (1972) 4555.
- 5 I.N. Juchnovski and I.G. Binev, *C.R. Acad. Bulg. Sci.*, **26** (1973) 659.
- 6 I.N. Juchnovski and I.G. Binev, *Tetrahedron Lett.*, (1974) 3645.
- 7 D.J. Croeger and R. Stewart, *Can. J. Chem.*, **45** (1967) 2163; R. Stewart and D.J. Croeger, *ibid.*, **45** (1967) 2173.
- 8 C.A. Fyfe, *Can. J. Chem.*, **47** (1969) 2231.
- 9 I.G. Binev and I.N. Juchnovski, *Commun. Dep. Chem. Bulg. Acad. Sci.*, **6** (1975), in press.
- 10 I.N. Juchnovski and I.G. Binev, *Chem. Phys. Lett.*, **12** (1971) 40; I.N. Juchnovski and I.G. Binev, *J. Mol. Struct.*, **7** (1971) 490.
- 11 I.N. Juchkovski and I.G. Binev, *C.R. Acad. Bulg. Sci.*, **24** (1971) 483.
- 12 R. Wache, *J. Pract. Chem.*, **39** (1889) 245; E. Von Meyer, *ibid.*, **37** (1887) 400, 410, 38 (1888) 336; R. Holtzwardt, *ibid.*, **39** (1889) 230.
- 13 S. Boldwin, *J. Org. Chem.*, **26** (1961) 3288.
- 14 H.U. Sieveking and W. Luttke, *Angew. Chem.*, **81** (1969) 431, 432; P. Kurtz, H. Gold and H. Disselnkötter, *Justus Liebigs Ann. Chem.*, **624** (1959) 1.
- 15 J.E. Bloor, B.R. Gilson and D.D. Shillady, *J. Phys. Chem.*, **71** (1967) 1238.
- 16 N. Mataga and K. Nishimoto, *Z. Phys. Chem.*, **13** (1953) 140.
- 17 A.N. Rodionov, *Usp. Khim.*, **42** (1973) 2152.
- 18 F.G. Bordwell and W.S. Mathews, *J. Amer. Chem. Soc.*, **96** (1974) 1216.
- 19 O.A. Reutov, K.P. Butin and I.P. Beletskaya, *Usp. Khim.*, **43** (1974) 35.
- 20 L. Sverdlov, M. Kovner and E. Kraynov, *Kolebatel'nye Spektry mnogoatomnykh molecul*, Nauka, Moscow, 1970, pp. 287 and 460.