BISPYRIDYL- AND BISQUINOLYLMETHANES. NMR-BASED CHARGE MAPPING OF THE CARBANIONS AND METAL LIGAND PROPERTIES

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Abstract - Nmr evidence is obtained for mixtures of geometrical stereoisomers of carbanions in DMSO solution of bis(4-)- and bis(2-pyridyl)methane (**1**) and (**2**), bis(2-pyridyl)acetonitrile (**3**), and bis(2-quinolyl)methane (**4**). When incorporated into π-charge/shift relationships the ^{13}C and ^{15}N nmr data provide access to charge demands c_X of the heterocycles, that is the fraction of π-charge withdrawn by the rings from the carbanionic carbon. Compounds (**3**) and (**4**) behave as ligands LH, whose anions L^- produce neutral chelates with divalent metal ions (Met = Zn^{2+}, Pd^{2+}). With Met = Co^{2+}, Cu^{2+}, Mn^{2+} the ligand LH **3** affords the dimer L_2.

The present paper reports the preparation of the carbanions of bis(4-pyridyl)methane (**1**), bis(2-pyridyl)methane (**2**), bis(2-pyridyl)acetonitrile (**3**), and bis(2-quinolyl)methane (**4**), and the study of their

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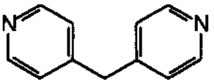
Dedicated to Professor Rolf HUISGEN on the occasion of his 75th birthday nmr spectra to investigate their stereochemistry, obtain the charge demands of the heterocycles as c_X^X values,[1,2] and charge mapping of the carbanions.



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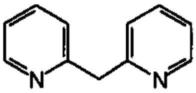

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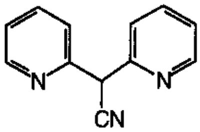

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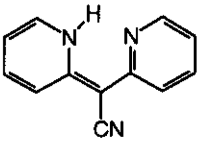

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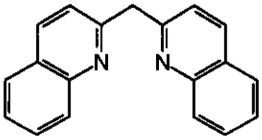

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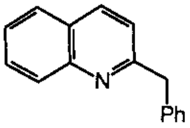

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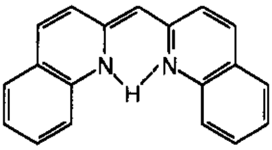

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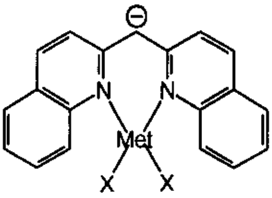
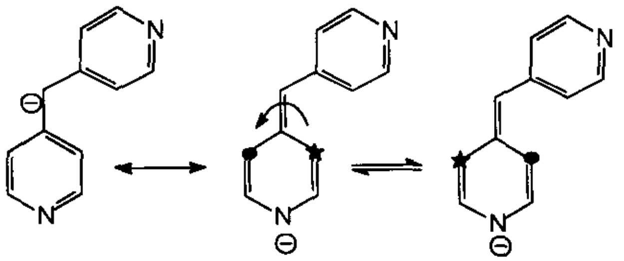


A

To complete the landscape we also report the charge demand of the 2-quinolyl group in the anion of 2-benzylquinoline (**5**) in order to compare the π-withdrawal of this heterocycle in the benzylic system $PhCH^-X$ with that in $^-CHX_2$. This investigation was prompted by the finding that in carbanions substituted by α- or γ-azinyl rings, a large amount of negative charge is transferred from the carbanionic carbon to the heterocycle and in particular to the nitrogen atoms. Geometrical isomerism has been detected by nmr in the carbanions of α- and γ-benzylpyridines and quinolines,[1] benzylazines[2] (pyridazine, pyrazine, pyrimidine), ω-substituted picolyl carbanions,[3] and carbanions of 2-benzyl-1,3-azoles[4,5] (oxazole, thiazole, imidazole). Finally, we explored whether bis(heteroaryl)methanes (**2**) - (**4**), like bis(2-benzothiazolyl)methane[5] and other heterocyclic congeners[6] can behave as a carbanionic ligand L^- to produce neutral metal chelates $[MetL_2]$ upon reaction with divalent transition metal acetates. Our previously reported quantitation of the π-deficient nature of azines (and pyridine in particular) agrees with the intuitive and traditional knowledge which, more than 30 years ago, suggested to Scheibe[7] that the methylene bridge of bis(2-quinolyl)methane could undergo the attack of a number of electrophilic reagents. Scheibe extensively investigated the preparation and behaviour of bis(2-quinolyl)methane[8-10] and, among other results, proposed the equilibrium of the methylene form of **4** with the enamine tautomer (**4a**)[9,10] and the spectroscopic detection of metal complexes to which the general structure (**A**) was assigned.[7,10]

RESULTS AND DISCUSSION

Nmr Spectra - The carbanions were prepared in DMSO solutions as previously reported[1-3,11-14] using methyl sulfinyl carbanion (dimsyl anion) as a base in a 2:1 excess. The reason for our choice of DMSO as a solvent for carbanions has been reported in previous papers[1-3, 11-14] and is essentially associated with the fact that carbanions are present as solvent-separated or free ions in this medium. The ^{13}C nmr data relating to the neutral compounds (**1** - **3**) and of their conjugate carbanions (**1**$^-$ - **3**$^-$) are shown in Table 1; those relating to **4** and **4**$^-$ in Table 2. In agreement with published reports[15] the bis(2-pyridyl)acetonitrile (**3**) exists in both $CDCl_3$ and the DMSO solution as the enaminic tautomer (**3a**): on the other hand, the bis(2-quinolyl)methane (**4**) is present in both $CDCl_3$ and DMSO solution as the methylene

