

## Charge Mapping in Carbanions. Weak Charge Demand of the Cyano Group As Assessed from a $^{13}\text{C}$ NMR Study of Carbanions of $\alpha$ -Activated Acetonitriles and Phenylacetonitriles: Breakdown of a Myth

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The  $^{13}\text{C}$  NMR values of the carbanions  $\text{XCH-CN}^-$  and their phenyl homologs  $\text{PhC(X)CN}^-$  were obtained in DMSO. By using previously proposed  $\pi$  charge- $^{13}\text{C}$  shift relationships (eqs 3 and 4), it is possible to compute the  $^{13}\text{C}$  NMR shift of the carbanionic carbon. In these relationships, the charge-dependent contribution of the  $^{13}\text{C}$  NMR shift is described by the charge demands ( $c_X$ ) of the different X groups. These quantities have been previously defined as the fraction of  $\pi$  charge transferred (delocalized) from an adjacent carbanionic center to group X. It is shown that it is possible to correlate with a high degree of precision (slope 0.96,  $r = 0.993$ ) computed and experimental shifts not only for the  $\text{XCH-CN}$  and the  $\text{PhC(X)CN}$  series (10 and 12 points, respectively), but also for 13 other  $^- \text{CHXY}$  carbanions 25-36 $^-$ . The only system that does not conform to the predictions of eq 3 is the ylid 11 $^-$ , obtained by deprotonation of cyanomethylenetriethylammonium iodide. The  $^{13}\text{C}$  NMR shifts of the phenylthio-substituted carbanions 12 $^-$  and 26 $^-$  are reproduced using a zero charge demand for the phenylthio group. This result experimentally validates theoretical indications that the stabilization provided by the PhS substituent to a  $\alpha$  carbanionic center is essentially nonmesomeric. Equations 1-4 are therefore confirmed as being highly predictive and of broad scope. It is definitely concluded that charge demands ( $c_X$ ) efficiently rank various organic functionalities X for their mesomeric electron-withdrawing power. The modest charge demand of the cyano group  $c_{\text{CN}}$  in  $\alpha$ -cyano carbanions is fully confirmed. In particular,  $c_{\text{CN}}$  is smaller than the charge demand of the 2- and 4-pyridyl groups  $c_{2\text{py}}$  and  $c_{4\text{py}}$ . This leads to a double-bond character of the bond between the carbanionic carbon and the carbon atom of the heterocycle in the anion. Because these results do not allow the description of  $\text{RCH-CN}$   $\alpha$ -cyano carbanions as  $\text{RCH=C=N}^-$  ketene imine nitranions, discussion is offered as to how this can be reconciled with the considerable increase in the acidity of cyanocarbon acids.

The problem of charge delocalization in cyano carbanions has been approached both theoretically<sup>1-4</sup> and spectroscopically (IR,<sup>5</sup> NMR,<sup>6</sup> photoelectron,<sup>7</sup> X-ray<sup>8</sup>). An essentially mesomeric mechanism of stabilization describing cyano carbanions as keteneimine nitranions (e.g.,  $\text{RCH-CN} \leftrightarrow \text{RCH=C=N}^-$ ) is favored by some authors<sup>1a,5</sup> and also reported in textbooks<sup>9</sup> and reviews.<sup>10</sup> This

conclusion is not universally shared and is clearly in contrast with the interpretation of our previous results.<sup>11-14</sup>

Charge demands  $c_X$  (previously<sup>11,13,14</sup> denoted as  $q_X$ ) of groups X have been defined<sup>11,13-15</sup> as the fraction of  $\pi$  charge withdrawn by X from an adjacent trigonal carbanion carbon. Numerical values of  $c_X$  depend on the system studied. Benzyl carbanions  $\text{PhCH-X}^-$  originated<sup>11</sup>  $c_X^{\text{Ph}}$  values, while symmetrically deactivated carbanions  $^- \text{CHX}_2$  (X = COR,  $\text{CO}_2\text{R}$ , CN,  $\text{SO}_n\text{R}$ ,  $\text{NO}_2$ , etc.) originated<sup>14</sup>  $c_X^{\text{X}}$  values. In our present notation of charge demand  $c_X$ , the subscript identifies the group X (X = COR,  $\text{CO}_2\text{R}$ , CN,  $\text{SO}_n\text{R}$ ,  $\text{NO}_2$ , etc.), while the superscript identifies the system from which the values have been obtained ( $c_X^{\text{Ph}}$  or  $c_X^{\text{X}}$ ). We have found<sup>11,14</sup> that the cyano group is endowed with comparatively small charge demands ( $c_{\text{CN}}^{\text{Ph}}$  and  $c_{\text{CN}}^{\text{CN}}$ ), and we associate this result with a limited or negligible negative charge transfer from the carbanionic carbon to the nitrogen atom of the cyano functionality.

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This picture of cyano carbanions is in agreement with an essentially localized  $\pi$  bonding between the carbanionic carbon and nitrile carbon atoms and a marginal involvement in the delocalization of the carbon nitrogen triple bond. Simultaneous, independent X-ray structural investigations on cyano carbanions<sup>5a</sup> confirm the correctness of our proposal.<sup>11-14</sup>

In a previous paper,<sup>16</sup> we provided experimental evidence that, regardless of any information derived from  $\pi$ -charge-<sup>13</sup>C relationships,<sup>17</sup> the resonance electron-withdrawing power of the cyano group is less than that of the pyridyl ring. To find definitive support for the numerical value of the charge demand of the cyano group, we needed to confirm that  $c_{CN}$  is comparatively small in as many different structures as possible, including di- and trisubstituted carbanions.

XCH <sub>2</sub> CN	XCH <sup>-</sup> CN	XCHCN   Ph	XC <sup>-</sup> CN   Ph
1, X = Ph	7, X = SO <sub>2</sub> Ph	13, X = Ph	19, X = 2-pyridyl
2, X = CONMe <sub>2</sub>	8, X = PO(OEt) <sub>2</sub>	14, X = CO <sub>2</sub> Me	20, X = 4-pyridyl
3, X = CO <sub>2</sub> Me	9, X = 2-pyridyl	15, X = COMe	21, X = 3-pyridazinyl
4, X = COPh	10, X = 4-pyridyl	16, X = COPh	22, X = 2-pyrazinyl
5, X = CN	11, X = NMe <sub>3</sub> <sup>+</sup> I <sup>-</sup>	17, X = CN	23, X = 2-pyrimidyl
6, X = SOPh	12, X = SPh	18, X = SO <sub>2</sub> Ph	24, X = 4-pyrimidyl

Consequently, we first examined the <sup>13</sup>C NMR spectra of the sodium salts of anions XCH<sup>-</sup>CN 1<sup>-</sup>-12<sup>-</sup>, substituents X being numerous electron-withdrawing functionalities which act by polar-inductive, polarizability, and/or resonance stabilization mechanisms. Second, we investigated the <sup>13</sup>C NMR spectra of the sodium salts of carbanions PhC<sup>-</sup>(CN)X 13<sup>-</sup>-24<sup>-</sup> in order to explore the response of charge demands to steric congestion.<sup>12,13</sup>

The previously reported parent equation (1)<sup>11,17</sup> relates the <sup>13</sup>C NMR shift of carbanionic carbon to the <sup>13</sup>C NMR shift of ethylene (122.8 ppm) to the shielding contributions

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

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

of the various *i* substituents directly bonded to the carbanionic carbon ( $A_i$ ), and to the  $\pi$  electron density on the carbanionic carbon  $q_C$ . In symmetrically disubstituted <sup>-</sup>CHX<sub>2</sub> carbanions, the  $\pi$  electron density on the carbanionic carbon is equal to the electron pair created by the deprotonation minus the fraction of  $\pi$  charge withdrawn by the substituent. Once having defined<sup>11,14</sup> this latter quantity as the charge demand  $c_X^X$  of the substituent X,  $\pi$  electron density  $q_C$  can be expressed by eq (2).

