J. Org. Chem. 1992, 57, 6435–6447

Structural Study and Reactivity of Carbanions in Solution: Phenyl- and 3-Pyridylacetonitriles

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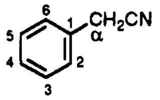
Received June 25, 1991 (Revised Manuscript Received July 15, 1992)

From the IR and ^{13}C NMR spectra of Li- or K-associated anionic species **1A,M** formed from phenylacetonitrile in THF, it appears that monomeric tight ion pairs and THF-solvated aggregates are in equilibrium at 0.25 M concentration; the 0.025 M THF solution of **1A,Li** only contains the monomer, the Li cation being likely located near the N atom of the CN moiety. In toluene–THF or hexane–THF solvent mixtures, solvated aggregates are predominant. In toluene–hexane, only desolvated aggregates are seen. Addition of increasing amounts of HMPA to THF solutions shows the formation of various Li solvates among which, according to low-temperature ^{31}P and ^{7}Li NMR determinations, the Li-di HMPA externally solvated ion pairs predominate. Solvent- or cryptand-separated ion pairs can also be characterized in DMSO or THF in the presence of cryptand. Li- or K-associated 3-pyridylacetonitrile anionic species **2A,M** behave as **1A,M** in toluene, in DMSO, and in THF in the presence of HMPA or of cryptand. In THF, as for **1A,Li**, **2A,Li** monomeric tight ion pairs are in equilibrium with THF-solvated aggregates at c = 0.25 M concentration, the Li cation interacting both with the CN moiety and the pyridyl ring; however, at c = 0.025 M aggregates are still present. **1A,M** and **2A,M** (M = Li, K) aggregates or **1A,Li** and **2A,Li** externally HMPA solvated ion pairs lead to predominant or exclusive 1,4-addition with benzylideneacetone. In THF 1,2-addition takes place with **1A,Li** while **2A,Li** leads to exclusive 1,4 addition; this discrepancy could be due to the fact that the equilibrium between monomeric tight ion pairs and aggregates is different in the two cases and to the different structure of the tight ion pairs, especially the strength of the anion–cation interaction.

Carbanions α to nitriles are very peculiar and useful reagents in organic synthesis,[1] mainly due to the electron-withdrawing ability of the cyano group[2] and to its small size. For instance, we have previously shown that lithiated arylacetonitriles are able to perform conjugate addition to the sterically hindered double bond of isophorone[3a] or of 10-methyl-$\Delta^{1(9)}$-octalin-2-one[3b] with a high yield, thus exhibiting a reactivity similar to that of high-order cuprates.[3c]

Since the knowledge of the structure of the species in solution may be of great help to understand their reactivity, this paper reports IR and NMR studies of the carbanionic species (**1A,M**) formed from phenylacetonitrile (**1**) in the conditions they are used in chemical reactions: countercation, solvent, and concentration.

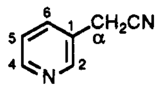


PhCHCN,M
1A,M

1

Recent work on arylmethyl anions with a nitrogen heterocyclic ring[4] has shown the important effect of the heteroatom in the ring on the charge delocalization; that is the reason why this study is extended to the carbanion **2A,M** derived from 3-pyridylacetonitrile (**2**).

In connection with the observed structures, some new experiments on the reactivity of **1A,M** and **2A,M** species toward 1,2 versus 1,4 addition to benzylideneacetone will be given.



3 - PyCHCN,M
2A,M

2

Some studies on the structure of phenylacetonitrile carbanion have been reported: the ^{1}H and ^{13}C NMR parameters of sodium-associated carbanion (**1A,Na**) in DMSO[5a] or in HMPA[5b] as well as those of lithium-associated anionic species (**1A,Li**) in THF[6] have been described. A few IR data (ν(C≡N) band) have also been given.[6,7a] The aggregation degree of lithiated phenylacetonitrile in THF has been determined by cryoscopy and pK_a measurements.[8] The structure has also been proposed by theoretical calculations.[9] Moreover, single-crystal X-ray analysis of the TMEDA-solvated dimeric lithiated phenylacetonitrile (**1A,Li**–TMEDA)$_2$[10] and of the complex (**1A,Li**–LDA)[11] came out recently.

Results and Discussion

Anionic species may exist in solutions as aggregates $(A^-M^+)_n$, tight ion pairs A^-M^+, solvent $A^-//M^+$ or cryptand

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Table I. IR Frequencies[a] (cm^{-1}) and Assignments of Phenylacetonitrile (1-h_5) and Anionic Species 1A,M-h_5

entry	1 1-h_5 liquid	2 1-h_5 THF	3[b] 1A,K-h_5 THF 222	4[b] 1A,K-h_5 THF	5[c] 1A,K-h_5 THF–tol. (40:60)	6[d] 1A,Li-h_5 THF–hex (80:20)	7[c] 1A,Li-h_5 THF	8[c] 1A,Li-h_5 THF–HMPA (74:26)	9[c] 1A,Li-h_5 THF–tol. (35:65)	10 1-h_5 DMSO	11[b] 1A,K-h_5 DMSO	12[c] 1A,Li-h_5 DMSO–THF (67:33)
ν(C≡N)	2253m	2249w	2096s (2083)m	(2100)w (2080) 2069s	(2100)w (2080) 2067s	2089s (2073) 2055w	2092s 2059w	(2112)w 2096s	2092w 2058s	2248w	2095m 2080s	2095s 2080m
8a	1602m	1600w	1585s	1582s	1582s	1583s	1584s	1586s	1586s	1601w	1579s	1582s
8b	1586w		1538w	1548w	1549w	1550w	1550w	(1574)w	1557w	1584w	1542w	1542w
19a	1495s	1494w	1484s	1485s	1485s	1486s	1487s	1486s	1487s	1496w	1484s	1486s
19b	1454s									1455w		
δCH_2	1415s	1417w										
14	1336w		1323w	1323w	1322w	1323w	1323w	1322w	1324w		1324w	1324w
ν_a(C–C–C)			1374m	1373m	1372m	1375m	1376m	1376m	1376m		1373m	1374m
"e"	1203w		1200w	1196w	1192w	1192w	1195w		(1191)w		1199w	1199w
9a	1184w		1169m	1171m	1173w	1172m	1171m	1170m	1174m		1171m	1171m
9b	1157w			1146w			1147w	1145w	1148w		1147w	1147w
18b	1076m											
18a	1029m											
12	1003w											
5	988w						984m		988m			
17a	969w											
ν_s(C–C–C)	940m		1292m	1289m			1289m	1290m	1288m		1289m	1290m

[a] The intensities of the bands are given as strong s, mean m, or weak w. Shoulders are indicated between brackets. $c = 0.25$ M. The bases used are as follows. [b] *t*-BuOK. [c] KHMDS or LHMDS. [d] *n*-BuLi.

$A^-[M^+]$ separated ion pairs, and free ions A^- which are in equilibrium:[7b]

$$(A^-M^+)_n \rightleftarrows n\ A^-\ M^+$$

$$A^-\ M^+ \rightleftarrows A^-//M^+ \rightleftarrows A^- + M^+$$

$$A^-\ M^+ + [\text{cryptand}] \rightleftarrows A^-[M^+] \rightleftarrows A^- + [M^+]$$

Different solvent and concentration conditions have been selected in order to shift these equilibria toward one predominating species.

The anionic species **1A,M** and **2A,M** have been generated in THF or in DMSO, the most frequently used solvents in carbanion chemistry, the countercation M being Li or K. They were prepared and handled under argon in the same way as in the chemical studies by action of 1.1–1.5 equiv of *n*-BuLi in hexane solution, LHMDS[12] in THF solution, KHMDS in toluene solution, or of freshly sublimated potassium tertiobutylate (*t*-BuOK) on the corresponding carbon acid, dissolved in the selected solvent. HMPA or cryptand 222 were added to the THF solution as complexants of Li or K, respectively. Toluene and hexane were either present as solvents of the organic bases or added to THF solutions, in order to lower the dielectric constant of the medium and favour ionic aggregation;[7b] in some cases, precipitation of a solid occurred.

IR and ^{13}C NMR spectra were usually performed with 0.25 M solutions, 0.025 M solutions were used to examine dilution effects in IR. Low-temperature ^{31}P and ^7Li NMR spectra were recorded on 0.12 M or 0.25 M THF–HMPA solutions.

Moreover, the IR assignments were strengthened by comparing the spectra of compounds labeled on the phenyl ring for **1A,M** and on the methylene group for **2A,M** with those of unlabeled species. IR and NMR data for anionic species will be examined and compared to those of neutral precursors.

IR and ^{13}C NMR Spectra of Neutral Precursors 1 and 2. The infrared spectra of phenylacetonitrile (**1**-h_5) and 3-pyridylacetonitrile (**2**-h_2) have been examined as pure liquids and in THF or DMSO solutions at the same concentrations as that of the carbanions. For **1**-d_5 the Raman spectrum of the pure liquid has been recorded. The observed frequencies and the intensities are listed in Table I (entries 1, 2, 10), Table II (entries 1, 2, 3), Table III (entries 1, 2, 7), and Table IV (entries 1, 5). The assignments of the bands are given in each table in terms of group frequencies.

The stretching ν(C≡N) vibrations of phenyl-h_5 and -d_5 and 3-pyridylacetonitriles-h_2 and -d_2 are observed in the 2250 cm^{-1} region, and their frequencies vary slightly with the nature of the solvent.

The observed bands for $PhCH_2CN$-h_5 and -d_5 in the 1700–1030 cm^{-1} region are mainly the five stretching carbon skeleton modes of the benzenic ring: 8a, 8b, 19a, 19b, and 14 according to the Wilson notation.[14] One of the two ν(C–C–C) modes of the bridge between the phenyl and the C≡N group lies at 1203 cm^{-1} for **1**-h_5 (Table I, entry 1); this mode couples, as usually met for monosubstituted benzenic compounds, with an in-plane ring deformation mode 1 or 12 and will be called "e". The second C–C–C mode is probably located at 940 cm^{-1} (Table I, entry 1) and 926 cm^{-1} (Table II, entry 1) for the h_5 and d_5 compounds, respectively. The other modes existing in this region are phenyl ring in-plane bending δ(CH) vibrations: 9a, 9b, 18a, and 18b which shift to lower frequencies in the d_5 compound. The assignments of these benzenic ring modes for the h_5 and d_5 compounds are in excellent agreement with those observed and calculated for toluene.[15] The deformation vibration of the CH_2 group is seen at 1415 (Table I, entry 1) and 1414 cm^{-1} (Table II, entry 1) in the h_5 and d_5 compounds.

The assignments of the bands for 3-pyridylacetonitrile (Tables III and IV) are very similar to those observed for phenylacetonitrile and agree quite well with those of the pyridine molecule ring.[16] The slight frequency shift observed for some skeleton modes, when going from **2**-h_2 to

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(12) The use of LDA as a base induces the formation of mixed aggregates.[11] It also may induce unwanted side reactions. See, for instance: (a) Zervos, M.; Wartski, L.; Seyden-Penne, J. *Tetrahedron* **1986**, *42*, 4963. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (c) Hall, P. L.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9571 and references cited therein. (d) Barnett, N. D. R.; Mulvey, R. E. *J. Am. Chem. Soc.* **1991**, *113*, 8187.