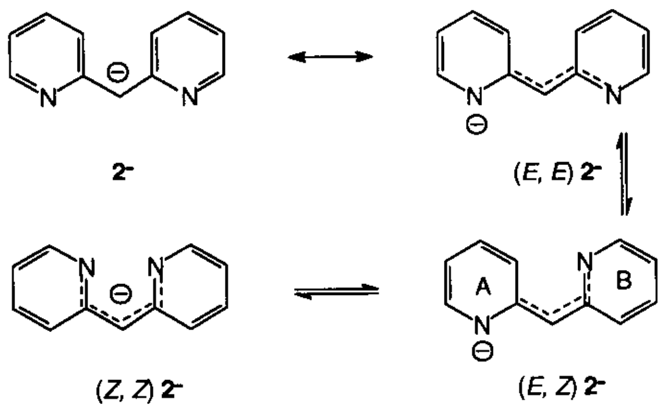


1$^-$ **1**$^-$**a** **1**$^-$**b**

Table 1 ^{13}C shifts and ^{15}N shifts of compounds (**1** - **3**), their conjugated carbanions ($\mathbf{1}^-$- $\mathbf{3}^-$), and metal chelates (**7** - **8**)[a]

Compd		1	2	3	4	5	6	CN	CH_2/CH^-	^1J/Hz
1		310.11	149.72	124.15	148.28	124.15	149.72		39.19	129.4
$\mathbf{1}^-$		256.38	147.67	113.31	147.25	113.31	147.67		83.97	148.1
2		315.0	159.27	123.43	136.51	121.47	149.01		46.34	128.0
$\mathbf{2}^-$		254.7	160.18[b]	118.24	132.05[b]	104.94[b]	147.86[b]		87.48[b]	145.0
		253.7	159.08[c]	116.98	131.42[c]	103.64[c]	148.14[c]		86.74[c]	146.5
		288		114.46						
	48°C	nd[d]	159.82	116.58	131.73	104.33	147.83		87.12	
3	$CDCl_3$	-	155.48	119.96	136.52	112.81	139.22	122.18	68.18	
			154.51	118.34	137.36	112.96	140.56	121.57	66.42	
$\mathbf{3}^-$		-	160.91	116.0	133.6	110.28	140.73	130.05	68.03	
6	$CDCl_3$	-	158.57	122.03	137.86	113.92	144.92	124.71	70.00	
7	$CDCl_3$	-	154.89	119.01	136.2	115.22	149.12	123.36	75.36	

[a] In DMSO solution unless otherwise indicated; [b]*ca.* 66%; [c] *ca.* 33%; [d] not detectable



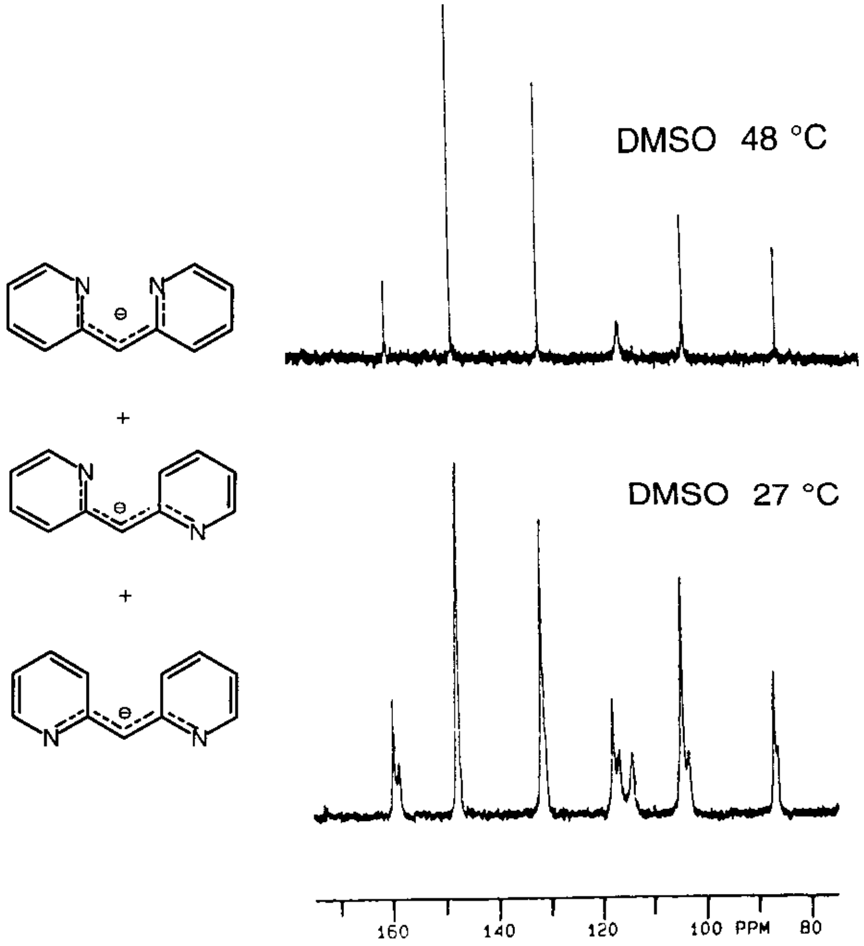


Figure 1. ^{13}C Nmr spectra of the anion ($\mathbf{2}^-$) of bis(2-pyridyl)methane in DMSO

Table 2. ^{13}C shifts and ^{15}N shifts of compound (**4**), its conjugated carbanion (**4**$^-$) and metal chelates (**10**)[a]