Carbanions 1<sup>-</sup>-12<sup>-</sup> are a special case of diactivated <sup>-</sup>CHXY carbanions in which Y = CN. We assume that the charge demand of the cyano group in the diactivated XCH<sup>-</sup>CN carbanions is equal to  $c_{CN}^{CN}$ , that is the charge demand exhibited by the cyano group in <sup>-</sup>CH(CN)<sub>2</sub> (0.207).<sup>14</sup> Analogously, the charge demand of group X in carbanions XCH<sup>-</sup>CN is assumed to be the same as the value presented by the X groups in symmetrically diactivated <sup>-</sup>CHX<sub>2</sub> carbanions ( $c_X^X$ ). Equations 3 and 4 can be derived<sup>13,14</sup> to predict the <sup>13</sup>C chemical shift of the carbanionic carbon in disubstituted carbanions 1<sup>-</sup>-12<sup>-</sup> and in trisubstituted carbanions 13<sup>-</sup>-24<sup>-</sup>, respectively.

$$\delta^{13}\text{C} = 122.8 + A_X + A_{CN} - 160(1 - c_{CN}^{CN} - c_X^X) \quad (3)$$

$$\delta^{13}\text{C} = 122.8 + A_X + A_{CN} + A_{Ph} - 160(1 - c_{CN}^{CN} - c_{Ph}^{Ph} - c_X^X) \quad (4)$$

We report that, using tabulated charge demand  $c_X^X$  values (Table I)<sup>16</sup> and  $A_i$  shift contributions, eqs 3 and 4 excellently predict the <sup>13</sup>C NMR shifts of the carbanionic carbon in 1<sup>-</sup>-12<sup>-</sup> (except for 11<sup>-</sup>) and in 13<sup>-</sup>-24<sup>-</sup>. The body of computed and experimental <sup>13</sup>C NMR shifts of  $\alpha$ -substituted acetonitrile anions is further expanded to reach a total of 23 points by incorporating the data of other disubstituted diactivated <sup>-</sup>CHXY carbanions 25<sup>-</sup>-36<sup>-</sup>.<sup>14</sup> In this way, we provide a convincing, definitive, and successful check of the validity of the  $\pi$  charge-<sup>13</sup>C relationship (1) and confirm the comparatively small value of the charge demand of the cyano group. In agreement with our earlier proposal, we conclude that ketene imine nitrone resonance structures RCH=C=N<sup>-</sup> are poor descriptors for  $\alpha$ -cyano carbanions. The modest charge demand of the cyano group indicates that cyano carbanions are not primarily stabilized by delocalization. Finally, the question of how this can be reconciled with the high acidity that the cyano group gives to cyanocarbon CH acids will be briefly discussed.

## Results

**NMR Data. (a) General.** <sup>13</sup>C NMR data in DMSO concerning the  $\alpha$ -substituted acetonitriles 1-12 and their conjugate carbanions 1<sup>-</sup>-12<sup>-</sup> are reported in Table II; data concerning the  $\alpha$ -substituted phenylacetonitriles 13-24 and their conjugate carbanions 13<sup>-</sup>-24<sup>-</sup> are given in Table III. The reasons for the choice of DMSO as a solvent have been explained and documented elsewhere.<sup>11,14,17</sup>

A number of  $\alpha$ -activated acetonitriles are sufficiently acidic to form their corresponding carbanions even in a protic solvent. The <sup>13</sup>C NMR spectra of neutral compounds have been recorded in MeOH; a methanolic solution of sodium methoxide was used for their carbanions (Table II). Given the CH acidity of these compounds, undeuterated methanol had to be used because protons of "active" methylenes undergo rapid deuterium exchange in CD<sub>3</sub>OD, even without base. The protic (MeOH) or aprotic dipolar (DMSO) nature of the solvent does not appreciably affect the chemical shifts of the anions. The carbanion shift differences found in the two solvent systems reproduce analogous differences found in the spectra of their neutral counterparts. However, one important difference between the two cases concerns the <sup>1</sup>J(C,H) coupling constants. Although deprotonated methylene is present as a doublet in the coupled spectra of the carbanions in DMSO, the methine <sup>1</sup>J(C,H) coupling (but not the couplings of the other aromatic or aliphatic carbon atoms) vanishes in the protic medium. This phenomenon is clearly due to a fast chemical exchange between the carbanionic species and either the protic solvent or the neutral precursor. Although the negligible amount of carbon acid present at equilibrium in MeOH does not influence the chemical shifts of the carbanion, the fast acid-base equilibrium affects the <sup>1</sup>J(C,H) coupling of the site involved in the deprotonation. This behavior, although primarily and initially shown for malononitrile (5),<sup>14</sup> is not peculiar only to cyano carbon acids; it is also observed with other CH acids of a very different nature, such as diethyl malonate.<sup>14</sup>

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Table I. Shielding Contributions  $A_i$  and Charge Demands of Various Groups<sup>a</sup>

X	$A_i$	$c_{\text{X}}^{\text{Ph}}$	$c_{\text{X}}^{\text{X}}$
Ph	13.00		0.29
CONMe <sub>2</sub>	5.88	0.42	0.275
CO <sub>2</sub> Me	6.20	0.40	0.268
CO <sub>2</sub> Et	6.00	0.40	0.268
COMe	14.90	0.51	0.325
COPh	9.30	0.56	0.341
CN	-14.60	0.28	0.207
SPh	9.4	0	0
SOPh	20.18	0.26	0.233
SO <sub>2</sub> Ph	17.46	0.28	0.206
PO(OEt) <sub>2</sub>	3.95	0.26	0.122
Me <sub>3</sub> N <sup>+</sup>	20.5	0	0
2-Py <sup>b</sup>	13.82	0.411	0.278
4-Py	12.70	0.408	0.277
2-Pym <sup>c</sup>	13.90	0.430	0.286
4-Pym	10.50	0.501	0.318
3-Pyd <sup>d</sup>	11.50	0.417	0.281
Pyz <sup>e</sup>	10.50	0.446	0.294

<sup>a</sup> See ref 16. <sup>b</sup> 2-Pyridyl. <sup>c</sup> 2-Pyrimidyl. <sup>d</sup> 3-Pyridazinyl. <sup>e</sup> Pyrazinyl.