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Table II. IR Frequencies[a] (cm^{-1}) and Assignments of Phenylacetonitrile (1-d_5) and Anionic Species 1A,M-d_5

entry	1 1-d_5 liquid	2[e] 1-d_5 liquid	3 1-d_5 THF	4[b] 1A,K-d_5 THF	5[b] 1A,K-d_5 THF 222	6[d] 1A,Li-d_5 THF–hex (80:20)	7[c] 1A,Li-d_5 THF	8[b] 1A,K-d_5 DMSO	9[c] 1A,Li-d_5 DMSO–THF (67:33)
9a + δCH_2		2294m							
19b + ν(C–C)	2278m		2278w						
$\nu(C\equiv N)$	2252s	2254m	2252w	(2092) 2070s	(2114) 2093s (2072)	2090s 2058m	2090s 2058m	(2114) 2090s (2072)	2090s
8a	(1577)		(1578)w	(1560)	(1558)	(1561)	(1562)	(1557)	
8b	1566m	1565w	1566w	1552s	1549s	1553s	1553s	1549s	1550s
19a	1380s	1380w	1380w	(1428)		(1430)	(1430)		
19b 19b + “e”	1347m			1415s	1417s	1416s	1416s	1416m	1416s
δCH_2	1414s	1414w	1417w						
14	1299w		1305w				(1175)		
13	1162w			1168m	1169m	1167m	1168m	1170m	1170m
9a	872w	872m							
“e” 19b + “e”	1130w	1130m		1352w		1351m (1340) 1317w	1351m (1340) 1317w	1351w	1351w
18b	847m	847m							
18a	823m								
	975w	974m							
12	961m	961s							
ν_s(C–C–C)	926m			1261w		1263w	1262w (1229)	1267w 1258m	1280w 1259w (1229)

[a] The intensities of the bands are given as strong s, mean m, or weak w. Shoulders are indicated between brackets. $c = 0.25$ M. The bases used are as follows. [b] *t*-BuOK. [c] KHMDS or LHMDS. [d] *n*-BuLi. [e] Raman spectrum.

Table III. IR Frequencies[a] (cm^{-1}) and Assignments of 3-Pyridylacetonitrile (2-h_2) and Anionic Species 2A,M-h_1

entry	1 2-h_2 liquid	2 2-h_2 THF	3[b] 2A,K-h_1 THF 222	4[c,d] 2A,Li-h_1 THF	5[c] 2A,Li-h_1 THF–HMPA (74:26)	6[c] 2A,Li-h_1 THF–HMPA (35:65)	7 2-h_2 DMSO	8[b] 2A,K-h_1 DMSO	9[c] 2A,K-h_1 DMSO–tol. (40:60)	10[c] 2A,Li-h_1 DMSO–THF (67:33)	11[c,e] 2A,K-h_1 tol.–THF (60:40)	12[d,e] 2A,Li-h_1 tol.–hex (80:20)
$\nu(C\equiv N)$	2256m	2255w	2111m 2095s	2117s (2104)	2107s	2111s (2094)	2253w	(2130) (2112) 2094s	(2108) 2094s	(2112) 2094s	2094s	2076s
8a	1593w	1592w	1560s	1568s	1560s	1558s	1593w	1560s	1560s	1560s	1565s	1571s
8b	1576m	1576w	1532w	1545m	1535m	1529m	1575w	1534w	1534w	1533w	1538w	1553m
19a	1479m	1478w	1476m (1471)	1483m (1478)	(1475) 1470m	(1475) 1470m	1479w	(1478) 1473m	1478m 1472m	(1478) 1472m	1473m	(1483) 1477m
19b	1426s	1426m	1426m	1430m	1426m	1424m		1425m	1426m	1426m	1428m	1432m
δCH_2	1413m	1413w										
ν_a(C–C–C) or “e”			1377m	1382m 1360w	1377m 1356m	1377m 1354m		1375m 1357m	1375m 1356m	1375m 1357m	1359m	1377m 1363m
14	1345w	1345w	1331w 1323m	1335m 1327w	1331w 1323m	1330w 1322m		1332w 1324m	1332w 1324m	1332w 1324m	1326w	(1337) 1330w
				1292w				1280w			1291w	
ν_s(C–C–C)			1276w	1267m				1264m		(1260)	1268m	1257m
				1227w								
3 or 9a	1216w	(1216)	1206w	1209m				1213m	1212m	1212m	1216m	1212m
15	1177w	1180w	1173w	1179m			1177w	1174w	1177m	1177m	1171m	1177m
	1125w	1125w		1125w			1126w	1130w	1129w	1129w	1128w	1126w
18b	1102w											
18a	1041w											
12	1027m	1026w		1104m	1112m (1104)	1115m 1103m	1104w	1105w	1105w	1104w	1102m	1104w

[a] The intensities of the bands are given as strong s, mean m, or weak w. Shoulders are indicated between brackets. $c = 0.25$ M. The bases used are as follows. [b] *t*-BuOK. [c] KHMDS or LHMDS. [d] *n*-BuLi. [e] Spectrum of the solid.

2-d_2, clearly indicates a small participation of the deformation coordinates of the CH_2 or CD_2 groups to these modes. This is particularly clear for the 19b mode which shifts from 1426 cm^{-1} (Table III, entry 1) in 2-h_2 to 1419 cm^{-1} (Table IV, entry 1) in 2-d_2.

The ^{13}C NMR parameters of 1 and 2 are given in Tables V and VI.

IR and NMR Spectra of Carbanionic Species 1A,M and 2A,M. The IR spectra of the carbanionic species observed in THF, THF–toluene, THF–HMPA, THF–cryptand 222, and DMSO solutions as well as those of some solids are given in Figures 1–9 and their band frequencies in Tables I–IV.

The nature of the predominant ionic species is mainly distinguished in the $\nu(C\equiv N)$ vibration region. Due to the possibility of Fermi resonance with harmonic or combination tone in that region, we have compared the bands observed for 1A,M-h_5 with 1A,M-d_5 and 2A,M-h_1 with 2A,M-d_1. Indeed, two bands are observed by IR for 1A,Li-h_5 compound in DMSO–THF (67:33 v/v) (Figure 1a) at 2095 and 2080 cm^{-1}. These two components are due to a Fermi resonance of the $\nu(C\equiv N)$ vibration with a combination tone level similar to that observed for the CH_3CN molecule.[13] These Fermi resonances are very sensitive to small frequency shifts of the levels and also to deuteration which shifts to lower frequency some skeleton vibration modes. Thus, the spectrum of the 1A,Li-d_5 in DMSO–THF (67:33 v/v) (Figure 1a) shows for the $\nu(C\equiv N)$ absorption only one component at 2090 cm^{-1}, a value intermediate between those of the two main com-

Table IV. IR Frequencies[a] (cm^{-1}) and Assignments of 3-Pyridylacetonitrile (2-d_2) and Anionic Species 2A,M-d_1

entry	1 2-d_2 liquid	2 2-d_2 THF	3[b] 2A,K-d_1 THF 222	4[c] 2A,Li-d_1 THF	4[c,d] 2A,Li-d_1 THF	5 2-d_2 DMSO-d_6	6[b] 2A,K-d_1 DMSO-d_6	7[c] 2A,Li-d_1 DMSO-d_6–THF (67:33)	7[c,d] 2A,Li-d_5 DMSO-d_6–THF (95:5)
ν(C≡N)	2258m	2252w	2101s	2118s	2119s 2102m	2249w	2095s	2097s	2095s
ν(CD)	2218w	2216w				2214w			
8a	1591w	1590w	1557m	1567m	1567m	1590w	1557s	1557s	1557s
8b	1573m	1572w	1528w	1542m	1543m	1572w	1531m	1531m	1531m
19a	1477s	1476w	1474m 1470m	1481m (1474)	1482m (1474)	1477w	1472m	(1474) 1472m	(1475) 1471m
19b	1419s	1419m	1424w 1407w	1430w 1409m	1410w	1419m	1408m (1402)	1425w 1408m	1425w 1408w
ν_a(C–C–C) or "e"			1384w 1375w (1345)	1394w 1380w 1360m	1394w 1381w 1360m		1385w (1360) 1348m	1389w 1373w 1347m	1389w 1373w 1347m
14	1337w	1335w	1329w 1321m	1334m 1325w	1335m 1322w	1338w	1331w 1322m	1331w 1322m	1331w 1322m
ν_s(C–C–C)			1373w	1292w (1262) (1228)			1274w 1257m 1234w	(1252)	(1252)
3 or 9a	1191w	1190w				1191w	1181w		
15	1125w	1125w		1134w		1126w	1133	1132w	
18b	1080w								
18a	1043w								
12	1029m			1105m					
	1016m	1016w					1104w	1104w	

[a] The intensities of the bands are given as strong s, mean m, or weak w. Shoulders are indicated between brackets. c = 0.25 M. The bases used are as follows. [b] *t*-BuOK. [c] LHMDS. [d] c = 0.025 M.

Table V. ^{13}C Chemical Shifts of Phenylacetonitrile (1) and Anionic Species 1A,M[a]

entry	species	M[b]	solvent (v:v)	C_α	CN	C_1	C_2 C_6	C_3 C_5	C_4
	1		THF	23.1	118	131.3	128.3	129.3	128.0
	1		DMSO	21.0	117.7	129.7	126.6	127.4	126.1
1	1A	Li	THF–tol. (35:65)	32.2 (+9.1)	150.3 (+32.3)	148.3 (+17)	119.4 (−8.9)		114.5 (−13.5)
2	1A	Li	THF	31.9 (+8.8)	144.3 (+26.3)	149.4 (+18.1)	118.2 (−10.1)	127 (−2.3)	112.0 (−16)
3	1A	Li	THF (0.06 M)	31.9 (+8.8)	143.1 (+25.1)	149.9 (+18.6)	118.1 (−10.2)	127.8 (−1.5)	111.7 (−16.3)
4	1A	Li	THF–HMPA (80:20)	33.9 (+10.8)	137.3 (+19.3)	151.4 (+20.1)	116.9 (−11.4)	127 (−2.3)	108.9 (−19.1)
5	1A	Li	THF–HMPA (35:65)	35.05 (+11.9)	134.3 (+16.3)	152.2 (+20.9)	116.5 (−11.8)	127.7 (−1.6)	107.5 (−20.5)
6	1A	K	THF	31.7 (+8.6)	141.6 (+23.6)	149.8 (+18.5)	117.8 (−10.5)	128.2 (−1.1)	111.8 (−16.2)
7	1A	K	DMSO	32.4 (+11.4)	134 (+16.3)	147.9 (+18.2)	115.8 (−10.8)	126.3 (−1.1)	108.7 (−17.4)
8	1A	K	THF 222	34.9 (+11.8)	134.5 (+16.5)	152.2 (+20.9)	116.4 (−11.9)	127.7 (−1.6)	107.7 (−20.3)

[a] c = 0.25 M. Variations Δδ (δ in **1A,M** − δ in **1**) are indicated by numbers with a sign in brackets. [b] The bases used are LHMDS or *t*-BuOK.

ponents observed for **1A,Li**-h_5. Such is also the case for the spectra of **1A,K**-h_5 (Figure 2a) in DMSO; **1A,K**-h_5 (Figure 2b) and **2A,K**-h_1 (Figure 4b) in THF in the presence of cryptand 222.

The ^{13}C parameters of **1A,M** and **2A,M** are given in Tables V and VI. The assignments rely on comparison with literature[4-6] and on the multiplicity of the signals determined by off-resonance technique. The low-temperature ^{31}P and ^{7}Li NMR chemical shifts for **1A,Li** and **2A,Li** in THF solutions with various amounts of HMPA are indicated in Table VII.