Compd		1	2	3	4	5	6	7	8	9	10	CH_2/CH^-	^1J/Hz
4	$CDCl_3$	-	159.53	121.90	136.50	127.53	126.10	129.47	129.10	148.0	126.91	49.13	130.0
		307.36	159.48	121.97	136.35	127.16	125.91	129.37	128.38	147.27	126.41	47.78	132.1
4$^-$		256.65	157.44	116.51	131.25	126.36	123.01	127.51	123.55	150.38	122.80	93.61	149.2
		240.41	159 61	118.38	131.25	126.36	123.01	127.51	124.25	150.38	122.80		
		231.48	158.59	117.05	130.12	126.36	121.31	127.51	124.92	150.87	122.80		
	45°C	nd[b]	159.58	117.90	132.03	127.36	122.5	128.69	124.78	151.69	123.98	94.64	147.7
10	$CDCl_3$	-	156.22	121.64	134.19	127 16	121.33	129.66	125.50	146.15	123.91	93.07	155.1

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[a] In DMSO solution unless otherwise indicated [b] not detectable.

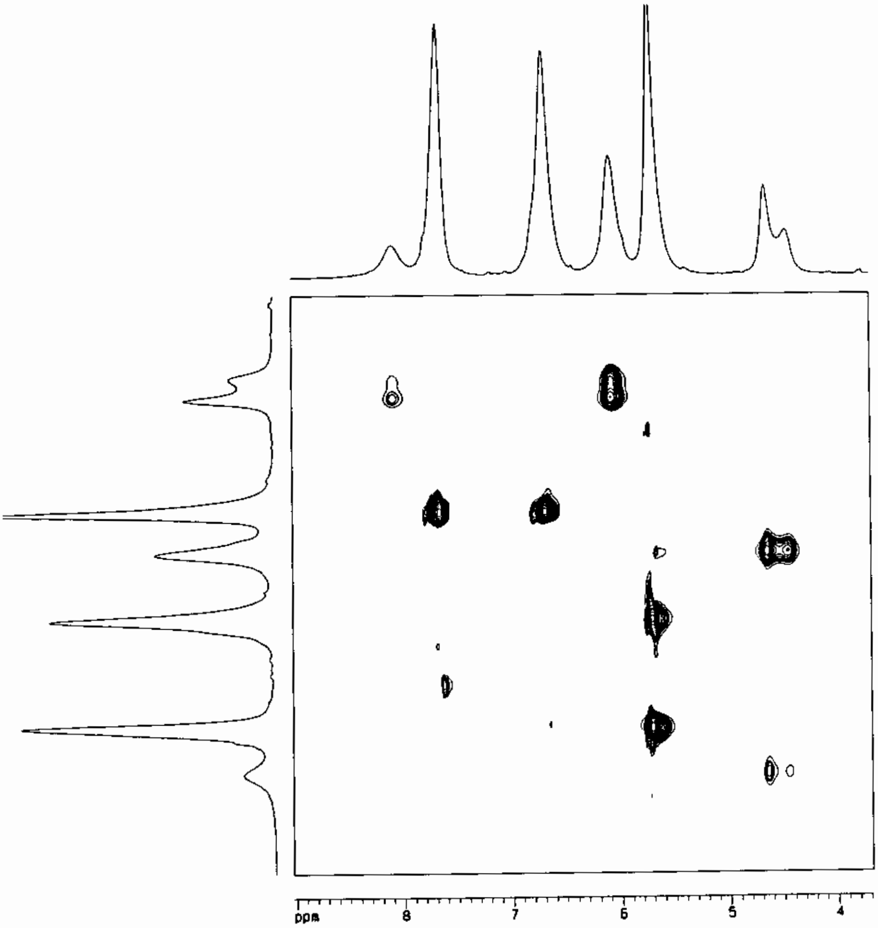


Figure 2. 2D NOESY experiment of anion (**2**$^-$)

tautomer, with only about 7% of the enaminic form(**4a**).The ^{13}C Nmr spectrum of anion (**5**$^-$) has already been reported,[1] that of the neutral is described in the Experimental. The ^{13}C nmr spectrum of anion (**1**$^-$) of bis(4-pyridyl)methane at 27 °C indicates the presence of the two stereoisomers (**1**$^-$**a**) and (**1**$^-$**b**): in particular, carbon atoms at positions 3 and 5 are under slow exchange on the nmr time scale and give rise to some broadening. A sharpening of the peaks was obtained upon increasing the temperature but at 50 °C free rotation was still not achieved. The temperature was not increased any further since the dimsyl anion is reported[16] to decompose above 60 °C. The ^{13}C nmr spectrum at 27 °C (Figure 1) and the ^{1}H nmr spectrum of anion (**2**$^-$) of bis(2-pyridyl)methane indicate the presence of the three isomers, (*E*,*E*) **2**$^-$, (*E*,*Z*) **2**$^-$, and (*Z*,*Z*) **2**$^-$. Two stereoisomers have all of the ^{13}C resonances in common with the exception of C-3; the third isomer has distinct ^{13}C resonances. All of the resonances are present as broad, structureless peaks. A NOESY phase-sensitive experiment (Figure 2) showed a marked NOE