(b) **Shift Assignment.** <sup>13</sup>C NMR shift assignments in the neutral compounds were based on coupling constants and on known<sup>18</sup> alkyl and cyano substituent effects. When ambiguities occurred, a complete analysis of the spectrum was performed and discrimination was based on multiplicities of patterns and on the values of long-range coupling constants. In the anions, in both the phenyl and the heterocyclic rings, the most shielded aromatic resonances were assigned to carbon atoms para to the carbanionic center. For resonances present at similar frequencies, discrimination between the two rings was based on signal intensities and on vicinal and long-range coupling constants.<sup>15</sup> Assignments that are not straightforward are reported in detail.

In compound **9**, the assignments of C(3) and C(5) were based on selective decoupling experiments, respectively, irradiating H(3) (7.42 ppm) and H(5) (7.34 ppm). In the corresponding anion **9**<sup>-</sup>, two isomers were present in a ratio of 3:1. We assigned the (*E*) form to the more abundant



isomer, considering that C(3) (double doublet) shows  $^3J(\text{C}, \text{H}\alpha) = ^3J(\text{C}, \text{H}\delta) = 6 \text{ Hz}$ . In the less abundant isomer, C(3) shows  $^3J(\text{C}, \text{H}\delta) = 6 \text{ Hz}$  and  $^3J(\text{C}, \text{H}\alpha) = 4.5 \text{ Hz}$ . The high-field compression shielding effect shown for phenyl rings<sup>15,19</sup> is also exerted by the cyano group, with C(3) moving 1 ppm to high field in the (*E*) form.<sup>20</sup> In anion **10**<sup>-</sup>, the magnetic nonequivalence of both C(3) and C(5), as well as of C(2) and C(6), provided<sup>16</sup> the most straightforward evidence for the geometrical isomerism in this system. Compound **14** was present in DMSO in two enolic forms in a ratio of 3:1. Compound **15** showed the ketonic form (10%), together with the two enolic forms (80% + 10%). Assignment of the aromatic carbons was not possible due to the overlap of peaks. In compound **19**, the assignment of carbon atoms C(3) and C(5) was based on

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(20) For shift assignment of **10**<sup>-</sup> see also ref 16.

a selective decoupling experiment performed by irradiating H( $\alpha$ ) (5.94 ppm).

**<sup>13</sup>C Shifts- $\pi$  Charge Relationships.** The majority of the shielding contributions  $A_i$  of the *i*th X groups directly bonded to the carbanionic center which have been considered in this paper have been reported previously<sup>11,14-16</sup> (Table I).

The trimethylammonium substituent Me<sub>3</sub>N<sup>+</sup> in anion **11**<sup>-</sup> cannot delocalize the adjacent negative charge by resonance. Analogously, theoretical indications suggest<sup>21</sup> that the phenylthio group PhS in anion **12**<sup>-</sup> does not participate in the delocalization of the negative charge by resonance. Consequently, we have attributed a zero charge demand to these substituents. As a result of this, we have assigned the "full" value of  $c_{\text{CN}}^{\text{Ph}} = 0.28$  to the charge demand of the cyano group.<sup>11</sup>

The  $\delta^{13}\text{C}$  shifts of the  $\alpha$ -substituted acetonitrile anions **1**<sup>-</sup>-**4**<sup>-</sup> and **6**<sup>-</sup>-**12**<sup>-</sup> computed by eq 3 are reported in Table IV. The malonitrile anion **5**<sup>-</sup> was excluded because it was the source of  $c_{\text{CN}}^{\text{CN}}$ . A plot of computed vs experimental values (except **5**<sup>-</sup> and **11**<sup>-</sup>) is shown in Figure 1.

To prove that the results of the charge demand treatment as applied to substituted acetonitrile anions were correctly coherent and homogeneous with those of other disubstituted deactivated carbanions, we have incorporated into the line of Figure 1 all of the data so far available for -CHXY systems belonging to the pyridyl<sup>16</sup> **25**<sup>-</sup>-**30**<sup>-</sup> and the deactivated series **31**<sup>-</sup>-**37**<sup>-</sup>.<sup>14</sup> Statistics of the correlations of computed vs experimental shifts are shown in Table V.

25 X = Ph	31 X = CO <sub>2</sub> Me	Y = COMe
26 X = SPh	32 X = CO <sub>2</sub> Et	Y = COPh
27 X = SOPh	33 X = CO <sub>2</sub> Et	Y = SOPh
28 X = SO <sub>2</sub> Ph	34 X = CO <sub>2</sub> Et	Y = SO <sub>2</sub> Ph
29 X = CO <sub>2</sub> Et	35 X = CO <sub>2</sub> Et	Y = PO(OEt) <sub>2</sub>
30 X = COPh	36 X = COMe	Y = SO <sub>2</sub> Ph
	37 X = COPh	Y = SO <sub>2</sub> Ph

To compute the  $\delta^{13}\text{C}$  shifts of the  $\alpha$ -substituted phenylacetonitrile anions **13**<sup>-</sup>-**24**<sup>-</sup> by eq 4, we used the  $c_{\text{X}}^{\text{X}}$  for the CN and X groups. We also had to establish the charge demand for the phenyl substituent. In the benzylic system PhCH-X, the charge demand of the phenyl ring  $c_{\text{Ph}}^{\text{Ph}}$  varies from 0.29 for Ph<sub>2</sub>CH<sup>-</sup> to 0.09 for PhCH-NO<sub>2</sub>. In making a guess of the charge demand of the phenyl ring in these trisubstituted carbanions, both the variable electronic nature of the phenyl ring and its steric effects need to be taken into account. We considered that the coupled action of both the cyano and the X groups in anions **14**<sup>-</sup>-**18**<sup>-</sup> cooperate in decreasing (the saturation effect)<sup>22</sup> the charge

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(22) In benzylic carbanions PhCH-X, the strong electron-withdrawing group X competes with the weak phenyl ring in delocalizing the charge; in -CHX<sub>2</sub>, the competition of two strong electron-withdrawing groups bonded to the same center causes a decrease in their charge-delocalizing capacity. This is a saturation phenomenon<sup>12,14,23</sup> because the effect of two X groups, quantified in terms of benzylic charge demands  $c_{\text{X}}^{\text{Ph}}$ , is less than additive in -CHX<sub>2</sub>.