The main trends observed in the IR spectra are the following: (i) According to the anion–cation interaction and the aggregation state of the various species, low-frequency ν(C≡N) bands related to the neutral precursors are seen. The ν(C≡N) infrared absorption band frequencies for **1A,M** or **2A,M** species, generated with 1.1 or 1.5 equiv of base, are lying in the 2120–2045 cm^{-1} region; small shoulders or bands around 2130 cm^{-1} only appear with larger amounts of base. Meth-Cohn et al.[6] observed ν(C≡N) infrared absorptions frequencies for **1A,Li** at 2160 and 2130 cm^{-1} using 1 equiv of LHMDS in THF and at 1905 cm^{-1} with 2 equiv of the same base; this last band has been assigned to a quasi dianion complex. It appears that in our conditions at least with LHMDS in THF, the formation of such complexes is avoided. It also strengthens the importance of the nature and amount of lithiated bases used to generate carbanions or enolates.[12]

(ii) The IR skeleton modes are also strongly affected (Figures 7A,B, 8A,B, and 9). Some of the benzenic ring C-C vibrations, which were of rather weak intensity in the neutral molecule **1**-h_5 (Table I, entry 1), become intense such as vibrations 8a and 19a in the **1A,M**-h_5 species (Table I). Their frequencies slightly decrease when going from the neutral precursor to the carbanions. The bands assigned to the vibration modes of the C–C–C bridge, that is to say the "e" mode at 1203 cm^{-1} coupled with a ν_a(C–C–C) benzenic ring mode and the ν_s(C–C–C) one located

Table VI. ^{13}C Chemical Shifts of 3-Pyridylacetonitrile (2) and Anionic Species 2A,M[a]

entry	species	M[c]	solvent (v:v)	C_α	CN	C_1	C_2 C_6	C_3 C_5	C_4
	2		THF	20.7	118.1	127.8	149.7		149.5
							135.7	124	
	2		DMSO	18.5	117.2	126	147.6		147.4
							134.4	122.4	
1	2A	Li	THF-tol. (75:25)	31.4 (+10.7)	137.3 (+19.2)	147.3 (+19.5)	140.6 (-9.1)		123.0 (-26.5)
							131.0 (-4.7)	123.5 (-0.5)	
2	2A	Li	THF	31.3 (+10.6)	137 (+18.9)	147.3 (+19.5)	140.5 (-9.2)		122.9 (-26.6)
							131 (-4.7)	123.5 (-0.5)	
3	2A	Li	THF-HMPA (87:13)	31.2 (+10.5)	135.3 (+17.2)	147.2 (+19.4)	141.0 (-8.7)		120.5 (-29)
							130.8 (-4.9)	122.7 (-1.3)	
4[b]	2A	Li	THF-HMPA (74:26)	31.7 (+11)	134.1 (+16)	147.5 (+19.7)	140.8 (-8.9)		119.9 (-29.6)
							130.1 (-5.6)	122.6 (-1.4)	
5	2A	Li	THF-HMPA (35:65)	32.6 (+11.9)	132.5 (+14.4)	147.8 (+20)	140.6 (-9.1)		119.3 (-30.2)
							129.3 (-6.4)	122.2 (-1.8)	
6	2A	Li	DMSO-THF (67:33)	30.5 (+9.8)	133.0 (+14.9)	144.9 (+17.1)	138.5 (-11.2)		118.9 (-30.6)
							129.4 (-6.3)	122.1 (-1.9)	
7	2A	K	DMSO	30.1 (+11.6)	132.6 (+15.4)	144.7 (+18.7)	138.1 (-9.5)		118.7 (-28.7)
							129.6 (-4.8)	122.0 (-0.4)	

[a] c = 0.25 M. Variations $\Delta\delta$ (δ in 2A,M − δ in 2) are indicated by numbers with a sign in brackets. [b] At low temperatures (−40 °C) two sets of signals are observed for C_1: 147.7 and 147.1; C_2: 140.7 and 140.0; C_5: 123.2 and 122.6 ppm. [c] The bases used are LHMDS or t-BuOK.

Table VII. ^{31}P[a] **and ^7Li**[b] **Chemical Shifts of 1ALi and 2ALi**[c] **(δ ppm, $W_{1/2}$, Hz)**

entry	species	concn (M)	T, °C	equiv of HMPA	free HMPA $\delta^{31}P$	complexed $\delta^{31}P$ ($W_{1/2}$)	equiv of HMPA/Li[d] found	δ^7Li ($W_{1/2}$, Hz)
1	1A,Li	0.25	20	4	24.99			-0.19 (12.8)
			-120	4	24.65	25.33 (31.9)	2.5	-0.35 (20.5)
2	2A,Li[e]	0.25	20	4	24.74			
			-60	4	24.35	25.01 (28.6)	2.6	
3	2A,Li	0.12	20	10	24.74			
			-100	10	24.35	25.02 (34.5)	2.7	-0.45 (24.5)

[a] $\delta^{31}P$ in ppm from H_3PO_4. [b] δ^7Li in ppm from LiBr/CD_3OD (c = 0.6M). [c] 1A,Li and 2A,Li are generated in THF using n-BuLi 1.6 M hexane solution. [d] The number of HMPA equiv per Li is calculated by relative integration of ^{31}P NMR peaks. [e] At lower temperature than −80 °C the solution is freezing.

at 940 cm^{-1} in 1-h_5, are shifted for **1A,M-h_5** to higher frequencies and appear as mean intense bands around 1373 and 1288 cm^{-1}, respectively. In the **1A,M-d_5** species (Table II) the 19a benzenic ring mode is expected to be lowered by 10 cm^{-1}, i.e., at 1370 cm^{-1}, a frequency very close to that of the "e" mode at 1373 cm^{-1}; consequently, the corresponding coordinates mix and two new modes are seen at approximately 1416 and 1351 cm^{-1}. The other ν_s(C–C–C) mode is observed at a slightly lower frequency than in the h_5 species around 1263 cm^{-1}. In **1A,M-d_5** one the 8b absorption appears at about 1550 cm^{-1} and is more intense than the 8a mode of the **1A,M-h_5** species at about 1582 cm^{-1}.

While the 8a and 19a absorption bands have almost the same intensities in **1A,M-h_5**, the 8a mode has an increased intensity compared to the 19a one in the **2A,M** carbanionic species (M = Li or K) (Tables III and IV). Moreover, the 8a frequency is lowered by 30 cm^{-1} relative to the neutral precursor while this difference is only 20 cm^{-1} for phenylacetonitrile. For most of the carbanionic species observed, several skeleton modes, 19a, "e" or ν_a(C–C–C) and 14 for **2A,M-h_1** or 19a, 19b, "e" or ν_a(C–C–C), and 14 for **2A,M-d_1** show at least two components; their presence may be assigned to the existence of two Z or E conformers[4] of the carbanion. The absence of splitting for the 19b mode in **2A,M-h_1**, compared to **2A,M-d_1** is probably related to the mixing with a δ(CD) coordinate, similar to that suggested for the δ(CH_2) coordinate in the parent neutral molecule 2-h_2, while this mixing should be absent for the δ(CH) coordinate.

The ^{13}C NMR signals are generally very sharp indicative of no ^{13}C–^7Li quadrupole interaction.[17] All the carbanionic **1A,M** and **2A,M** species exhibit a large $^{13}C\alpha$–H one bond coupling constant (164.4 Hz) showing thus the planarity of this carbon.[17] The significant ^{13}C shift variations are upfield C_4 shifts, always larger in **2A,M** than in **1A,M**, and downfield CN shifts: their magnitudes also vary according to the anion–cation interaction and aggregation state.

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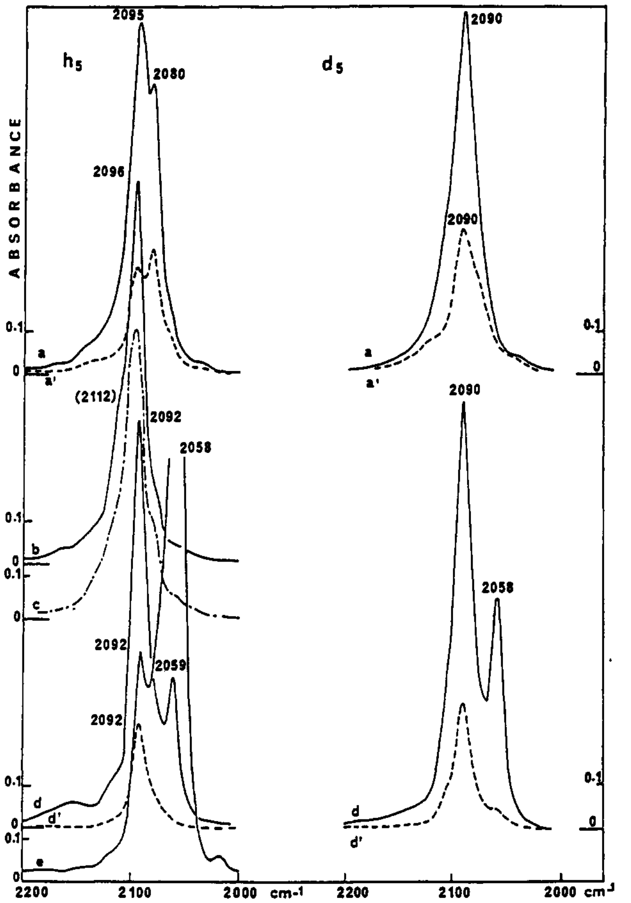


Figure 1. Infrared absorption spectra in the ν(C≡N) vibration region of lithium carbanions **1A,Li**-h_5 or -d_5 in solution. The solvents are DMSO–THF (67:33 v/v) (a) and (97:3 v/v) (a′); THF–HMPA (74:26 v/v) (b) and (35:65 v/v) (c); THF (d,d′); toluene–THF (65:35 v/v) (e). The base used is LHMDS. The concentrations are 0.25 M (a–e) and 0.025 M (a′, d′).

(1) Structure of Solvent- or Cryptand-Separated Ion Pairs and Free Ions. The Δδ $^{13}C_\alpha$, ^{13}CN, $^{13}C_1$, and $^{13}C_4$ chemical shift variations (Table V, entries 5, 7, and 8) as well as the ν(C≡N) vibrations are very close for **1A,Li**-h_5 in THF–HMPA (35:65 v/v) 2096 cm^{-1} (Figure 1c), **1A,K**-d_5 in THF 222, 2093 cm^{-1} (Figure 2b), **1A,K**-d_5 in DMSO, 2090 cm^{-1} (Figure 2a) or **1A,Li**-d_5 in DMSO, 2090 cm^{-1} (Figure 1a) solutions. These species are therefore solvent- or cryptand-separated ion pairs or free ions.

From the Δδ ^{13}CN of +16.3 to 16.5 ppm and the Δν(C≡N) frequency lowering of 157–160 cm^{-1}, it appears that the negative charge is not highly delocalized into the CN moiety, the CN group mainly exhibiting a –I effect in carbanion stabilization, as already proposed by Bordwell.[2] Charge delocalization into the phenyl ring is the most important for **1A,Li** in THF–HMPA as estimated by C_4 shielding (–20.5 ppm) when going from the neutral precursor to the anionic species;[17] this value is quite larger than in the related ketone or ester enolate,[18,19a] a fact which is in agreement with the previously quoted CN effect. Such a charge delocalization into the **1A,Na** species has already been shown through the influence of the phenyl ring para substituent[7] on the ν(C≡N) frequency. Nevertheless, this charge delocalization is not as high as in some nonfunctionalized benzylic carbanions, i.e., norbornyl- or cyclohexyl-substituted ones.[21] This charge delocalization which polarizes the phenyl ring is responsible for the large intensity increase of some phenyl ring vibrational modes (Figure 7A, c,e; 7B, b,e,c,f) as seen before.