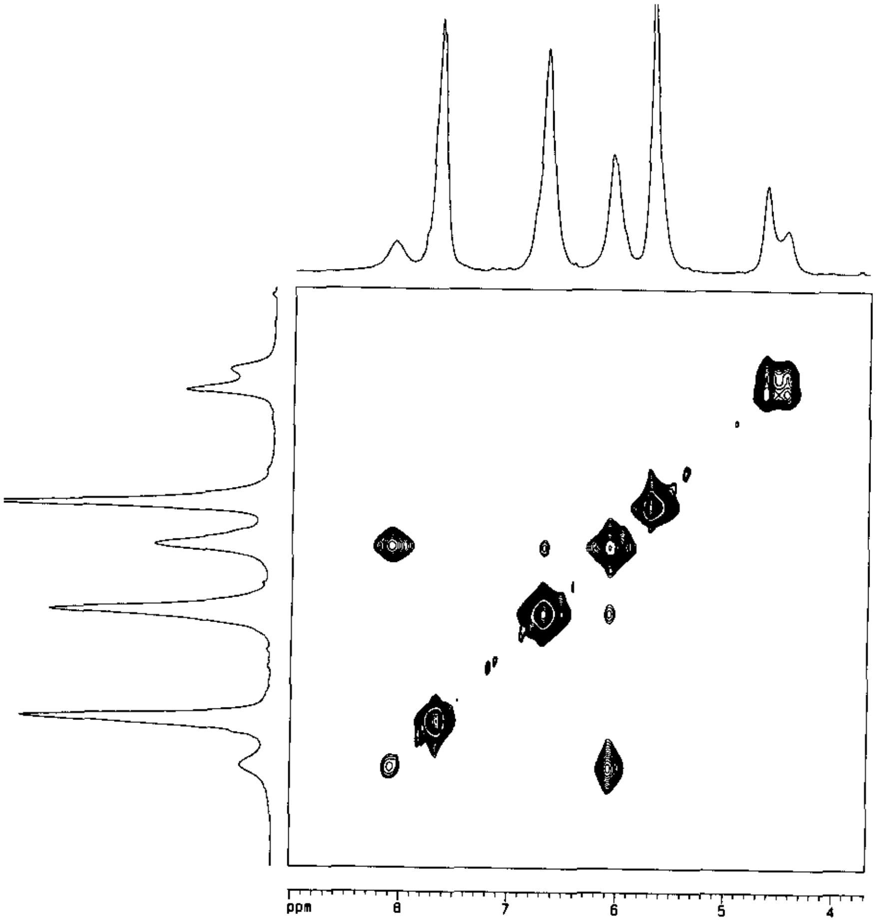
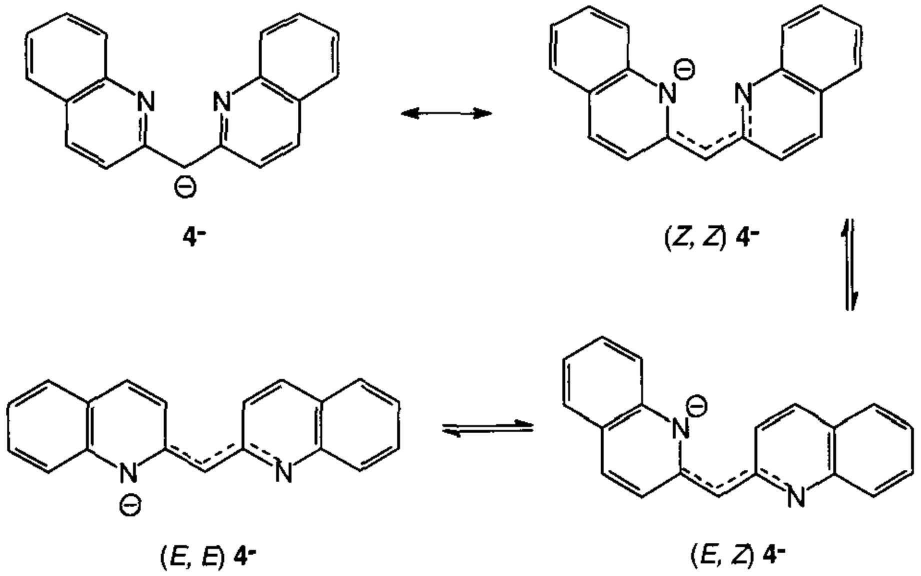


Figure 3. 2D exchange experiment on anion (**2**$^-$)

between the carbanion proton and the protons at position 3 of the (*E*,*Z*)**2**$^-$ and the (*Z*,*Z*)**2**$^-$ isomers are certainly present. In the same experiment (Figure 3) we found chemical exchange between the peak at 6 ppm and the peak at 8 ppm. The lower field peak must be assigned to C-3 of ring A of (*E*,*Z*) **2**$^-$ on the basis of the shielding effect exerted by the sp^2 lone pair on the nitrogen of ring B.[17] Assignment of these resonances to H-3 was confirmed by the results of HETCOR experiments. This conclusion clearly supports the presence of the stereoisomer (*E,Z*) **2**$^-$. Integration of the peaks at 6 and 8 ppm indicated an approximate ratio of 1:2. This is in line with what was found on analyzing ^{13}C spectra when three almost equally intense resonances were attributed to C-3. In the proton decoupled ^{13}C spectrum at 48 °C all of the multiple peaks collapse into a single set of resonances and, under these conditions, the three isomers undergo fast equilibration (Figure 1).

The nmr spectra of anion (**3**$^-$) of bis(2-pyridyl)acetonitrile at 27 °C show only one set of sharp peaks: this result can be interpreted as being due to a single isomer or, more probably, as the outcome of rapidly interconverting stereoisomers.