Table II.  $^{13}\text{C}$  NMR Data for Neutral  $\alpha$ -Substituted Acetonitriles  $\text{XCH}_2\text{CN}$  and Conjugated Carbanions Sodium Salts  $\text{XCH}^-\text{CN}$ 

compd	X	state <sup>a</sup>	solvent <sup>b</sup>	$\text{CH}_2/\text{CH}^-$	$J/\text{Hz}$	CN	other groups
1	Ph	N	DMSO	22.6	137.4	119.03	$C_i = 131.23, C_o = 127.78, C_m = 128.73, C_p = 127.27$
		A <sup>c</sup>	DMSO	33.6	150.0	137.43	$C_i = 148.9, C_o = 115.9, C_m = 127.6, C_p = 109.0$
2	CONMe <sub>2</sub>	N	DMSO	24.68	135.3	116.04	$\text{CO} = 162.87, \text{Me} = 37.39, 35.14$
		A	DMSO	32.11	<i>d</i>	130.93	$\text{CO} = 172.97, \text{Me} = 35.34$
3	CO <sub>2</sub> Me	N	MeOH	22.37	137.1	112.87	$\text{CO} = 163.57, \text{Me} = 51.27$
		A	DMSO	24.24	137.3	114.89	$\text{CO} = 164.65, \text{Me} = 52.84$
			MeOH	32.39	<i>e</i>	129.35	$\text{CO} = 175.27, \text{Me} = 48.44$
			DMSO	33.59	166.4	129.32	$\text{CO} = 171.70, \text{Me} = 48.28$
4	COPh	N	MeOH	27.79	134.4	113.65	$\text{CO} = 177.17, C_i = 133.72, C_o = 127.17, C_m = 127.64, C_p = 133.04$
		A	DMSO	29.97	134.9	115.73	$\text{CO} = 189.50, C_i = 134.50, C_o = 128.27, C_m = 128.74, C_p = 134.10$
			MeOH	56.48	169	126.56	$\text{CO} = 182.32, C_i = 140.79, C_o = 124.89, C_m = 126.56, C_p = 127.71$
			DMSO	52.18	165.2	127.32	$\text{CO} = 179.97, C_i = 142.65, C_o = 125.48, C_m = 127.21, C_p = 127.82$
5	CN <sup>f</sup>	N	MeOH	6.27	144.0	111.27	
		A	DMSO	8.40	144.2	111.88	
			MeOH	-0.78	<i>e</i>	130.31	
			DMSO	-0.25	175.3	130.36	
6	SOPh	N	DMSO	43.41	149.8	112.95	$C_i = 142.07, C_o = 124.28, C_m = 129.30, C_p = 131.83$
		A	DMSO	37.53	175.3	128.63	$C_i = 150.59, C_o = 124.44, C_m = 126.63, C_p = 126.35$
7	SO <sub>2</sub> Ph	N	MeOH	43.67	147.0	110.29	$C_i = 136.74, C_o = 127.60, C_m = 128.58, C_p = 134.06$
		A	DMSO	44.71	147.1	112.12	$C_i = 137.32, C_o = 128.17, C_m = 129.68, C_p = 135.07$
			MeOH	35.55	<i>e</i>	127.08	$C_i = 148.49, C_o = 123.77, C_m = 127.32, C_p = 129.14$
			DMSO	37.40	176.1	126.26	$C_i = 151.20, C_o = 124.03, C_m = 127.95, C_p = 128.79$
8	PO(OEt) <sub>2</sub> <sup>g</sup>	N	DMSO <sup>h</sup>	14.95	135.4	114.46	$\text{CH}_2 = 62.81, \text{Me} = 16.03$
		A	DMSO <sup>h</sup>	3.57	161.3	131.36	$\text{CH}_2 = 58.80, \text{Me} = 16.39$
9	2-Py	N	DMSO <sup>h</sup>	25.56	136.1	118.12	$C_2 = 151.15, C_3 = 122.75, C_4 = 137.27, C_5 = 122.57, C_6 = 149.38$
		A	DMSO <sup>h</sup>				
			<i>E</i> (75%)	40.80	163.2	133.18	$C_2 = 166.05, C_3 = 111.53, C_4 = 133.19, C_5 = 104.98, C_6 = 148.19$
			<i>Z</i> (25%)	40.80	163.2	133.18	$C_2 = 166.05, C_3 = 112.51, C_4 = 132.84, C_5 = 105.08, C_6 = 148.19$
10	4-Py	N	DMSO <sup>h</sup>	22.30	138.2	118.29	$C_2 = C_6 = 150.30, C_3 = C_5 = 123.41, C_4 = 140.61$
		A	DMSO <sup>h</sup>	39.47	165.0	130.79	$C_2^i = 146.76, C_3^i = 110.60, C_4 = 153.93, C_5 = 111.71, C_6 = 147.24$
11	Me <sub>3</sub> N <sup>+</sup>	N	DMSO <sup>h</sup>	52.83	150.8	111.94	$\text{Me} = 53.32$
		A	DMSO <sup>h</sup>	68.32	166.7	132.79	$\text{Me} = 57.74$
12	SPh	N	DMSO <sup>h</sup>	18.44	149.8	117.72	$C_i = 132.66, C_o = 129.26, C_m = 129.46, C_p = 127.41$
		A	DMSO <sup>h</sup>	2.22	180.3	139.00	$C_i = 150.56, C_o = 122.85, C_m = 127.66, C_p = 122.20$

<sup>a</sup> N for neutrals and A for anions. <sup>b</sup> Solutions are 0.33 M unless differently stated. <sup>c</sup> Reference 11. <sup>d</sup> Covered by solvent peaks. <sup>e</sup> Absence of coupling constant because under fast exchange. <sup>f</sup> Reference 14. <sup>g</sup> Bottin-Strzalko, T.; Seyden-Penne, J.; Pouet, M. J.; Simmonin, M. P. *J. Org. Chem.* 1978, 43, 4346-4351. <sup>h</sup> 0.50 M solutions. <sup>i</sup> Positions facing to cyano group.

demand of the phenyl ring almost as much as the powerful nitro group does in the phenylnitromethane anion  $\text{PhCH}^-\text{NO}_2$  ( $c_{\text{Ph}}^{\text{Ph}} = 0.09$ ). We therefore assumed that the coupled action of the CN and the X group is equivalent to one nitro group, and so we chose the value of 0.09 for the phenyl charge demand in carbanions 14<sup>-</sup>-18<sup>-</sup>. In carbanions 13<sup>-</sup> and 19<sup>-</sup>-24<sup>-</sup>, it is conceivable that, in addition to the saturation effect, there is also a steric effect. In substituted benzhydryl  $\text{Ph}_2\text{C}^-\text{X}$  carbanions,<sup>12,13</sup> the experimental shift of carbanionic carbon was accounted for by assuming that one phenyl ring exerts the same charge demand in the corresponding benzyl carbanion  $\text{PhCH}^-\text{X}$ , while the charge demand of the second phenyl ring is zero. Carbanions 19<sup>-</sup>-24<sup>-</sup> are trisubstituted carbanions: two of the substituents are six-membered aromatic rings and one of them is a heterocyclic azine. Providing the substitution of one phenyl for a heterocyclic azine system is taken into account, the situation in carbanions 19<sup>-</sup>-24<sup>-</sup> is therefore similar to that in the  $\text{Ph}_2\text{C}^-\text{X}$  series. On the basis of this reasoning, we assigned the value  $c_{\text{Ph}}^{\text{Ph}} = 0.05$  to carbanions 13<sup>-</sup> and 19<sup>-</sup>-24<sup>-</sup>. We have the  $c_{\text{Het}}^{\text{Ph}}$  for the charge demands of the heterocyclic azines<sup>11,15</sup> and, as in our previous paper,<sup>16</sup> we exploited eq 5,<sup>14</sup> which relates  $c_{\text{X}}^{\text{Ph}}$  and  $c_{\text{X}}^{\text{X}}$ , in order to obtain  $c_{\text{Het}}^{\text{X}}$ .

$$c_{\text{X}}^{\text{Ph}} = 2.216c_{\text{X}}^{\text{X}} - 0.205 \quad (n = 8, r = 0.990) \quad (5)$$

#### The $\delta^{13}\text{C}$ shifts of the $\alpha$ -substituted phenylacetonitrile

(23) Bordwell, F. G.; McCollum, G. J. *J. Org. Chem.* 1976, 41, 2391-2396.

anions 13<sup>-</sup>-24<sup>-</sup>, computed by means of eq 4, are reported in Table IV; the statistics of the line are shown in Table V.