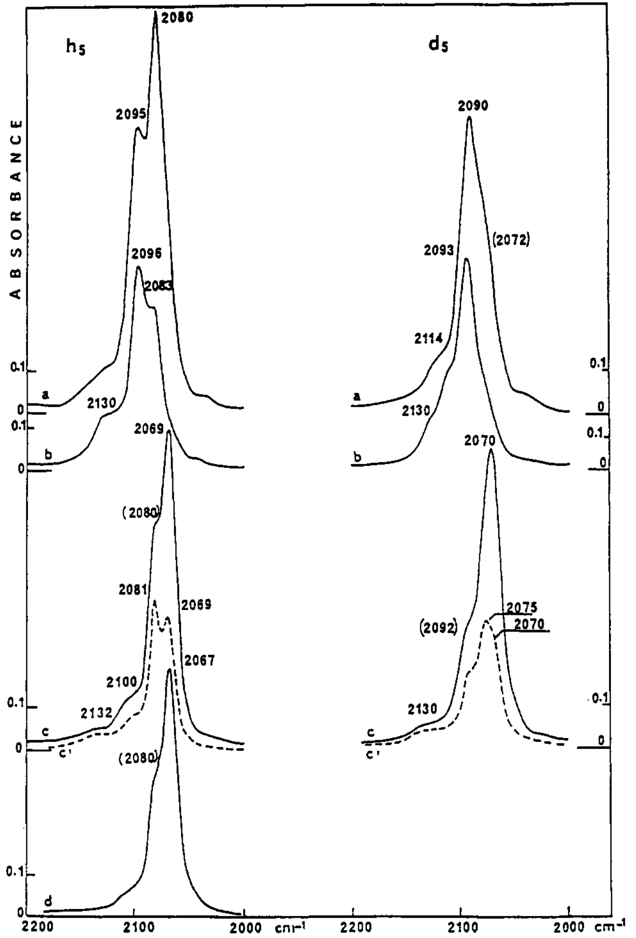
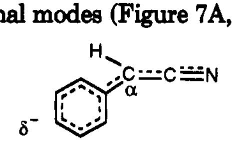
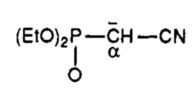


Figure 2. Infrared absorption spectra in the ν(C≡N) vibration region of potassium carbanions **1A,K**-h_5 or -d_5 in solution. The bases used are *t*-BuOK (a, b, c, c′) or KHMDS (d). The solvents are DMSO (a); THF in presence of 1.2 equiv of cryptand 222 (b); THF (c, c′); toluene–THF (60:40 v/v) (d). The concentrations are 0.25 M (a–d) and 0.025 M (c′).



1A$^-$



$(EtO)_2\overset{\displaystyle O}{P}–\bar{C}H_\alpha–CN$

3A$^-$

The influence of a nitrile group on charge delocalization can also be compared in phenylacetonitrile carbanion **1A$^-$** and in the diethyl cyanomethylphosphonate **3A$^-$**;[22] the Δδ ^{13}CN chemical shift variation (+16.3 ppm) for **1A,K** in THF 222 and **3A,K** in DMSO 222 is the same, indicative of a similar electronic reorganization around the nitrile moiety for both species. However, when going from the neutral precursor to the anion, C_α is shifted to more positive values in **1A,K** (ΔδC_α = +11.7 ppm) and to more negative ones in **3A,K** (ΔδC_α = –11.4 ppm), a fact indicating a better charge delocalization ability of the phenyl group related to the phosphoryl one.

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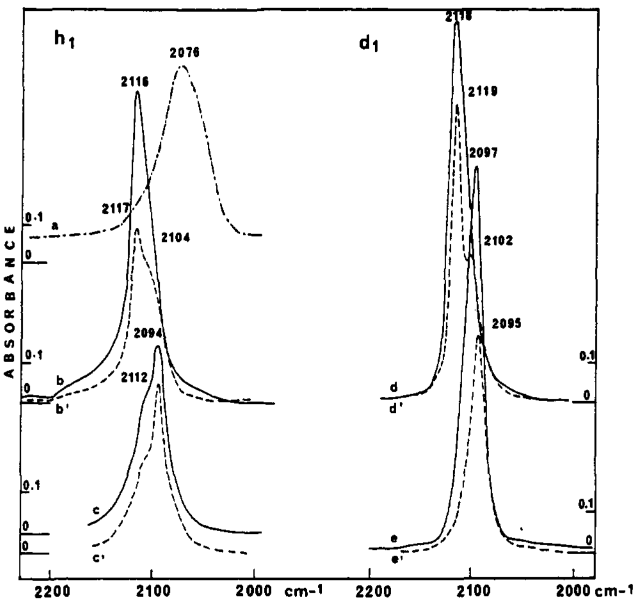
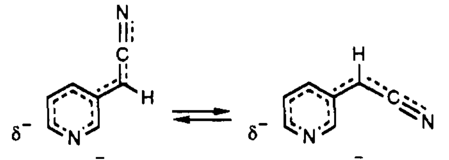


Figure 3. Infrared absorption spectra in the $\nu(C{\equiv}N)$ vibration region of lithium carbanions **2A,Li**-h_1 or -d_1 in solution (b, b′, c, c′, d, d′, e, e′) or in the solid state (a) precipitated from a solution in toluene–hexane (80:20 v/v). The bases used are *n*-BuLi (a) or LHMDS (b, b′, c, c′, d, d′, e, e′). The solvents are THF (b, b′, d, d′); DMSO–THF (67:33 v/v) (c) and (95:5 v/v) (c′); DMSO-d_6–THF (67:33 v/v) (e) and (95:5 v/v) (e′). The concentrations are 0.25 M (b, d, e), 0.22 M (c), 0.033 M (c′), and 0.025 M (b′, d′, e′).

The IR spectra of **2A,K**-d_1 in THF 222 (Figure 4e) or **2A,Li** in THF–HMPA (35:65 v/v) (Figure 5d) exhibit a $\nu(C{\equiv}N)$ absorption around 2101 cm^{-1}. The two bands observed at 2111 and 2094 cm^{-1} for **2A,Li**-h_1 (Figure 5d) are probably due to a Fermi resonance such as in the case of **2A,K**-h_1 (Figure 4b). In DMSO, **2A,K**-d_1 or **2A,Li**-d_1 presents also only one $\nu(C{\equiv}N)$ absorption at 2095 and 2097 cm^{-1}, respectively (Figures 4f and 3e). These results confirm the existence of only solvent- or cryptand-separated ion pairs or free ions in these solutions.

In these species, two conformers **2A$_1^-$** and **2A$_2^-$** in equilibrium can be characterized by the splitting in two components of IR skeleton modes 19a, "e" or 14 (Table III, entries 3, 6, 8, 10; Table IV, entries 3, 6, 7; Figures 8A,B and 9), only one band being observed for these modes in **1A$^-$**. A similar equilibrium has been pointed out by Bank and Dorr[4] in benzylpyridine systems.



2A$_1^-$ **2A$_2^-$**

From the ^{13}C NMR data (Tables V and VI) and the $\Delta\nu(C{\equiv}N)$ frequency lowering (154 cm^{-1}) it appears that the charge density around the C_α–CN moiety is very similar in **2A$^-$** and **1A$^-$**: the chemical shift variations of these two carbons $\Delta\delta$ in THF–HMPA (35:65 v/v) for instance are very close (Table V, entry 5 and Table VI, entry 5): +11.9 ppm for $^{13}C_\alpha$ in both cases and, respectively, +16.3 and +14.4 ppm for ^{13}CN. However, electron delocalization into the heteroaromatic ring of **2A$^-$**, as estimated from C_4 shielding (−30.2 ppm, Table VI, entry 5) is larger than into the phenyl ring of **1A$^-$** (−20.5 ppm, Table V, entry 5): such an ability of the 3-pyridyl moiety to accommodate a negative charge better than the phenyl one is in agreement with the previous findings of Bank and Dorr.[4]

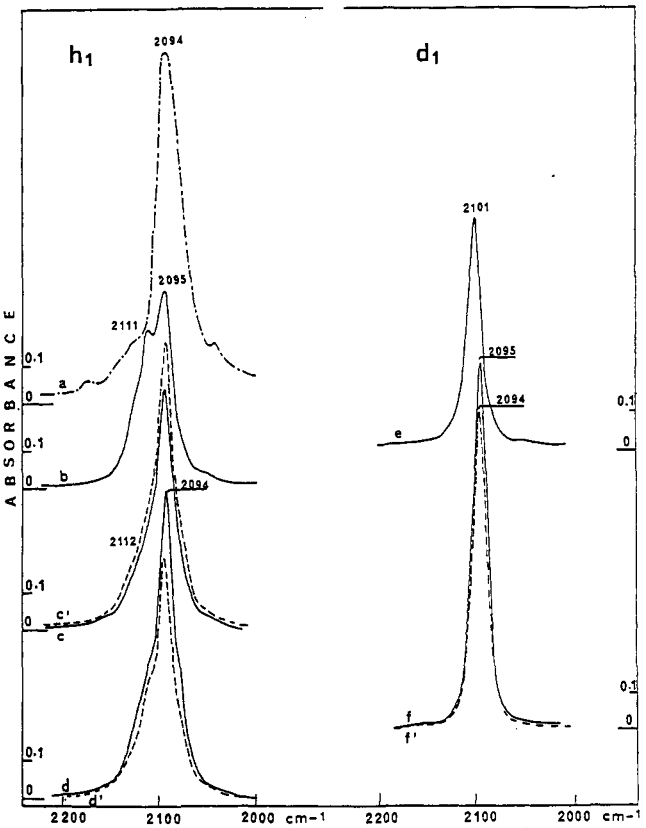


Figure 4. Infrared absorption spectra in the $\nu(C{\equiv}N)$ vibration region of potassium carbanions **2A,K**-h_1 or -d_1 in solution (b, c, c′, d, d′, e, f, f′) or in the solid state (a) precipitated from a solution in toluene–THF (60:40 v/v). The bases used are KHMDS (a, d, d′) or *t*-BuOK (b, c, c′, e, f, f′). The solvents are THF in the presence of 1.2 equiv of cryptand 222 (b, e); DMSO (c, c′); toluene–DMSO (60:40 v/v) (d) and (10:90 v/v) (d′); DMSO-d_6 (f, f′). The concentrations are 0.25 M (b, c, d, e, f), 0.05 M (c′), 0.037 M (d′), and 0.025 M (f′).

(2) Structure of Aggregates. (i) Phenylacetonitrile 1A,M Aggregates. In THF using *n*-BuLi (THF–hexane (80:20 v/v)) (Table I, entry 6) or LHMDS as bases (Figure 1d; Table I, entry 7), three $\nu(C{\equiv}N)$ absorptions are observed for **1A,Li**-h_5: a band at 2055 or at 2059 cm^{-1} and a shoulder at 2073 cm^{-1} can be assigned to solvated aggregates and the one located at 2089 or at 2092 cm^{-1} to monomeric tight ion pairs; these species are in equilibrium at 0.25 M concentration. At 0.025 M concentration, only monomeric tight ions pairs can be characterized by IR in pure THF (Figure 1d′). This is in agreement with Bauer and Seebach's cryoscopic determination at a similar concentration,[8a] although at −108 °C, and with Streitweiser's pK_a measurements.[8b] As more hexane is present in THF solution (THF–hexane (63:37 v/v)) the previous shoulder at 2073 cm^{-1} becomes clearly a band (Figure 6a) showing thus the increase of the amount of these aggregates at 0.25 M when using *n*-BuLi as a base. Moreover a crystalline solid whose $\nu(C{\equiv}N)$ lies at 2065 cm^{-1} has been isolated from a THF–hexane (25:75 v/v) solution (*c* = 0.12 M).