The ^{13}C nmr spectrum of anion (**4**$^-$) of bis(2-quinolyl)methane at room temperature is extremely complex. A sharpening of the peaks occurs at higher temperatures although, in this case, complete collapse into a single set of resonances could not be achieved at 48 °C.The spectra clearly indicate the presence of all of the three stereoisomers (*E,E*) **4**$^-$, (*E,Z*) **4**$^-$, and (*Z,Z*) **4**$^-$. The identification of carbon atoms of the heterocycle are reported in Table 2, independently of their assignment to specific stereoisomers.



4$^-$

(*Z, Z*) **4**$^-$

(*E, E*) **4**$^-$

(*E, Z*) **4**$^-$

Theoretical modelling of the relative energies of **2**$^-$ and the cyano system **3**$^-$, their barriers to interconversion and their charge distributions was undertaken using the AM1 SCF-MO Hamiltonian and the MOPAC program system,[18] in conjunction with the COSMO continuum solvation correction (Table 3). At the gas phase level, the three geometrical isomers reveal energies within 2.0 kcal mol^{-1} of each other, with the (*E,Z*) form being marginally the more stable. This low energy difference is consistent, within the error of the calculations, in the observation of three separate species in solution. When the COSMO solvation model is applied to **3**$^-$ to correct for the dielectric shielding of the DMSO solvent, the relative energies show a slightly smaller spread of 1.5 kcal mol^{-1}, with the lowest energy form now being the (*E,E*) isomer (Table 3). From the nmr spectra only a single set of resonances is apparent for the cyano carbanion (**3**$^-$). To investigate whether this could be due to rapid interconversion of the three isomers, we located the transition states for the (*Z,Z*) to the (*E,Z*) and for the (*E,Z*) to the (*E,E*) interconversion. In the gas phase for **2**$^-$, the barriers were respectively 8.1 and 10.0 kcal mol^{-1}, reducing to 6.0 and 3.9 in a solvent of dielectric constant 45. Addition of a cyano group modifies these barriers to 3.7 and 5.1 in the gas phase and to 2.1 and 1.9 in solution. Whilst the absolute magnitude of these barriers are probably too low to correspond to separate nmr signals, the trend apparent for the cyano group strongly supports the interpretation that the barriers to interconversion are significantly lower for this system.

Table 3. Calculated AM1 enthalpies (kcal mol^{-1}) for **2**$^-$ and **3**$^-$

Anion	(*Z,Z*)	(*E,Z*)	(*E,E*)
2$^-$ ($\varepsilon = 1$)	47.6	46.3	48.0
2$^-$ ($\varepsilon = 45$)	-21.5	-19.5	-19.8
3$^-$ ($\varepsilon = 1$)	66.5	66.0	66.6
3$^-$ ($\varepsilon = 45$)	-1.1	-1.5	-2.6

Charge Demands - Charge demands are defined as the fraction of π-charge transferred from the charged cabon atom to the substituent X:[11-13] they are based on dependable π-charge/^{13}C shift[14] and π-charge/^{15}N shift[20] relationships. In charge demand notation, the subscript identifies the substituent group and the *superscript identifies the system or family of carbanions.* Thus, benzyl carbanions PhCH$^-$X originated the c_X^{Ph} values, whereas symmetrically disubstituted carbanions X$_2$CH$^-$ originated the c_X^X values. Equation (1) allows the empirical calculation of the π electron density q_C^π [1,2,14] on a trigonal disubstituted carbanionic carbon $^-$CHXY, *once the chemical shift of the carbanionic carbon* and the shielding contributions A_i of the i groups bonded to it are known. In di-activated carbanions X$_2$CH$^-$ (where X = Y) the charge demand

$$\delta^{13}C = 122.8 + \Sigma A_i - 160(q_C^\pi - 1) \quad (1)$$

c_X^X is related to the experimentally obtained q_C^π as shown *in relationship* (2). *In benzyl carbanions PhCH$^-$X* the charge demand c_X^{Ph} is related to the value of q_C^π as shown in relationship (3), where c_{Ph} is the charge

$$c_X^X = (2 - q_C^\pi)/2 \quad (2)$$

$$c_X^{Ph} = 2 - c_{Ph} - q_C^\pi \quad (3)$$

$$c_{ring}^{ring} = \Sigma\Delta\, q_{C\text{-ring}}^\pi + \Sigma\Delta\, q_N^\pi \quad (4)$$

where

$$\Delta q_{C\text{-ring}}^\pi = -\,\Delta\delta^{13}C_{ring}/160 \quad (5)$$

$$\Delta\, q_N^\pi = -\,\Delta\delta^{15}N/366.34 \quad (6)$$

delocalized by the phenyl group. When X is a nitrogen heteroaromatic ring in PhCH$^-$X and $^-$CHX$_2$, the fraction of π-charge delocalized by the rings, c_{ring}^{ring} (c_{Ph}, c_{Het}^{Ph}, c_{Het}^{Het}) can be calculated as shown in Eq. 4 by *summing* the local variations of the π electron densities of all of the positions of the (heterocyclic) ring. Eq (6) reports the charge sensitivity of ^{15}N according to the ^{15}N shift/ π-charge relationship we have recently proposed.[20] Eq 3 or Eq 4 can provide the charge demand in benzyl carbanions and Eq 2 or Eq 4 in bis(heteroaryl)methyl *carbanions (Het)$_2$CH$^-$. The approach going through* Eq 2 and Eq 3 gives values that are predominantly influenced by the uncertainity of q_C^π. This method has the great advantage that it uses only one shift/π-charge relationship based on ^{13}C shifts and provides charge demands for heterocycles that are homogeneous with those previously[2,3,11,12] obtained for several other EWGs. Eq 4 instead involves a high number of terms in the summation of all of the local π-charge densities. The summation of the calculated total number of electrons on the rings (the phenyl and the heterocycle in $PhCH^-Het$, or the two heterocycles in $(Het)_2CH^-$) and on the carbanionic carbon CH^- must be as nearly as possible equal to the total number of π electrons of the system, that is 14 in $\mathbf{1}^-$ and $\mathbf{2}^-$, and 22 in the benzofused $\mathbf{4}^-$ (Eq 7 and 8). Results are reported in Table 4 to show the excellent agreement between these numbers and confirm the consistency and reliability of the method in providing charge mapping in these heterocycle-substituted carbanions.