### Discussion

**Assessment of the Carbon Shift- $\pi$ -Charge Relationships.** Although empirical, eq 3 and 4 predict  $^{13}\text{C}$  chemical shifts of carbanions very precisely, and the values of the charge demands  $c_{\text{X}}$  we have previously proposed are here confirmed as reliable figures. We have also shown that eq 5 can be safely used to obtain  $c_{\text{X}}^{\text{X}}$ , once  $c_{\text{X}}^{\text{Ph}}$  values are known.

Within the  $\alpha$ -substituted acetonitrile series, carbanions  $\text{Me}_3\text{N}^+\text{CH}^-\text{CN}$  (11<sup>-</sup>) and  $\text{PhSCH}^-\text{CH}$  (12<sup>-</sup>) are particularly interesting. Both groups enhance the acidity of the parent carbon acid (acetonitrile) by several  $\text{pK}_a$  units.<sup>24-26</sup> For the phenylthioacetonitrile anion (12<sup>-</sup>), agreement with the experiment is very good, and this supports the idea that the phenylthio PhS group does not delocalize the  $\pi$  charge (charge demand equal to zero). The considerable acidifying effect of the arylthio or alkylthio groups<sup>24</sup> is associated with an extra nonmesomeric stabilization of the contiguous carbanionic center.<sup>21</sup> In contrast, for ylid 11<sup>-</sup>, the experimental  $^{13}\text{C}$  shift of the carbanionic carbon is considerably

(24) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* 1976, 41, 1885-1886.

(25) (a) Bordwell, F. G.; Van der Puy, M.; Vanier, N. R. *J. Org. Chem.* 1976, 41, 1883-1885. (b) Bordwell, F. G.; Zhang, X. *J. Org. Chem.* 1990, 55, 6078-6079.

(26) Bordwell, F. G. *Acc. Chem. Res.* 1988, 21, 456-463.

Table III.  $^{13}\text{C}$  NMR Data for Neutral  $\alpha$ -Substituted Phenylacetonitriles  $\text{PhCH}(\text{X})\text{CN}$  and Conjugated Carbanions Sodium Salts  $\text{PhC}^-(\text{X})\text{CN}$ 

compd	X	state <sup>a</sup>	solvent <sup>b</sup>	benzylic positions					CN	other groups
				C <sub>α</sub>	C <sub>i</sub>	C <sub>o</sub>	C <sub>m</sub>	C <sub>p</sub>		
13	Ph	N <sup>c</sup>	DMSO	40.68	136.52	127.32	129.07	127.88	120.18	
		A	DMSO	55.46	152.87	119.65	128.30	114.37	133.12	
14	CO <sub>2</sub> Me	N	DMSO	42.31	130.65	128.01	129.14	128.10	116.68	CO = 165.83, Me = 53.58
		A	DMSO	54.59	141.25	120.66	127.00	117.29	127.42	CO = 167.53, Me = 48.26
15	COMe	N	DMSO <sup>d</sup>	86.64 <sup>e</sup>	132.70	126.95	128.29	126.15	120.97	CO = 168.25, Me = 21.68
		A	DMSO	86.04 <sup>f</sup>	132.83	129.05	128.64	126.99	119.05	CO = 169.15, Me = 19.68
16	COPh	N	DMSO	73.12	140.41	122.30	126.99	119.25	129.27	CO = 182.14, Me = 28.13
			DMSO	45.89 <sup>g</sup>		h			117.83	CO = 190.37
		DMSO	88.19 <sup>i</sup>		h			120.72	CO = 167.82	
		DMSO	87.82 <sup>j</sup>		h			119.14	CO = 168.00	
A	DMSO	73.29	140.46	123.00	127.03	120.05	128.63	CO = 181.76, C <sub>i</sub> = 145.61, C <sub>o</sub> = 126.84, C <sub>m</sub> = 127.35, C <sub>p</sub> = 127.03		
	DMSO	27.21	127.67	127.16	129.57	129.80	113.92			
17	CN	N	DMSO	27.11	141.12	117.90	127.98	116.72	126.24	
		A	DMSO	27.11	141.12	117.90	127.98	116.72	126.24	
18	SO <sub>2</sub> Ph	N	DMSO	60.94	125.64	130.26	128.93 <sup>k</sup>	130.26	114.23	C <sub>i</sub> = 134.69, C <sub>o</sub> = 129.28, C <sub>m</sub> = 129.74, C <sub>p</sub> = 135.43
		A	DMSO	59.85	147.48	119.37	127.57	117.84	125.23	C <sub>i</sub> = 138.21, C <sub>o</sub> = 124.66, C <sub>m</sub> = 128.20, C <sub>p</sub> = 129.85
19	2-Py	N	DMSO <sup>l</sup>	43.58	135.49	127.61	128.97	128.00	119.57	C <sub>2</sub> = 155.23, C <sub>3</sub> = 122.25, C <sub>4</sub> = 137.67, C <sub>5</sub> = 123.11, C <sub>6</sub> = 149.58
		A	DMSO <sup>l</sup>	61.95	142.28	121.47	126.98	115.99	131.25	C <sub>2</sub> = 161.39, C <sub>3</sub> = 115.23, C <sub>4</sub> = 133.12, C <sub>5</sub> = 108.06, C <sub>6</sub> = 147.25
20	4-Py	N	CDCl <sub>3</sub> <sup>m,i</sup>	41.53	133.35	127.22	128.97	128.36	117.54	C <sub>2</sub> = C <sub>6</sub> = 149.38, C <sub>3</sub> = C <sub>5</sub> = 122.10, C <sub>4</sub> = 144.68
		A	DMSO <sup>l</sup>	59.21	141.41	122.82	127.84	118.41	129.68	C <sub>2</sub> = C <sub>6</sub> = 147.67, C <sub>3</sub> = C <sub>5</sub> = 112.15, C <sub>4</sub> = 148.85
21	3-Pyd	N	DMSO <sup>l</sup>	41.85	134.78	127.82	129.32	128.48	118.94	C <sub>3</sub> = 158.51, C <sub>4</sub> = 126.35, C <sub>5</sub> = 128.22, C <sub>6</sub> = 151.42
		A	DMSO <sup>l</sup>	60.60	140.96	122.24	127.16	117.27	129.47	C <sub>3</sub> = 161.33, C <sub>4</sub> = 119.54, C <sub>5</sub> = 123.59, C <sub>6</sub> = 139.24
22	Pyr	N	DMSO <sup>l</sup>	41.22	134.56	127.65	129.14	128.29	118.79	C <sub>2</sub> = 151.15, C <sub>3</sub> = 143.53, C <sub>5</sub> = 144.36, C <sub>6</sub> = 144.45
		A	DMSO <sup>l</sup>	61.63	140.90	121.92	127.17	117.72	128.78	C <sub>2</sub> = 156.92, C <sub>3</sub> = 139.90, C <sub>5</sub> = 126.50, C <sub>6</sub> = 141.48
23	2-Pym	N	DMSO <sup>l</sup>	45.69	134.66	128.00	129.13	128.39	119.05	C <sub>2</sub> = 164.52, C <sub>4</sub> = C <sub>6</sub> = 158.32, C <sub>5</sub> = 120.66
		A	DMSO <sup>l</sup>	66.25	141.16	123.00	126.98	117.33	129.44	C <sub>2</sub> = 168.54, C <sub>4</sub> = C <sub>6</sub> = 155.21, C <sub>5</sub> = 105.62
24	4-Pym	N	CDCl <sub>3</sub> <sup>m,i</sup>	45.10	133.00	127.89	129.57	130.00	117.73	C <sub>2</sub> = 159.19, C <sub>4</sub> = 163.71, C <sub>5</sub> = 119.12, C <sub>6</sub> = 158.41
		A	DMSO <sup>l</sup>	65.84	139.92	123.28	127.13	118.82	127.74	C <sub>2</sub> = 157.05, C <sub>4</sub> = 162.46, C <sub>5</sub> = 111.48, C <sub>6</sub> = 149.98