In toluene solution (toluene–THF (65:35 v/v)), using LHMDS as a base, aggregates presenting a $\nu(C{\equiv}N)$ at 2058 cm^{-1} (Figure 1e) are the predominant species (*c* = 0.25 M).

All these aggregates exhibit a much lower frequency shift of the $\nu(C{\equiv}N)$ absorption compared to that of cryptated ion pairs at 2093 cm^{-1} (Figure 2b). This is indicative of a weakening of the CN force constant due a strong interaction with the Li cation. For these aggregates the $\Delta\delta$ ^{13}CN downfield shift variation ($\Delta\delta$ = +32.3 ppm, Table V,

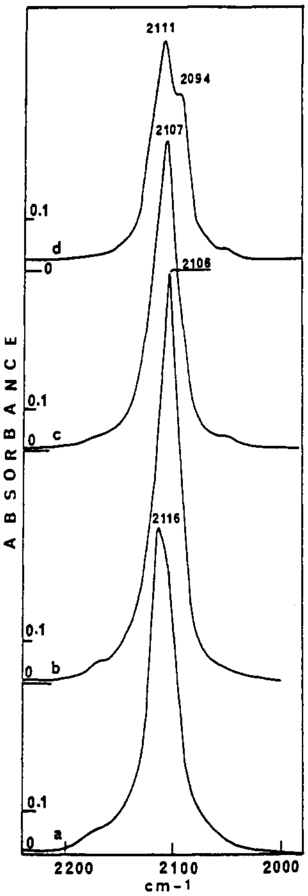


Figure 5. Infrared absorption spectra in the $\nu(C{\equiv}N)$ vibration region of a 0.25 M solution of **2A,Li-**h_1 in THF with different amounts of HMPA added. THF-HMPA (100:0 v/v) (a); (87:13 v/v) (b); (74:26 v/v) (c); (35:65 v/v) (d). The base used is LHMDS.

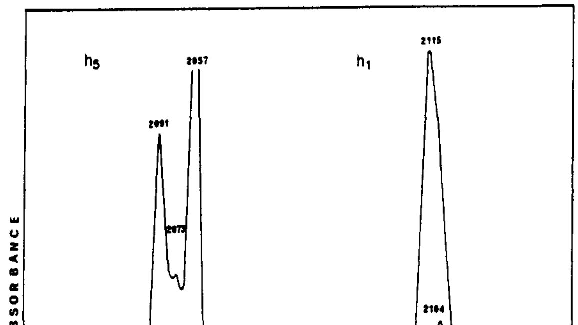


Figure 6. Infrared absorption spectra in the $\nu(C{\equiv}N)$ vibration region of lithium carbanions **1A,Li-**h_5 (a) and **2A,Li-**h_1 (b, b′) in solution. The solvents are THF–hexane (63:37 v/v) (a); THF–toluene (50:50 v/v) (b) and (5:95 v/v) (b′). The bases used are *n*-BuLi (a) and LHMDS (b, b′). The concentrations are 0.25 M (a, b) and 0.025 M (b′).

entry 1) related to that of solvent-separated ion pairs ($\Delta\delta$ = +16.3 ppm, Table V, entry 5) also shows the strongest interaction of the cation with the nitrile moiety.

Furthermore the aromatic skeleton vibrations in the aggregates, whose $\nu(C{\equiv}N)$ lie at 2058 cm^{-1} (Table I, entry 9, Figure 7A, a) and in the solid state at 2065 cm^{-1}, are not very different from those of the cryptated ion pairs (Table I, entry 3, Figure 7B, c). It seems that, as in the crystalline

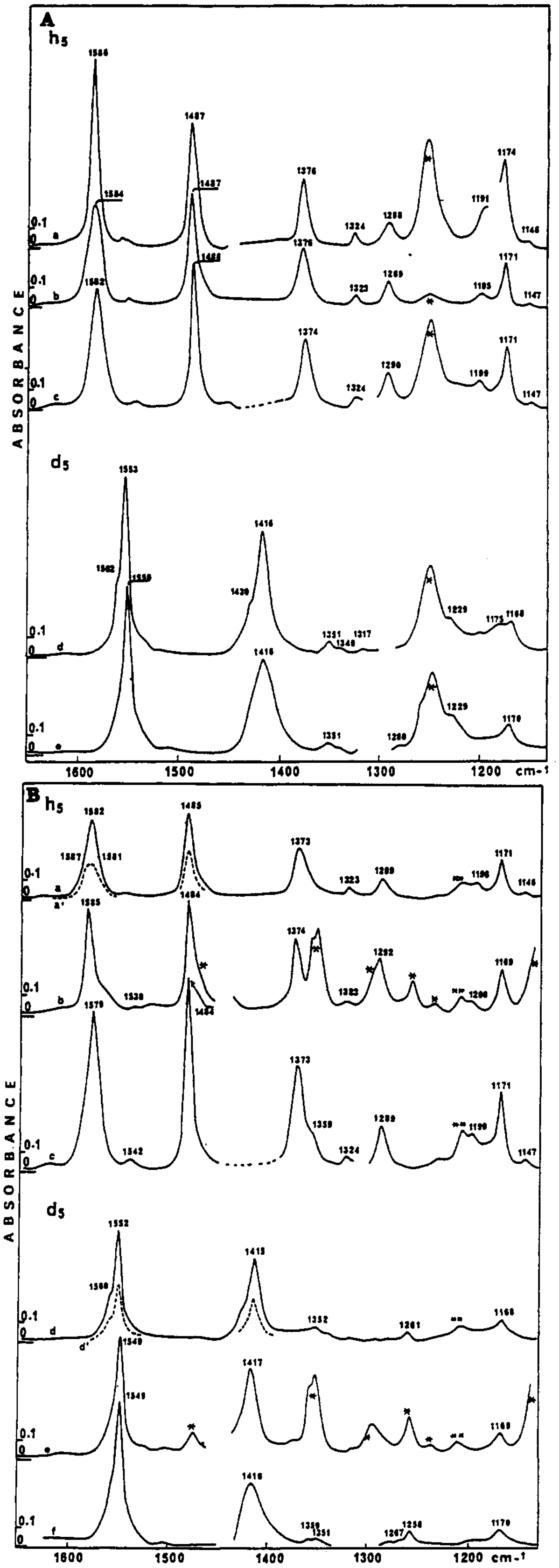


Figure 7. (A) Infrared absorption spectra in the skeleton vibrations region of a 0.25 M solution of **1A,Li-**h_5 or -d_5. The solvents are toluene–THF (65:35 v/v) (a); THF (b, d); DMSO–THF (65:35 v/v) (c, e). The base used is LHMDS. *Absorption band of HMDS (for b HMDS is evaporated). (B) Infrared absorption spectra in the skeleton vibrations region of a 0.25 M or 0.025 M (---) solution of **1A,K-**h_5 or -d_5. The base used is *t*-BuOK. The solvents are THF (a, a′, d, d′); THF in the presence of 1.2 equiv of cryptand 222 (b, e); DMSO (c, f). *Absorption bands of cryptand 222 (b, e). **Absorption bands of *t*-BuOH.

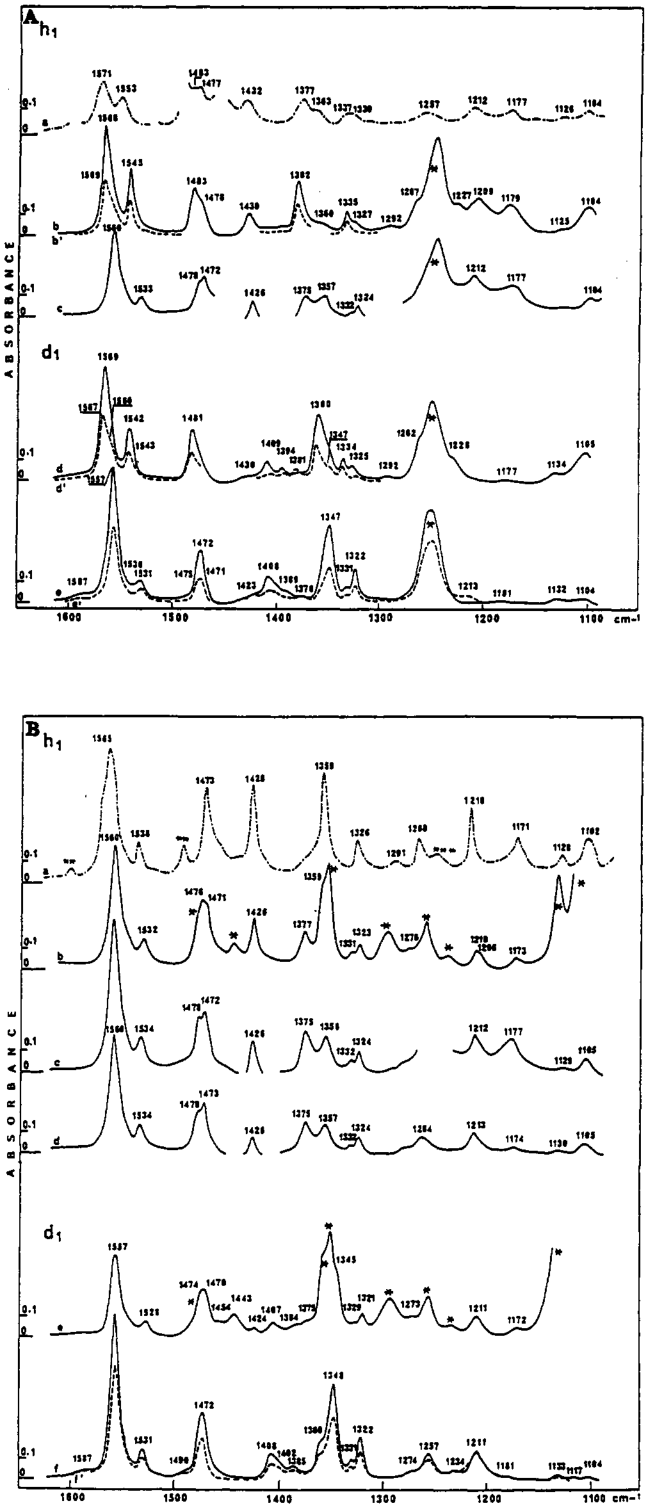


Figure 8. (A) Infrared absorption spectra in the skeleton vibrations region of **2A,Li**-h_1 or -d_1 in solution (b, b′, c, d, d′, e, e′) or in the solid state (a) precipitated from a solution in toluene–hexane (80:20 v/v). The bases used are *n*-BuLi (a) or LHMDS (b, b′, c, d, d′, e, e′). The solvents are THF (b, b′, d, d′); DMSO–THF (67:33 v/v) (c); DMSO-d_6–THF (67:33 v/v) (e) and (95:5 v/v) (e′). The concentrations are 0.25 M (b, d, e), 0.22 M (c), 0.025 M (b′, d′, e′). *Absorption band of HMDS. (B) Infrared absorption spectra in the skeleton vibrations region of **2A,K**-h_1 or -d_1 in solution (b, c, d, e, f, f′) or in the solid state precipitated from a solution in toluene–THF (60:40 v/v) (a). The bases used are KHMDS (a, c), *t*-BuOK (d, f, f′), *t*-BuOK with 1.2 equiv of cryptand 222 added (b, e). The solvents are THF (b, e); toluene–DMSO (60:40 v/v) (c); DMSO (d); DMSO-d_6 (f, f′). The concentrations are 0.25 M (b–f), 0.025 M (f′). *Absorption band of cryptand 222. **Absorption band of toluene. ***Absorption band of traces of HMDS.