$$q^{\pi}_{Het} + q^{\pi}_{Ph} + q^{\pi}_{C} = \text{total number of } \pi \text{ electrons} \quad (7)$$

$$2\, q^{\pi}_{Het} + q^{\pi}_{C} = \text{total number of } \pi \text{ electrons} \quad (8)$$

The theoretically (AM1) calculated π-electron density q_C on the carbanionic carbons of $\mathbf{2}^-$ corresponded to a π-charge of -0.38, -0.36 or -0.32 for the (*Z,Z*), the (*E,Z*), and the (*E,E*) isomers respectively, in reasonable agreement with those estimated from experiment (Table 4). Stabilisation of this centre with a cyano group increases this charge density to -0.46, -0.46, and -0.41 respectively.

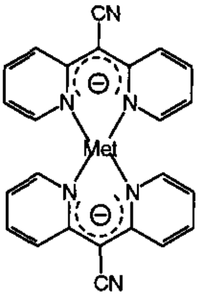
Chelate Formation - On the basis of our previous experience of the formation of neutral metal chelates $[MetL_2]$ with bis(2-benzothiazolyl)methane[5] and related heterocycles[6] we submitted compounds (**2** - **4**) to the action of transition metal acetates. Precipitation of the neutral chelates (**6**) and (**7**) was observed upon treatment of a methanolic solution of compound (**3**) with $Zn(AcO)_2$ and $Pd(AcO)_2$. On the contrary, an analogous treatment of ligand (**3**) with $Co(AcO)_2$ or $Mn(AcO)_2$ led to the isolation of the dimer (**9**). Treatment of the ligand (**3**) with $Cu(AcO)_2$ afforded both the chelate (**8**) as a green precipitate and the dimer (**9**) recovered from the mother liquors. The formation of the dimer (**9**) can be accounted for by assuming a metal-catalysed electron transfer (oxidation) of a metal-complexed carbanionic species,

Table 4 Experimental π-electron densities (q) for anions (**1**$^-$ - **4**$^-$) and charge demands (c) of heteroaryl substituents.

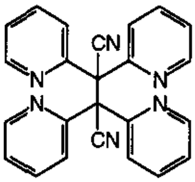
Compd.			A_i	c_X[a]	q_{Het}[b]	q_C[c]	$2q_{Het} + q_C$[d]
1$^-$	4py		12.70	0.299	6.314	1.401	14.030
2$^-$	2py	I	13.82	0.303	6.330	1.394	14.053
		II	13.82	0.303	6.338	1.394	14.069
		III	13.82	0.302	6.280	1.398	13.957
		48°C	13.82	0.302		1.396	
	mean (I+II+III)				6.316		
4$^-$	2qui	I	15.86	0.310	10.351	1.381	22.082
		II	15.86	0.310	10.287	1.381	21.995
		III	15.86	0.310	10.301	1.381	21.983
		45°C	15.86	0.313		1.374	
	mean (I+II+III)				10.313		
5$^-$			15.86[e]	0.305		1.390	

[a] Charge demand of the heteroaryl substituent obtained using Eq 2. [b] π-Electron density resident on the heteroaryl substituent ($q_{Het} = 6 + c_{Het}$ where c_{Het} is obtained from Eq 4 [c] π-Electron density resident on the carbanionic carbon obtained from Eq 1. [d] Total π-electron density of the anionic system (to be compared with the theoretical value of 14 π-electrons and 22 π-electrons respectively). [e] Values obtained from Eq 3 using q_C from Eq 1 with A_{Ph} = 13 ppm.

either initially formed or deriving from the metal chelate [MetL$_2$]. No chelates were obtained by simply mixing the bis(2-quinolyl)methane (**4**) and metal acetates. However, when NaOH or MeONa was added to the methanolic solution, ligand (**4**) afforded the corresponding neutral chelate(**10**)(deep red) with Zn(AcO)$_2$. The chelates are insoluble in hydroxylic solvents but moderately soluble in CHCl$_3$ and other organic solvents. The ^{13}C nmr data of chelates (**6**) and (**7**) are shown in Table 1, and that of chelate (**10**) in Table 2: they provide unequivocal evidence for the carbanionic nature of the ligands in the complexes. In particular, the bridge carbon linking the two heterocycles is a methine with a large ^1J(CH). With zinc acetate, the bis(2-benzothiazolyl)methane (BBTMH) affords the zinc chelate [Zn(BBTM)$_2$]: on the basis of its tetrahedral structure,[5] it is highly probable that the zinc chelates (**6**) and (**10**) also have a similar arrangement around the metal. Conversely, the palladium chelate should present a planar arrangement, as in the case of the chelate of bis(2-benzoxaxolyl)methane (BBOMH) with palladium [Pd(BBOM)$_2$].[6]



6: Met = Zn
7: Met = Pd
8: Met = Cu



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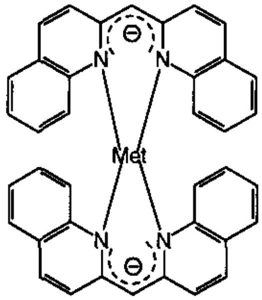