<sup>a</sup> N for neutrals and A for anions. <sup>b</sup> Solutions are 0.33 M unless differently stated. <sup>c</sup> Pagani, G. A.; Bradamante, S. *J. Org. Chem.* 1980, 45, 105–114. <sup>d</sup> Enolic form only. <sup>e</sup> First enolic form (85%). <sup>f</sup> Second enolic form (15%). <sup>g</sup> Ketonic form (10%). <sup>h</sup> Only aromatic shifts of the major isomer of the three ones present, are reported, but not assigned: C<sub>i</sub> = 135.55, 132.82; others: 130.48, 128.49, 128.4 (2), 127.40, 126.74. <sup>i</sup> First enolic form (80%). <sup>j</sup> Second enolic form (10%). <sup>k</sup> Assignments can be interchanged. <sup>l</sup> 0.50 M solutions. <sup>m</sup> Compound unstable in DMSO solution.

Table IV. Comparison of Experimental and Computed  $^{13}\text{C}$  NMR Shifts of the Carbanionic Carbon in  $\text{XCH}^-\text{CN}$  and  $\text{PhC}^-(\text{X})\text{CN}$ 

X	XCH <sup>-</sup> CN		PhC <sup>-</sup> (X)CN	
	computed	exptl	computed	exptl
Ph	40.72	33.6 <sup>a</sup>	61.72 <sup>b</sup>	55.46 <sup>a</sup>
CONMe <sub>2</sub>	31.20	32.11 <sup>a</sup>		
CO <sub>2</sub> Me	30.40	32.39 <sup>c</sup>	57.80	54.59 <sup>c</sup>
		33.59 <sup>c</sup>		
COMe			75.62	73.12 <sup>c</sup>
COPh	45.18	56.48 <sup>c</sup>	72.58	73.29 <sup>c</sup>
		52.18 <sup>a</sup>		
CN			27.24	27.11 <sup>a</sup>
SPh	2.40 <sup>d</sup>	2.22 <sup>a</sup>		
SOPh	38.78	37.53 <sup>a</sup>		
SO <sub>2</sub> Ph	31.74	35.55 <sup>c</sup>	59.14	59.85 <sup>a</sup>
		37.40 <sup>a</sup>		
PO(OEt) <sub>2</sub>	4.79	3.57 <sup>a</sup>		
Me <sub>3</sub> N <sup>+</sup>	13.50 <sup>d</sup>	68.32 <sup>a</sup>		
2-Py	39.62	40.80 <sup>a</sup>	60.62 <sup>b</sup>	61.95 <sup>a</sup>
4-Py	38.34	39.47 <sup>a</sup>	59.34 <sup>b</sup>	59.21 <sup>a</sup>
2-Pym			61.98 <sup>b</sup>	66.25 <sup>a</sup>
4-Pym			63.70 <sup>b</sup>	65.84 <sup>a</sup>
3-Pyd			58.78 <sup>b</sup>	60.60 <sup>a</sup>
Pyr			59.86 <sup>b</sup>	61.63 <sup>a</sup>

<sup>a</sup> DMSO. <sup>b</sup> The "partial" value of  $c_{\text{Ph}}^{\text{Ph}} = 0.05$  is used instead of  $c_{\text{Ph}}^{\text{Ph}} = 0.09$ . <sup>c</sup> MeOH. <sup>d</sup> The "full" value of  $c_{\text{CN}}^{\text{Ph}} = 0.28$  is used instead of  $c_{\text{CN}}^{\text{CN}} = 0.207$ .

lower field than computed. This is the only recorded case of a failure of eq 3 to predict the correct carbanionic shift. The variance may be due to a number of different reasons. Equation 3 may break down because of the presence of the positive charge of the trimethylammonio group (an incorrect evaluation of  $A_1$  because the paramagnetic contribution of the trimethylammonio group is not constant between the neutral model  $\text{CH}_2=\text{CHNMe}_3^+$  and

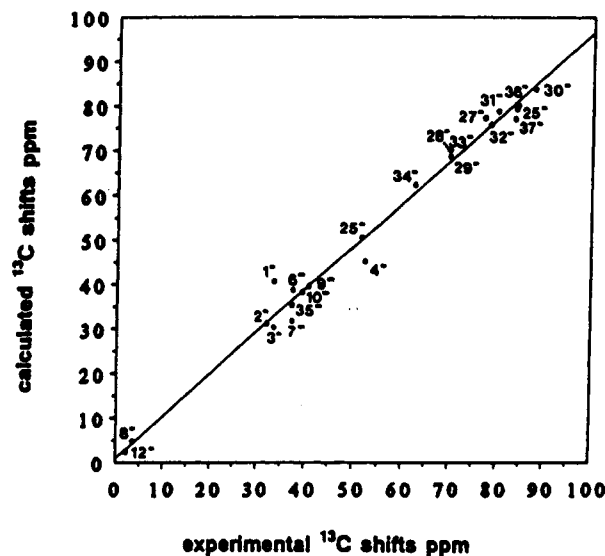


Figure 1. Plot of experimental vs calculated  $^{13}\text{C}$  shifts of the carbanionic carbon in  $\alpha$ -substituted acetonitrile anions and other disubstituted deactivated carbanions.  $[\delta^{13}\text{C}_{\text{calcd}} = (0.956 \pm 0.024)\delta^{13}\text{C}_{\text{exp}} + (0.902 \pm 0.604)]$ ,  $r = 0.993$ ,  $n = 23$ .

the anion<sup>27</sup>) or it may be that the positive charge enhances the charge demand of the cyano group. There are also other possible explanations but, without further experimental evidence, any further discussion is only speculative.

**Delocalization in Cyano Carbanions.** The existence of geometrical isomerism in  $9^-$  and room temperature

(27) According to our approach,<sup>11,17</sup> the  $A_1$  term already incorporates such a contribution in the assumption that the excitation energy term remains constant on going from the neutral model  $\text{RCH}=\text{CHX}$  to the anion.