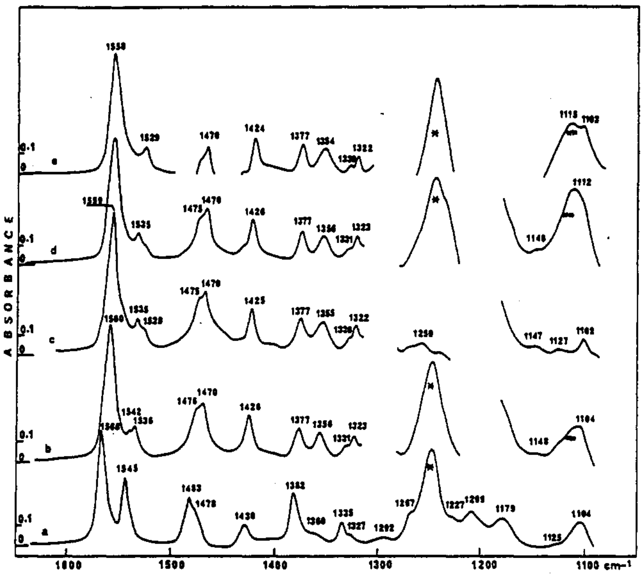
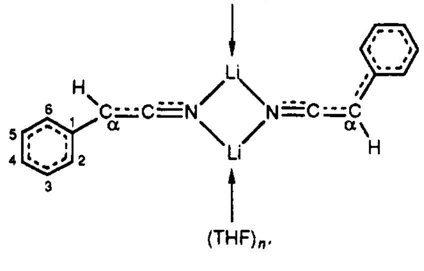


Figure 9. Infrared absorption spectra in the skeleton vibrations region of a 0.25 M solution of **2A,Li** in THF with different amounts of HMPA added. The bases used are LHMDS (a, b, d, e) or *n*-BuLi (c). The solvents are THF–HMPA (100:0 v/v) (a); (87:13 v/v) (b); (74:26 v/v) (d); (35:65 v/v) (e); THF–hexane–HMPA (50:24:26 v/v/v) (c). *Absorption band of HMDS. **Absorption band due to ν(PO) perturbated by LHMDS in excess.

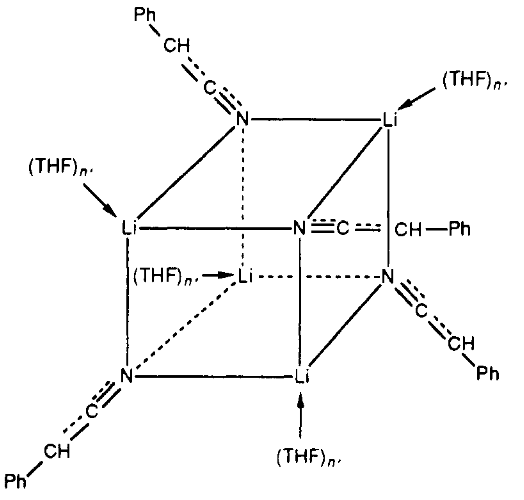
solid,[10] the lithium cation is located in the vicinity of the CN nitrogen. This hypothesis is strengthened by the following observations: (i) the large frequency increase of the "e" mode or of the ν_s(C–C–C) mode located, respectively, at 1376 and 1288 cm^{-1} (Table I, entry 9, Figure 7A, a) is in excellent agreement with the shortening of the C_1–C_α and C_α–CN bonds (C_1–C_α = 1.432 Å and C_α–CN = 1.382 Å), determined by X-ray crystallography, compared to the C–C single bond length of approximatively 1.5 Å in the parent molecule **1**; (ii) the small frequency decrease (−14 and −7 cm^{-1}) for 8a and 19a modes, for instance (Table I, entry 9), and their large intensity increase when comparing the spectra of the parent molecule **1** with that of these aggregates also indicate charge delocalization into the phenyl moiety producing a deformation of the phenyl ring. Such a deformation is observed in the solid,[10c] the C_6–C_1–C_2 and C_3–C_4–C_5 angles being, respectively, 115.7° and 118.6°.

We therefore assign to the soluble aggregates whose ν(C≡N) is observed at 2073 cm^{-1} and to the solid one observed at 2065 cm^{-1} a dimeric structure $(\mathbf{1A,Li})_2(\mathrm{THF})_n$ similar to that determined by X-ray crystallography,[10] showing a ν(C≡N) at 2065 cm^{-1} with TMEDA being the ligand instead of THF in the latter case.



$(\mathbf{1A,Li})_2(\mathrm{THF})_n$

For the aggregates whose ν(C≡N) is lying at 2058 cm^{-1} a tetrameric cubic structure $(\mathbf{1A,Li})_4(\mathrm{THF})_n$ could be envisioned with three Li cations around the nitrile moiety. A more detailed quantitative study of the THF–hexane solvent effect confirms these assignments.[19b]



(**1A**,**Li**)$_4$(THF)$_n$

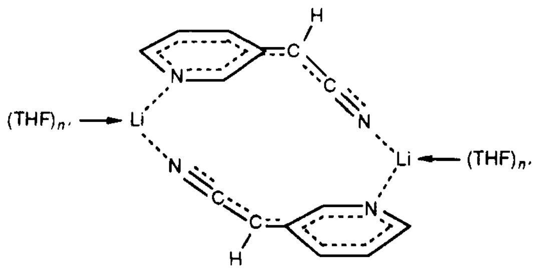
Finally, in toluene-hexane solution (80:20 v/v) using n-BuLi as a base (c = 0.25 M) another solid precipitated which exhibits a ν(C$\equiv$N) absorption at 2045 cm^{-1}. This latter species is probably an unsolvated aggregate (**1A**,**Li**)$_n$, the Li cation being also in the vicinity of the C$\equiv$N nitrogen. Unsolvated aggregates of LDA have been recently studied by X-ray crystallography.[12d]

The **1A**,**K** species formed in THF with t-BuOK or KHMDS (Figure 2c,d) are soluble aggregates characterized by a lower ν(C$\equiv$N) absorption at 2069 or 2067 cm^{-1}, respectively, related to the cryptand-separated ion pairs in THF (2093 cm^{-1}). These aggregates have probably a polymeric structure similar to that of (**1A**,**Li**)$_n$(THF)$_{n'}$ although the cation–anion interaction is somewhat weaker as indicated by the smaller $\Delta\nu$(C$\equiv$N) frequency shift (24 cm^{-1} compared with 35 cm^{-1}). The smaller ^{13}CN chemical shift variation ($\Delta\delta$ = +23.6 ppm) for (**1A**,**K**)$_n$(THF)$_{n'}$ compared to (**1A**,**Li**)$_4$(THF)$_n$ ($\Delta\delta$ = +32.3 ppm) is also consistent with this interpretation (Table V, entries 6 and 1).

(ii) 3-Pyridylacetonitrile 2A,M Aggregates. As in the case of **1A**,**Li**, several ν(C$\equiv$N) absorptions are observed for **2A**,**Li** in THF and in THF–toluene solutions, but surprisingly, they are located either at higher or at lower frequency than those of cryptated ion pairs **2A**,**K**: 2101 cm^{-1} (Figure 4e). In THF solution, at c = 0.25 M a large absorption is observed at 2116 cm^{-1} while at c = 0.025 M, next to the previous band, a shoulder appears at 2104 cm^{-1} (Figure 3b,b′). In THF–toluene solution (5:95 v/v) at c = 0.025 M (Figure 6b′) the major absorption is located at 2104 cm^{-1} while smaller ones appear at 2116 and 2087 cm^{-1}. From these results, we assign the 2116 cm^{-1} absorption to monomeric tight ion pairs and the two other absorptions to various solvated aggregates which are in equilibrium.

Species whose ν(C$\equiv$N) lies at 2087 cm^{-1} are probably solvated aggregates with a Li cation–nitrile interaction (**2A**,**Li**)$_n$(THF)$_{n'}$ similar to (**1A**,**Li**)$_n$(THF)$_{n'}$.

For the solvated species observed at 2104 cm^{-1}, the Li cation–nitrile moiety interaction is no longer similar to that previously proposed implying only the CN nitrogen lone pair. The main interaction probably involves both the pyridyl ring and the nitrile moiety, Li being located in the anion plane. A dimeric structure (**2A$_2$**,**Li**)$_2$(THF)$_n$ could be proposed.

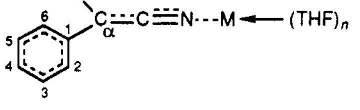


(**2A$_2$**,**Li**)$_2$(THF)$_n$

When using n-BuLi in toluene (toluene–hexane (80:20 v/v)) a white solid precipitated at c = 0.25 M exhibiting a band at 2076 cm^{-1} (Figure 3a) which is also assigned to unsolvated aggregates to which a structure similar to that of (**1A**,**Li**)$_n$ could be attributed as they present the largest frequency lowering $\Delta\nu$(C$\equiv$N) = 25 cm^{-1}. This is in agreement with a strong interaction of the Li cation with the nitrile moiety. Moreover, the skeleton vibrations pattern shows the presence of two conformers for the pyridyl ring 19a, "e" and 14 modes (1483 and 1477 cm^{-1}, 1377 and 1363 cm^{-1}, 1337 and 1330 cm^{-1} (Figure 8A, a)). It was not possible to obtain single crystals of (**2A**,**Li**)$_n$ probably due to the presence of several conformers.[23]

In THF–toluene (40:60 v/v), KHMDS being the base, the precipitate formed, which does not contain HMDS according to its IR spectrum, exhibits a ν(C$\equiv$N) absorption at 2094 cm^{-1} (Figure 4a), i.e., at lower frequency than cryptated ion pairs as well as a single set of skeleton vibrations (1473, 1359, and 1326 cm^{-1}) (Figure 8B, a, Table III, entry 11): it should correspond to an aggregate (**2A**,**K**)$_n$ involving essentially the C$\equiv$N moiety, under a single conformation. Fortuitously, this aggregate and the solvent-separated ion pairs in DMSO (Figure 4f) have ν(C$\equiv$N) absorption at the same frequency. This fact is not totally unexpected, as Corset and Loupy[24] have previously shown that in DMSO the contact ion pairs for potassium cyanide and the free ions exhibit the same ν(C$\equiv$N) absorption.

(3) Structure of the Tight Ion Pairs. (a) Phenylacetonitrile 1A,M Tight Ion Pairs. Tight ion pairs are observed in THF with Li and K. They are characterized by a ν(C$\equiv$N) frequency at 2092 cm^{-1} for **1A**,**K**-d_5 in THF (Figure 2c) or 2090 cm^{-1} for **1A**,**Li**-d_5 in THF (Figure 1d) which is very close to that of the **1A**,**K**-d_5 cryptand-separated ion pairs in THF at 2093 cm^{-1} (Figure 2b). Such is also the case for the skeleton vibration modes. However, in conditions where aggregates are probably not present for **1A**,**Li** in 0.06 M THF solution,[8] the $\Delta\delta$ ^{13}CN chemical shift variation of +25.1 ppm is closer to that of the solvated aggregates whose ν(C$\equiv$N) lie at 2058 cm^{-1} (+32.3 ppm) compared to that of the solvent-separated ion pairs (+16.3 ppm) (Table V, entries 3, 1, 5). The same trend holds for $\Delta\delta$ C$_\alpha$, $\Delta\delta$ C$_1$, and $\Delta\delta$ C$_4$. All these results are in agreement with a –C$\equiv$N···M interaction in the tight ion pairs, thus suggesting the following monomeric structure.