10: Met = Zn

CONCLUSION

The results of nmr investigation provide evidence that in DMSO the solvent-separated or free anions (**1**$^-$, **2**$^-$ and **4**$^-$) are constituted by slow interconverting stereoisomers; in the cyano-substituted (**3**$^-$), free rotation is observed. In agreement with our previous observations[3,21] theoretical calculations indicate that a high negative charge density is resident on the carbanionic carbon of **3**$^-$ contiguous to the cyano group. As a result, the double bond character of the bond between the carbanionic carbon and the heterocycle is decreased and, consequently, also the charge transfer onto the heterocycle. Because of all this, the barrier to rotation around the bond between the carbanionic carbon and the heterocycle in **3**$^-$ is easier than in **2**$^-$. The high charge demand of the pyridyl ring in bis(pyridyl)methanes is comparable with that of the methoxycarbonyl group in malonic ester.[12] ^{15}N Nmr indicates that most of the negative charge withdrawn by the heterocycle is present on the nitrogen atoms.

The structure of the neutral chelates obtained with divalent transition metals is different from that envisaged by Scheibe many years ago. The presence of the base is not necessary for the formation of chelates (**6**) and (**7**), but it is to obtain the chelate (**10**).

EXPERIMENTAL

^{1}H and ^{13}C Nmr specta were recorded on Bruker AC-300, Bruker AMX-500 WB and Varian XL-300 instruments using Me$_4$Si as external standard. The temp for the DMSO solutions was 27 °C. ^{15}N Nmr spectra were recorded at 27 °C on a Varian XL-300 spectrometer, operating at 30.45 MHz and (if possible) using 0.50 M solutions in DMSO. ^{15}N Nmr shifts were measured relative to aniline as external standard. The aniline standard was checked against neat nitromethane and the chemical shifts related to liquid NH$_3$, using a conversion factor of 380.23 ppm for the chemical shift of neat nitromethane. The acquisition parameters for ^{15}N measurements (gated decoupled experiment) were: a spectral width of 15,000 Hz, 32 K data points, a pulse delay of 20 s, a pulse angle of *ca.* 70° for 30 µs, zero filling and line broadenings of 1-3 Hz, the number of transient of were 2000-3000. Anion solutions (0.5 M in DMSO) were in 10 mm o.d. tubes containing an internal 5 mm coaxial tube with neat DMSO-d_6 providing the internal deuterium lock. Coupling constant values, *J*, are given in Hz throughout. Elemental analyses were performed by the microanalysis laboratory of our department using a Perkin-Elmer 240 instrument. Mps are uncorrected. Anhydrous solvents were prepared by continuous distillation over sodium sand, in the presence of benzophenone and under nitrogen or argon, until the blue color of sodium ketyl was permanent. The extracts were dried over Na_2SO_4. Bis(4-pyridyl)methane (**1**)[22] was prepared by reduction of the corresponding ketone.[23]

2-Benzylquinoline (**5**) - ^{13}C-Nmr (300 MHz, $CDCl_3$) δ 160.18 (C-2), 120.85 (C-3), 135.67 (C-4), 126.87(C-5), 125.06 (C-6), 127.60 (C-7), 128.67 (C-8), 146.39 (C -9), 125.51 (C-10), 128.07 (C_o), 127.60 (C_m), 125.37 (C_p), 138.57 (C_{ipso}), 43.62 (CH_2).

2-(β-Styryl)quinoline - A solution of quinaldine (1.01 g, 7.05 mmol) in DMSO (4 ml) was added dropwise to a solution of benzaldehyde (0.77 g, 7.26 mmol) in DMSO (4 ml); after few minutes a solution of sodium hydroxide was added (50%, 3 ml). After 24 h at room temperature the mixture was poured onto water (70 ml), extracted with ether (5x80 ml). The solvent was removed from the dried extracts to give the crude product as a yellow oil (1.49 g) which was flash chromatographed on silica gel (CH_2Cl_2- AcOEt 3:1 v/v) to give the compound as a yellow solid (0.21 g, 13 %) mp 94-95 °C (lit.,[24] 100-101 °C)

Bis(2-pyridyl)methane (**2**) - A mixture of bis-2-pyridilacetonitrile (1.43 g, 5.86 mmol) with sulphuric acid (70%, 5.5 ml) was heated at 120-130 °C for 6 h. After cooling the mixture was poured onto ice (50 ml) and the solution was made alkaline by sodium hydroxide (20%, 22 ml). The solution was extracted with ether (5x80 ml), dried and evaporated to give dark oil (0.99 g). The crude product was purified by distillation under reduced pressure (bp 145 °C at 0.10 mmHg, lit.,[25] bp 106-110 at 0-5 mmHg) to give a light yellow oil (0.88 g, 88.2%).

Bis(2-pyridyl)acetonitrile (**3**) - Pure powdery sodium amide (3.98 g, 0.10 mol) was obtained by placing an aliquot of a 50% suspension of sodium amide in toluene in a flask under nitrogen and evaporating the solvent under reduced pressure. The amide was suspended in anhydrous glyme (90 ml) and under stirring and in nitrogen atmosphere, a solution of 2-pyridilacetonitrile (5.84 g, 49.40 mmol) in the same solvent (50 ml) was added dropwise, maintaining the temperature at 0 °C. The mixture was brought to room temperature and then a solution of 2-bromopyridine (7.87 g, 49.80 mmol) in the same solvent (50 ml) was added. After stirring for 9 h at 80 °C, the reaction mixture was poured onto ice (200 ml) and extracted with chloroform (10x250 ml); the solvent was removed from the dried extracts to leave a crude product (5.16 g) which was submitted to flash chromatography on silica gel with ethyl acetate-hexane (5:2, v/v) to provide the product like yellow solid (3.49 g, 36.2%), mp 127-129 °C (lit.,[15] 129-130 °C).