Table V. Linear Correlation Parameters of Experimental ( $x$ ) vs Computed ( $y$ )  $^{13}\text{C}$  NMR Shifts of the Carbanionic Carbon in XCH-CN, XCH-Y, and PhC(X)CN

entry	system	slope	intercept	$r$	$n$	X
1	XCH-CN	$0.902 \pm 0.080$	$2.128 \pm 1.214$	0.970	10	Ph, CONMe <sub>2</sub> , CO <sub>2</sub> Me, COPh, SOPh, SO <sub>2</sub> Ph, PO(OEt) <sub>2</sub> , 2-pyridyl, 4-pyridyl, SPh
2	XCH-CN	$0.893 \pm 0.051$	$1.501 \pm 0.811$	0.989	9	as entry 1 - Ph
3	XCH-Y	$0.956 \pm 0.024$	$0.902 \pm 0.604$	0.993	23	as entry 1 + 25 - 37
4	PhC(X)CN	$0.954 \pm 0.074$	$2.740 \pm 0.839$	0.972	12	Ph, CO <sub>2</sub> Me, COMe, COPh, CN, SO <sub>2</sub> Ph, 2-pyridyl, 4-pyridyl, 3-pyridazinyl, 2-pyrazinyl, 2-pyrimidyl, 4-pyrimidyl
5	PhC(X)CN	$0.973 \pm 0.056$	$1.026 \pm 0.661$	0.985	11	as entry 4 - Ph

anisochrony of C(3) and C(5) in  $10^-$  is unequivocal proof of the high double-bond character between the carbanionic center and the carbon atom of the pyridyl ring, associated with a high rotational barrier along this bond. This means that the negative charge prefers to delocalize into the heterocycle rather than toward the cyano group. Further validation of this has been provided in our previous paper<sup>16</sup> on  $\omega$ -substituted 4-picoly carbanions 4-PyCH<sup>-</sup>X, in which the pyridyl ring was used as a probe for monitoring the delocalization of the negative charge. The carbon atoms C(3) and C(5) in anion  $20^-$  are equivalent, and so the presence of a further electron-withdrawing group, albeit as weak as that of the phenyl ring, is sufficient to promote the symmetrization of the pyridyl ring. If the cyano group were a strong resonance electron acceptor, it would symmetrize the pyridyl ring in anion  $10^-$ , but since carbons 2 and 6 and carbons 3 and 5 are nonequivalent, the cyano group is not strong enough to withdraw electron density away from the 4-pyridyl.

The small values of the charge demands of the cyano group  $c_{\text{CN}}^{\text{Ph}}$  and  $c_{\text{CN}}^{\text{CN}}$ , as well as the results obtained with the anions of pyridylacetonitriles  $9^-$  and  $10^-$ , establish beyond any doubt that this group is very weak in delocalizing the negative charge of an adjacent carbanionic center by mesomeric mechanisms. These results do not support the view that the ketene imine nitrone  $\text{CH}_2=\text{C}=\text{N}^-$  is a major contributor to the description of  $\alpha$ -cyano carbanions. It is worth ascertaining whether this conclusion is also supported by other theoretical and experimental data.

The problem of delocalization of the negative charge in  $\alpha$ -cyano carbanions (the transfer of the negative charge from the carbanionic carbon to the nitrile functionality) has often been addressed both theoretically and spectroscopically (including IR, NMR, and X-ray investigations). The view that extensive delocalization occurs<sup>1a,2,5a</sup> has been questioned.<sup>11-14</sup> Theoretical studies on cyano carbanions have been carried out within the framework of the effect exerted by substituents X on methyl-substituted carbanions  $^-\text{CH}_2\text{X}$ ,<sup>1,2,4,28</sup> but the comparison of theoretical results from different sources may be misleading (early theoretical investigations have been shown<sup>29</sup> to be inadequate because diffuse functions were not included in the basis set). Hopkinson et al.<sup>1a</sup> calculated that the  $^-\text{CH}_2\text{CN}$  species is 6 kcal/mol less stable than the ketene imine "tautomer"  $\text{CH}_2=\text{C}=\text{N}^-$ , but according to Schleyer,<sup>3c</sup> the C-metallated species  $\text{MCH}_2\text{CN}$  is 9.7 kcal/mol more stable than the N-metallated  $\text{CH}_2=\text{C}=\text{NM}$ . Further, and different, difficulties are met in comparing theoretical and experimental results. Experimental results describe properties of the carbanions in a certain phase state, and interactions between the anions and both the positive counteraction

and the solvent (e.g., the hydrogen bonding) must be considered. Schleyer<sup>30</sup> has differentiated the description, and hence the computation, of "bare" anions and the corresponding system in which interactions occur with the cation. At the CNDO level Schleyer<sup>3c</sup> has approached the description of (dimeric) metal complexes of acetonitrile anion with water and Jorgensen<sup>31</sup> has considered the direct hydrogen-bonding interaction of the bare acetonitrile anion with water. Finally, the NMR information source we used provides the  $\pi$  electron density at the carbanionic carbon, although the majority of original papers reports total atomic charges rather than their  $\sigma$  and  $\pi$  contributions. In short, any useful comparison between experimental and theoretical results requires dealing with a computed species that mimics the structure of the anion ascertained (or supposed) to be present under the experimental conditions.

The charge demands  $c_{\text{CN}}^{\text{Ph}}$  and  $c_{\text{CN}}^{\text{CN}}$  have been obtained from  $^{13}\text{C}$  spectra of the sodium salts of respectively  $\text{PhCH}^-\text{CN}$  and  $^-\text{CH}(\text{CN})_2$ . We believe that the phenylacetonitrile and malononitrile anions are solvent-separated or free anions in DMSO. We have discussed this point elsewhere,<sup>11,13,14</sup> basing our belief on the dissociating properties of DMSO,<sup>32</sup> its good coordinating capacity toward the sodium cation,<sup>33</sup> and the insensitivity of NMR shifts to the presence of a cryptand for the counteraction.<sup>11</sup> Since the charge demands obtained from the above anions can be successfully applied to the anions studied in the present paper, the cyano carbanions we have described here should also be considered solvent-separated or free anions. We are also convinced that cyanocarbanions are reluctant to hydrogen bond. Proof for this is provided by the almost identical  $\text{pK}_a$  values of malononitrile in water<sup>34</sup> [ $\text{pK}_a = 11.41$  ( $\text{H}_2\text{O}$ )] and in DMSO<sup>26</sup> [ $\text{pK}_a = 11.0$  (DMSO)], a behavior which is dramatically different from that of comparably acidic carbon acids possessing hydrogen bonding groups (carbonyl and nitro).<sup>26</sup> The constancy of malononitrile  $\text{pK}_a$  in water and in DMSO is further evidence that the ketene imine nitrone does not substantially contribute to the mesomerism of the malononitrile anion. If it did, the nitrogen atom of the nitrone would be highly susceptible to hydrogen bonding (hard-hard interaction), something which is not supported by experimental evidence. An analogous conclusion can also be drawn from the reported similarity of the  $^{13}\text{C}$  shifts of the malononitrile anion in DMSO and in methanol.<sup>14</sup>