M = Li or K

A similar structure can be assigned to the K tight ion pairs **1A**,**K** (Table V, entry 6). Indeed, the $^1J_{\mathrm{CH}}$ magnitude for **1A**,**Li** (164.4 Hz) corroborates the planarity of the C$_\alpha$ carbon.[22a,17] The C$_1$–C$_\alpha$ and C$_\alpha$–CN bonds in these ion pairs have a similar double-bond character as compared

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[23] We are grateful to Prof. G. Boche for his help in these experiments which were performed in Marburg by one of us (D.C.).

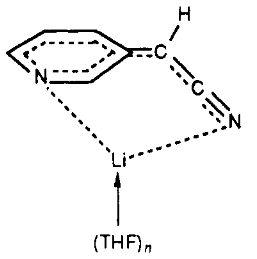
[24] (a) Loupy, A.; Corset, J. *C. R. Acad. Sci. Paris* **1974**, *279(C)*, 713. (b) Loupy, A.; Corset, J. *J. Sol. Chem.* **1976**, *5*, 817.

to that observed in the solvent-separated ion pairs since the frequency of the "e" or ν_s(C–C–C) modes does not vary much (Tables I and II).

The addition of increasing amounts of HMPA to the THF solutions of **1A,Li** tight ion pairs (20–65% v/v) exhibits a slight modification in the IR ν(C≡N) absorption (Figure 1b,c). However, $\Delta\delta$ ^{13}CN and $\Delta\delta$ ^{13}C$_4$ vary progressively (Table V, entries 4 and 5). It is likely that various solvates of the lithiated ion pairs are coexisting in fast equilibrium at the ^{13}C NMR time scale. The higher the HMPA content, the larger $\Delta\delta$ ^{13}C$_4$ negative shift and the smaller $\Delta\delta$ ^{13}CN positive shift are, i.e., the weaker the anion–cation interaction. ^{31}P and ^{7}Li NMR (Table VII) were performed on **1A,Li** generated in THF solution containing 25% HMPA (v/v). The mode of formation of the carbanionic species is of prime importance to observe two ^{31}P signals at low temperature; i.e., it is necessary to freeze the solution and then warm it to room temperature before performing the variable-temperature ^{31}P determination. One observes then a poorly resolved quintet at δ = 25.33 ppm next to an absorption at δ = 24.65 ppm at −120 °C. If such a prefreezing process is not performed, an average ^{31}P signal is only seen. ^{7}Li spectrum run in the same conditions shows a poorly resolved triplet at −0.35 ppm. From these results it appears that the major solvate contains 2 HMPA per lithium cation. These results are similar to those recently obtained by Reich and Green[20] in the case of Et$_3$PhB$^-$Li$^+$. However, it must be pointed out that ^{31}P and ^{7}Li NMR determinations were performed at low temperature, while IR and ^{13}C determinations are run at room temperature so that the HMPA solvation number might be different in both cases.

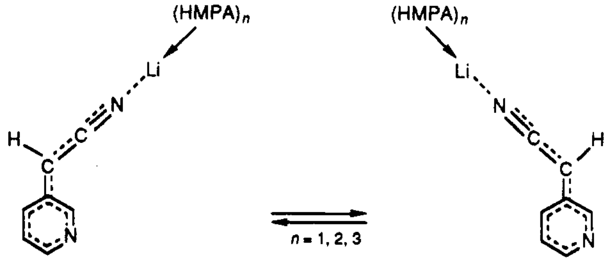
(b) 3-Pyridylacetonitrile 2A,M Tight Ion Pairs. Due to the presence of the aromatic heterocyclic nitrogen, the structure of 3-pyridylacetonitrile **2A,M** tight ion pairs is expected to be different from those of phenylacetonitrile analogs.

In THF, the ν(C≡N) absorption of the lithium-associated species **2A,Li-d_1** lies at a higher frequency 2118 cm^{-1} (c = 0.25 M) (Figure 3d), than the K-cryptated ion pairs **2A,K-d_1** 2101 cm^{-1} (Figure 4e). This indicates that the Li cation–anion interaction is different from that observed in lithiated phenylacetonitrile tight ion pairs **1A,Li** ν(C≡N): 2092 cm^{-1}. The skeleton vibrations pattern (Figure 9a) of **2A,Li-h_1** in THF at c = 0.25 M shows a highly predominant conformer, characterized by absorptions at 1483, 1382, and 1335 cm^{-1} (Table III, entry 4). The **2A,Li** $\Delta\delta$ ^{13}CN chemical shift variation (+18.9 ppm) (Table VI, entry 2) is smaller than the **1A,Li** $\Delta\delta$ ^{13}CN one (+26.3 ppm, Table V, entry 2) and closer to that of the solvent-separated ion pairs **2A,Li** ($\Delta\delta$ = +14.4 ppm, Table VI, entry 5); a larger $\Delta\delta$ C$_4$ chemical upfield shift is observed in **2A,Li** ($\Delta\delta$ = −26.6 ppm, Table VI, entry 2) related to **1A,Li** ($\Delta\delta$ = −16 ppm, Table V, entry 2). The value of $^{1}J_{\mathrm{CH}}$ = 164.4 Hz for **2A,Li** in THF is in agreement with the planarity of C$_\alpha$ carbon. These features as well as the skeleton band intensities enhancement (Figure 9a), when going from the neutral precursor to the carbanion, indicate an interaction of the cation with the heterocyclic aromatic ring. The proposed model for the monomeric tight ion pairs **2A$_2$,Li** is as follows: the Li cation should lie in the plane of the pyridyl anion and be in interaction both with the nitrile moiety and the nitrogen at the meta position of the pyridyl ring. This structure takes into account the presence of a single conformer. However, contrary to the case of **1A,Li** to which monomeric tight ion pairs assignment also relies upon literature data,[8] there is no other strong evidence of the fact that the previous species are indeed monomeric. Thus, in the case of **2A,Li**, only differently aggregated species should coexist.



2A$_2$,Li(THF)$_n$

The addition of increasing amounts of HMPA, 13–65% v/v to the 0.25 M solution of **2A,Li** in THF (Figure 5) induces the formation of another species as evidenced by IR: the ν(C≡N) appears at 2106 cm^{-1} and the presence of two conformers in equilibrium is assigned by different skeleton vibrations at 1476 and 1470 cm^{-1}, 1377 and 1356 cm^{-1}, 1330 and 1323 cm^{-1} (Table III, entry 5, Figure 9b,c,d). At least at low HMPA content, the following HMPA externally solvated contact ion pairs structure could be proposed:

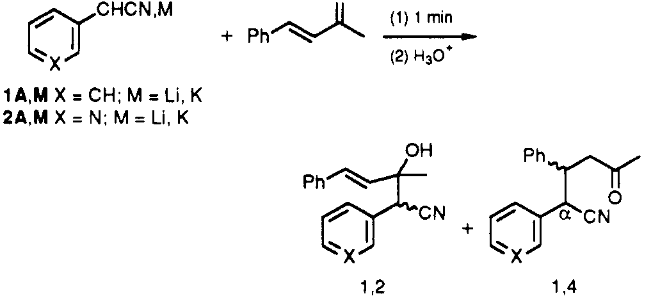


2A$_2$,Li(HMPA)$_n$ **2A$_1$,Li(HMPA)$_n$**

As in the case of **1A,Li**, $\Delta\delta$ ^{13}C$_4$ chemical upfield shift variation indeed increases with higher amounts of HMPA, −26.6 ppm in pure THF (Table VI, entry 2), −29 ppm in THF–HMPA (87:13 v/v) (Table VI, entry 3), −29.6 ppm in THF–HMPA (74:26 v/v) (Table VI, entry 4), and −30.2 ppm in THF–HMPA (35:65 v/v) (Table VI, entry 5), in agreement with a weakening of the anion–cation interaction.

As previously shown, the low-temperature ^{31}P NMR determinations confirm these interpretations and an average of 2.7 bound HMPA molecules per Li cation could be estimated.

Reactivity. The regioselectivity of the reaction of **1A,M** and **2A,M** reagents on benzylidene acetone has been compared, under kinetic control, at low temperature in different solvents, at various concentrations, and with Li and K as associated cations (Table VIII). The γ-ketonitrile resulting from 1,4-addition and the allylic alcohol arising from 1,2-addition in the case of **1A,Li** were characterized by ^{1}H NMR and mass spectra.



1A,M X = CH; M = Li, K
2A,M X = N; M = Li, K

From these results, it appears that **2A,M** species give only 1,4-addition in THF (M = Li, entries 8, 9), toluene

Table VIII. Reactivity of 1A,M and 2A,M toward Benzylideneacetone

entry	reagent	base[a]	solvent	concn/M	temp/°C	1,2/1,4 ratio[b]
1	**1A,Li**	LHMDS	THF	0.06	−78	97/3
2	**1A,Li**	LHMDS	THF	0.25	−90	30/70
3	**1A,Li**	*n*-BuLi	THF–hex 95:5 (v/v)	0.06	−78	87/13
4	**1A,Li**	*n*-BuLi	THF–hex 80:20 (v/v)	0.25	−78	65/35[d]
5	**1A,Li**	*n*-BuLi[c]	tol.–THF–hex 60:20:20 (v/v/v)	0.25	−90	<1/99
6	**1A,Li**	*n*-BuLi	THF–HMPA 74:26 (v/v)	0.25	−78	<1/99[d]
7	**1A,K**	*t*-BuOK	THF	0.25	−78	<1/99
8	**2A,Li**	*n*-BuLi	THF–hex 95:5 (v/v)	0.06	−90	<1/99
9	**2A,Li**	*n*-BuLi	THF–hex 80:20 (v/v)	0.25	−90	<1/99
10	**2A,Li**	*n*-BuLi[c]	tol.–THF–hex 60:20:20 (v/v/v)	0.25	−90	<1/99
11	**2A,Li**	*n*-BuLi	THF–HMPA 74:26 (v/v)	0.25	−78	<1/99
12	**2A,K**	KHMDS	THF–tol. 40:60 (v/v)	0.25	−78	<1/99

[a] 1.2 equiv of base. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] The carbanionic solution was heterogeneous. [d] Reference 35.

(M = Li or K, entries 10, 12), and THF–HMPA (M = Li, entry 11) while the results observed with **1A,M** depend upon the cation, the solvent, and when M = Li, the concentration. 1,2-Addition occurs next to 1,4-addition with **1A,Li** in THF, the 1,2/1,4 ratio increasing when the concentration decreases (entries 2 and 1; 4 and 3); such a concentration effect on the 1,2/1,4 regioselectivity has never been described up to now to our knowledge. Using toluene at *c* = 0.25 M instead of THF leads only to 1,4 addition product (entry 5). Such is also the case for **1A,Li** in THF–HMPA (entry 6) or **1A,K** in THF (entry 7).