Bis(2-quinolyl)methane (**4**) - A mixture of quinaldine (7.88 g, 55.03 mmol) and 2-chloroquinoline (6.00 g, 36.67 mmol) was heated at 200 °C under nitrogen for 2 h. After cooling, potassium hydroxide (10%, 100 ml) was added and the mixture was stirred for 1 h and then extracted with ether (4x200 ml). The dried solution was evaporated to give the dark red crude product (7.63 g), which, washed with petroleum ether, was flash-chromatographed on silica gel (CH_2Cl_2-AcOEt 3:1, v/v) to give the red pure product (1.99 g, 20.1%), mp 101-102 °C (lit.,[9a] mp 102-103 °C).

1,2-Dicyano-1,1,2,2-tetra(2-pyridyl)ethane (**9**) - To a solution of bis-2-pyridylacetonitrile (0.181 g, 0.93 mmol) in methanol (25 ml) a solution of $Mn(AcO)_2 \cdot 4H_2O$ (0.114 g, 0.47 mmol) in the same solvent (10 ml) was added dropwise. After stirring for 24 h at room temperature and under nitrogen, the product was obtained as a white solid (22 mg, 12%), mp 194 °C. ^{1}H-Nmr (300 MHz, $CDCl_3$): δ 7.17 (4H, dd, J = 7.3, J = 4.8 Hz, H-5); 7.50 (4H, d, J = 8.0 Hz, H-3); 7.64 (4H, td, J = 8.0, J = 1.8 Hz, H-4); 8.40 (4H, d, J = 4.8 Hz, H-6). Anal. Calcd for $C_{24}H_{16}N_6$: C, 74.21; H, 4.15; N, 21.64. Found: C, 74.35; H, 4.08; N, 21.67. M$^+$, 388, 361, 310, 271, 195, 194, 169, 156, 140, 78, 69. Analogous results were obtained with $Co(AcO)_2 \cdot 4H_2O$.

Metal chelates of bis(2-pyridyl)acetonitrile (**6**) and (**7**)- To a solution of bis(2-pyridyl)acetonitrile (196 mg, 1 mmol) in MeOH (25 ml) under nitrogen a solution of $Zn(AcO)_2 \cdot 2H_2O$ (127 mg, 0.58 mmol) in the same solvent (5 ml) was added dropwise. After 3 days the chelate (**6**) as a yellow solid was filtered (14.6 mg, 5.5%), mp > 250 °C. ^{1}H-Nmr (300 MHz, $CDCl_3$) δ 6.58 (2H, t, J = 5.5, H-5), 7.53 (2H, ddd, J = 8.8, J = 5.5, J = 1.8, H-4), 7.56 (2H, d, J = 5.5, H-6), 7.70 (2H, d, J = 8.8, H-3). Anal. Calcd for $C_{24}H_{16}N_6Zn$: C, 63.52; H, 3.55; N, 18.52. Found: C, 63.69; H, 3.32; N, 18.72.

Analogously, the Palladium complex (**7**) was obtained (46 % yield) as an orange solid, mp 228-230 °C (decomp), starting from the ligand (**3**) (53.3 mg, 0.27 mmol) and $Pd(AcO)_2$ (30.1 mg, 0.13 mmol) in MeOH (20 ml). ^{1}H-Nmr (300 MHz, $CDCl_3$) δ 6.42 (2H, td, J = 6.2, J = 1.9, H-5), 7.04 (2H, d, J = 6.2, H-3), 7.37 (2H, ddd, J = 8.6, J = 6.2, J = 1.0, H-4), 7.41 (2H, dd, J = 6.2, J = 1.0, H-6). Anal. Calcd for $C_{24}H_{16}N_6Pd$: C, 58.25; H, 3.26; N,16.98. Found: C, 58.07; H, 3.38; N, 17.04.

Reaction of bis(2-pyridyl)acetonitrile (**3**) *with copper acetate. formation of the chelate* (**8**) *and the dimer* (**9**) - To a solution of bis(2-pyridyl)acetonitrile (**3**) (214 mg, 1.1 mmol) in MeOH (35 ml) a solution of $Cu(AcO)_2$ (118 mg, 0.59 mmol) in the same solvent (15 ml) was added dropwise. The chelate (**8**) precipitated immediately as a green solid (116 mg, 43%), mp 196 °C. Anal. Calcd for $C_{24}H_{16}N_6Cu$: C, 63.8; H, 3.5; N,18.6. Found: C, 63.5; H, 3.8; N, 18.4. A white precipitate (10.4 mg) was recovered from the filtered mother solution after one night and it was identified as the dimer (**9**).

Zinc chelate (**10**) *of bis(2-quinolyl)methane* (**4**) - To a solution of $Zn(AcO)_2 \cdot 2H_2O$ (44.1 mg, 0.2 mmol) in MeOH (2 ml) a solution of NaOH (7.4 mg, 0.185 mmol) in the same solvent (1 ml) was added: to this mixture a solution of the ligand (**4**) (100 mg, 0.37 mmol) in MeOH (7 ml) was added dropwise. The chelate (**10**) precipitated immediately as a deep red solid (29.9 mg, 27%), mp 172 °C. Anal. Calcd for $C_{38}H_{26}N_4Zn$: C, 75.56; H, 4.34; N, 9.28. Found: C, 75.39; H, 4.30; N, 9.29.

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