There is, therefore, good overall agreement between our experimental results and those provided by theory. Both

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the large  $\pi$  electron density on the carbanion carbon of  $\alpha$ -cyano carbanions and the small charge demand of the cyano group are in agreement with Hopkinson results.<sup>1a</sup> The following charges were computed to reside on the carbon atoms of  $-\text{CH}_2\text{X}$ :  $-0.886$  for  $\text{X} = \text{CN}$ ,  $-0.770$  for  $\text{X} = \text{CHO}$ ,  $-0.874$  for  $\text{X} = \text{CH}=\text{CH}_2$ , and  $-0.503$  for  $\text{X} = \text{NO}_2$ . Our results also agree with more recent, high-level computations on the acetonitrile anion. According to Schleyer,<sup>3c</sup> C-metallated acetonitrile is more stable than N-metallated ketenimine nitrane. This suggests a larger  $\pi$  charge density on carbon than on nitrogen atoms. Finally, "the noticeable shortening of the C-C bond length and the modest extension of the C $\equiv$ N linkage"<sup>3c</sup> (a result obtained both by computational<sup>3c</sup> and X-ray<sup>8</sup> investigations) is in line with an essentially localized negative charge on the carbanionic carbon both in the computed bare  $\alpha$ -cyano carbanion and in the solid state. This is a case of agreement between experimental, theoretical, and structural results, at variance with another case in which the existence of solvent interactions prevents the possibility of comparing theoretical and structural results.<sup>35</sup>

Finally, in terms of reactivity,  $\alpha$ -cyano carbanions are known to react with electrophiles at the nitrogen atom only in very rare cases, either with silyl-based species<sup>36</sup> or when severe steric congestion is present at the carbanionic carbon.<sup>37</sup>

**Acidity of Cyanocarbon Acids and Delocalization in the Conjugate Anions.** In DMSO, phenylacetonitrile is a carbon acid only 2  $\text{pK}_a$  units weaker ( $\text{pK}_a = 21.9$ )<sup>26</sup> than phenylacetone ( $\text{pK}_a = 19.9$ ),<sup>26</sup> despite a large difference in  $\rho_{\text{CN}}$  and  $\rho_{\text{COMe}}$ . It is recognized that the stabilization of phenylacetone anion is largely provided by delocalization in the enolate. If the cyano group cannot provide stabilization by resonance, what is the mechanism which enables this group to provide such a high degree of acidity to cyanocarbon acids? We doubt that the polar-inductive-field effects are primarily responsible, despite the high value of  $\sigma_I$  for the cyano group. In fact, substituent effect analysis<sup>13</sup> has shown that the sensitivity of the DMSO acidity of deactivated carbon acids to polar-inductive-field effects is only 0.81 times that provided by resonance effects. The stabilization that polar-inductive-field effects can provide is therefore only marginal. We believe that the answer to this question was suggested many years ago by Bordwell,<sup>38</sup> when he considered the energetic balance associated with the structural reorganization undergone by the carbon acid on its way to the carbanion. In discussing the strongly acidifying effect of the nitro group in nitromethane as compared with the small effect exerted by the  $\text{MeSO}_2$  group in dimethyl sulfone, Bordwell pointed out that the  $\text{CH}_2=\text{NO}_2^-$  contributor is very important for  $\text{CH}_2\text{NO}_2^-$  because of the near-equivalence of the C=N and N=O bond energies. In contrast, the relatively poor conjugative stabilization provided by the  $\text{CH}_3\text{SO}_2=\text{CH}_2^-$  contributor is much less important in stabilizing the anion. In cyano carbanions, the strong  $\pi$  interaction between the carbanionic carbon and the cyano carbon atom (as shown by structural investigations<sup>9</sup>) gives this linkage a high double-bond character which is certainly very valuable in terms of anion

stabilization. It is the formation of this new double bond that stabilizes  $\alpha$ -cyano carbanions and therefore causes the considerable acidity of their neutral precursors.

## Conclusion

In addition to several other experimental results (the solvent insensitivity of cyanocarbon acidity,<sup>11</sup> the solvent insensitivity of the NMR parameters of conjugated carbanions,<sup>14</sup> the product distribution of the collapse of cyano carbanions with electrophiles,<sup>39</sup> the violation<sup>11,40</sup> of the reactivity-selectivity principle based on the  $\rho$  response<sup>26</sup> of acidity to substituent effects in aryl-substituted acetonitriles), as well as computational and structural investigations on cyano carbanions, our experimental charge-demand approach points to the *inadequacy* of ketene imine nitrane in satisfactorily describing such carbanionic species. The VB representation of delocalization introduces an inconsistency due to oversimplification because it requires a simultaneous bond extension of the triple C $\equiv$ N bond, something which is hardly supported by either theoretical or structural data. Cyano carbanions provide a new challenge to our understanding (or at least to our representation) of chemical bonding in these species.

## Experimental Section

**NMR Data.** <sup>13</sup>C NMR spectra were recorded at 25 °C either on a Varian XL-100 or XL-300 or a Bruker 80 spectrometer, operating at 25.14, 75.47, and 20.12 MHz, respectively, and were measured relative to  $\text{Me}_4\text{Si}$  as external standard; <sup>13</sup>C NMR shifts were recorded using 0.33 or 0.50 M solutions in DMSO. The DMSO-*d*<sub>6</sub> solvent provided the internal deuterium lock. Anion solutions in DMSO (10-mm o.d. tubes) were provided with an internal 5-mm coaxial tube containing neat DMSO-*d*<sub>6</sub>.

**Materials and Preparation of the Carbanions.** Phenylacetonitrile, methyl cyanoacetate, malononitrile, 2-pyridylacetonitrile, 4-pyridylacetonitrile, diphenylacetonitrile, and phenylthioacetamide were commercially available. *N,N*-dimethyl cyanoacetamide,<sup>41</sup> benzoylacetonitrile,<sup>42</sup> phenylsulfonylacetonitrile,<sup>43</sup> phenylsulfonylacetonitrile,<sup>44</sup> cyanomethylenetriethylammonium iodide,<sup>45</sup> methyl  $\alpha$ -cyanophenylacetate,<sup>46</sup>  $\alpha$ -acetylphenylacetone,<sup>47</sup>  $\alpha$ -benzoylphenylacetone,<sup>48</sup> phenylmalononitrile,<sup>49</sup>  $\alpha$ -(phenylsulfonyl)phenylacetone,<sup>50</sup>  $\alpha$ -(2-pyridyl)phenylacetone,<sup>51</sup>  $\alpha$ -(4-pyridyl)phenylacetone,<sup>51</sup>  $\alpha$ -(3-pyridazinyl)phenylacetone,<sup>51b</sup>  $\alpha$ -(2-pyrazinyl)phenylacetone,<sup>51b</sup>  $\alpha$ -(2-pyrimidyl)phenylacetone,<sup>51b</sup> and  $\alpha$ -(4-pyrimidyl)phenylacetone<sup>51b</sup> were prepared according to reported procedures. Anions were prepared following a previously described procedure.<sup>11,14,15</sup>

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