These results indicate that tight ion pairs **1A,Li** (*c* = 0.06 M) and **2A,Li** (*c* = 0.06 M) predominating in THF[25] are responsible either for the major 1,2 or the 1,4-additions observed. The opposite behavior of these tight ion pairs is certainly related to their different structure, especially the strength of the anion–cation interaction. In **1A,Li**, the nitrile–lithium interaction is loose enough to allow the lithium–enone complexation known to favor the 1,2-addition.[28] On the contrary, such an electrophilic assistance does not take place with **2A,Li**, the cation being strongly complexed both by the pyridyl ring and by the nitrile moiety. On the other hand, with **1A,Li** the amount of 1,4-addition increases when aggregated species are characterized either in THF (*c* = 0.25M, entry 2) or in toluene (entry 5). 1,4-addition is probably due to these aggregates which coexist with monomeric tight ion pairs. Fox and Renaud[29] have recently shown by electroanalytical methods that the more associated species of Li dialkylamides are better electron donors than the less associated ones. Seebach and al.[30] have pointed out, in the case of lithiated derivatives of alanine diketopiperazine, that single-electron transfer processes might take place with aggregated species while monomeric species should react by an ionic mechanism. As it is well-known that radical reactions on α,β unsaturated ketones are strongly favored at the C_4 position,[31] a single-electron transfer from **1A,Li** aggregates could be postulated.

On the other hand, by adding increasing amounts of HMPA to the THF solution of **1A,Li** the anion–cation interaction becomes weaker: the lithium cation is no longer available for α-enone complexation, thus favoring 1,4-addition. With K as a counter ion, no electrophilic assistance takes place so that no 1,2-addition is observed whatever the species present in solution.

Conclusion

We have shown that in associating media such as THF, THF–toluene, or THF–hexane **1A,M** and **2A,M** solvated aggregates are in equilibrium with monomeric tight ion pairs. In toluene–hexane solutions **1A,M** and **2A,M** unsolvated aggregates precipitate. **1A,Li** and **2A,Li** diHMPA externally solvated ion pairs or separated ion pairs predominate according to the amount of HMPA added to THF solutions.

From our results it clearly appears, as already proposed by Cohen[32] for addition of sulfur stabilized carbanions to α-enones, that solvent-separated ion pairs **1A,M** and **2A,M** lead to 1,4-addition to benzylideneacetone. As in the case of Cohen's system **1A,Li** tight ion pairs lead to 1,2-addition likely via a polar mechanism, implying electrophilic assistance while **2A,Li** ion pairs do not, due to their peculiar structure. Moreover, **1A,M** and **2A,M** aggregates are also reactive species which favor 1,4-addition to this α-enone; a SET mechanism could then be postulated.

Experimental Section

Solvents and Materials. Solvents and reagents were dried and purified prior to use. THF was distilled from Na metal/

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(25) For **1A,Li** (0.06 M), according to Seebach,[8] monomeric tight ion pairs are observed by conductimetry at low temperature, where the experiments were run, in agreement with our results at room temperature. In the case of **2A,Li**, we surmise that a similar assumption is valid. Nevertheless, it must be quoted that **2A,Li** gives 1,2-addition to α,β unsaturated aldehydes in similar conditions:[26] it is known, in hydride reductions of carbonyl compounds, that electrophilic assistance is required for ketones while it is not the case for aldehydes.[27]

(26) Pellet, A. Thesis, ICMO, University of Orsay, 1988. Pellet, A.; Wartski, L. Unpublished results.

(27) Seyden-Penne, J. *Reductions par les alumino- et borohydrures en synthèse organique*; Ed. Technique et Documentation Lavoisier: Paris, 1988; p 40.

(28) Loupy, A.; Lefour, J. M.; Deschamps, B.; Seyden-Penne, J. *Nouv. J. Chim.* **1980**, *4*, 121.

(29) Renaud, P.; Fox, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 5702.

(30) Seebach, D.; Weber, T. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag, Berlin, **1986**, 190.

(31) Giese, B. *Radicals in Organic Synthesis*: *Formation of Carbon–Carbon Bonds*; Organic Chemistry Series, Baldwin, J. E., Ed.; Pergamon Press: New York, 1986; p 24.

(32) Cohen, T.; Abraham, W. D.; Myers, M. *J. Am. Chem. Soc.* **1987**, *109*, 7923.

benzophenone ketyl and kept under an argon atmosphere. DMSO, toluene, and HMPA were distilled over CaH_2 under an inert atmosphere. Phenylacetonitrile and 3-pyridylacetonitrile are commercial (Aldrich) and distilled prior to use. *n*-BuLi (1.6 M in hexane), LHMDS (1 M in THF), and KHMDS (0.5 M in toluene) are Aldrich commercial solutions; *t*-BuOK(Merck) was sublimated before use.

Preparation of Deuteriated Compounds. Toluene-*d*$_5$. $AlCl_3$ (1.7 g) was added to dry toluene (20 mL). Anhydrous DCl was bubbled through the stirred solution for 1.5 h, and 3 mL D_2O was then carefully added to the mixture. After usual workup and distillation, 13.5 g of ring-deuteriated toluene were obtained.

Purity was checked by IR and NMR spectroscopy. Deuterium content on the ring: 93%.

Benzyl-*d*$_5$ Bromide. Toluene was brominated with *N*-bromosuccinimide.[33]

Benzyl-*d*$_5$ Cyanide. This compound was prepared according to literature procedure.[34]

3-Pyridylacetonitrile-*2*-*d*$_2$. This compound was obtained by exchange of 3-pyridylacetonitrile with D_2O at 65 °C during 24 h. Isotopic purity was checked by NMR. Deuterium content: 96%.

Preparation of Solutions. All experiments were carried out under argon in a dry flask equipped with a rubber septum for the introduction of the reagent via syringe.

Starting material (phenylacetonitrile **1** or 3-pyridylacetonitrile **2**, 10^{-3} mol) was dissolved in the required amount of solvent so that the final solution was 0.25 M; 0.06 and 0.025 M solutions were obtained by dilution with THF of the 0.25 M solution. To the magnetically stirred solution was added *n*-BuLi, LHMDS, or KHMDS (1.2–1.5 mmol) by a syringe. The solution was stirred at room temperature for 15 min. An aliquot amount of this solution was taken out via a syringe and either introduced under an argon atmosphere into the NMR tube or transferred to the infrared cell.

IR Spectra. Infrared spectra have been scanned on a Perkin 983 spectrometer. The frequencies are given with a precision of ±1 cm^{-1} for sharp bands. The cell thickness is 0.003 and 0.020 cm for the dilute solution. They are equipped with CaF_2 windows. The solvent spectra were substracted from the solution spectra so that the figures show the absorption of the solute. The preparation of the anion solutions and the filling of the cells were performed under argon in a glovebag.

When the carbanion species were prepared with bases such as LHMDS or KHMDS, there is formation of hexamethyldisilazane (HMDS) in the solution. The spectra of these solutions always present a strong band about 1248 cm^{-1}. In the spectrum Figure 6A, b, the HMDS was evaporated.

When the carbanion species were prepared with *t*-BuOK, there was formation of *t*-BuOH in the solution. The spectra of these solutions always show a slight band at about 1210 cm^{-1}.

NMR Spectra. ^{13}C spectra were recorded on a Bruker AM 200 spectrometer. ^{31}P and ^{7}Li spectra were performed on a Bruker AM 250 spectrometer. The temperature of the probe was 20 °C. ^{13}C, ^{31}P, ^{7}Li spectra were determined by using the FT technique.

^{13}C NMR spectra (50, 33 MHz, 5-mm tube, ^{2}H lock). The ^{2}H resonance of D_2O contained in a capillary located inside the 5-mm tube provided the ^{2}H external lock. The carbon chemical shifts are reported in ppm downfield from tetramethylsilane. The proton coupled ^{13}C NMR spectra were obtained by using the off-resonance technique, and the $^{1}J_{CH\alpha}$ coupling constant was determined by carrying out the NMR spectra without any decoupling.

^{31}P NMR spectra (101, 26 MHz, 10-mm tube, ^{2}H lock). A 5-mm tube filled with CD_2Cl_2 located inside the 10-mm tube was used for the ^{2}H external lock to perform low-temperature spectrum recording. The ^{31}P chemical shifts are reported in ppm on the δ scale relative to a solution of pure H_3PO_4.

^{7}Li NMR spectra (97, 20 MHz, 10-mm tube, ^{2}H lock). A 5-mm tube filled with a 0.6 M LiBr solution in CD_3OD was used both for the ^{2}H external lock and as an external standard.

The low-temperature NMR spectra were recorded on a Bruker AM 250 spectrometer equipped with a variable-temperature unit. The sample was cooled under a nitrogen stream, and the probe temperatures were monitored with a thermocouple and are accurate within 5 °C.

General Procedure for 1,2/1,4-Addition of Phenylacetonitrile or 3-Pyridylacetonitrile to Benzylidene Acetone. In a 25-mL oven-dried double-necked round-bottomed flask fitted with an argon bubbler, a thermometer, and a magnetic stirring bar was placed 10^{-3} mol of phenylacetonitrile or 3-pyridylacetonitrile in the required amount of solvent (THF, HMPA, or toluene) so that the final concentration of the solution was 0.25 M. The reaction mixture was cooled to −78 °C, and 1.3–1.5 equiv of base (LHMDS, KHMDS, *n*-BuLi or *t*-BuOK) was added via a syringe followed by stirring for 30 min. Benzylidene acetone (1.2×10^{-3} mol) formerly dissolved in the appropriate solvent was added via a syringe within 1 min to the stirred reaction mixture at −78 or −90 °C. The solution was immediately quenched with 1 mL of 2 M HCl. Quenching by a cooled solution at −70 °C of acetic acid in THF gives the same result (Table VIII, entry 9). After being warmed to 0 °C, the reaction mixture was diluted with 10 mL of ether. The organic layer was washed with brine and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to afford an oil which was examined by NMR and purified by silica gel chromatography.

2-(3-Pyridyl)-3-phenyl-5-oxohexanenitrile. White solid: mp 90.5 °C (chromatography on silica gel column: CH_2Cl_2/ether 1/1). IR: 2250, 1720 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$ δ ppm): diastereoisomers mixture A/B 70/30: 8.55 (m, 1 H, 3-Py); 8.4 (d, 0.7 H, 3-Py); 8.3 (d, 0.3 H, 3-Py); 7.5 (ddd, 0.3 H); 7.15 (m, 6.7 H, Ph and 3-Py); 4.5 (d, $J = 5.8$ Hz, 0.7 H, $H_{\alpha A}$); 4.15 (d, $J = 6.9$ Hz, 0.3 H, $H_{\alpha B}$); 3.7 (ddd, 0.3 H); 3.6 (ddd, 0.7 H); 3.1 (m, 2 H); 2.2 (s, 2 H, Me_A); 2.1 (s, 1 H, Me_B). MS *m*/*e* (relative intensity): 264 (9); 147 (15); 118 (33); 43 (100). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.60; O, 6.06. Found: C, 77.10; H, 6.15; N, 10.34; O, 6.12.

The corresponding 1,2 and 1,4 adducts related to phenylacetonitrile have already been described.[35]

Acknowledgment. We thank Mr. J. M. Dedieu for running ^{31}P and ^{7}Li NMR spectra and performing variable-temperature experiments. We are indebted to Dr. M. C. Roux for having carried out some 1,2/1,4-addition reactions and Dr. M. F. Lautie and N. Ratovelomanana for the synthesis of deuterated compounds. We thank the Rhône-Poulenc Agrochimie for generous financial support.

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