α-Substituted Toluenes as Carbon Acids: Structural Reorganization and Free Energy Changes upon Carbanion Formation

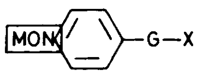
Silvia Bradamante and Giorgio A. Pagani *

Dipartimento di Chimica Organica e Industriale dell'Università and Centro CNR Speciali Sistemi Organici, Via C. Golgi 19, 20133 Milano, Italy

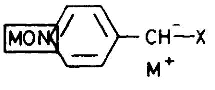
^{1}H, ^{13}C, and ^{19}F n.m.r. data of benzyl carbanions $PhCH^{-}X$ (VI) and p-$FC_6H_4CH^{-}X$ have been found to be appropriate monitors for probing the structural reorganization undergone by the precursor carbon acids $PhCH_2X$ upon deprotonation. Even in the highly dissociating Me_2SO as solvent benzyl carbanions exhibit ion-pairing phenomena: these have been proved by the effect exerted by the [2.2.1]cryptand on ^{13}C shifts, and by changing the countercation. ^{13}C Parameters of benzyl anions (VI) provide experimental access to negative π charge density maps through equation (1). It is shown that the solvent greatly assists delocalization of the negative charge in these systems. The substituent-induced variations of the *para*-monitor in the anions are linearly related to pK_a variations of the precursor acids. Carbanions appear to belong to two different classes depending on the mechanism with which the charge stabilizes the system. Thus, in enolate and nitronate anions the stabilization is provided by extensive charge transfer from the carbanion carbon, in contrast to carbanions activated by the third-row elements (P,S) and by the cyano group. Substituent electron demands q_X (the amount of charge transferred to the activating substituent X) govern the charge distribution in the anions in related ways, the acidity of the precursor acids $PhCH_2X$, and the sensitivities of these latter to remote aryl substitution.

Carbanions are intermediates of primary importance in organic chemistry;[1,2] substituent stabilization of carbanions, analogous to carbocations,[3] is provided both by intra- and intermolecular mechanisms: the intramolecular effect of substituents has been inferred from the ionization constants in solution of the precursor carbon acids,[4—7] while the role played by dispersion forces in the intermolecular process of stabilization[8] has been investigated by obtaining acidities in the gas phase.[9] Details concerning geometries, delocalization, and energies of carbanions have been provided by a number of *ab initio* computations.[10]

In the present work we report how the different groups X influence the structural reorganization undergone by α-substitituted toluene carbon acids $PhCH_2X$ (I) upon deprotonation. We obtained information of structural content by performing a detailed n.m.r. study in Me_2SO on benzyl carbanions (VI).†,[11] From this approach it can be shown that: (i) the effects originated by substituents X determine both the structural reorganization of the carbanions and the acidities of their precursors, (ii) acidities of toluene and of methane carbon acids (I) and (VIII) respectively, as determined by Bordwell and his co-workers in Me_2SO,[6] are related to experimental electron demands of substituents X, q_X, as determined from charge–^{13}C relationships,[12] (iii) functionalized carbanions exhibit, relative to other anionic species we have previously studied,[13] ion pairing even in Me_2SO, and (iv) the phenylogy principle, proposed for oxygen acids,[14b] applies as well as to carbon acids (I), (VIII), and (IX). In fact α-substituted toluenes (I), reproducing the design of families (I)—(V),[11,14] are iso-Hammett phenyl homologues of methane carbon acids CH_3X (VIII), while p-substituted toluenes p-$XC_6H_4CH_3$ (IX) are true Hammett phenyl homologues.



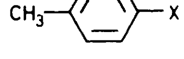
(I) G = CH_2
(II) G = CHPh
(III) G = O
(IV) G = NH
(V) G = NMe
(VI) G = CH^{-}
(VII) G = N^{-}



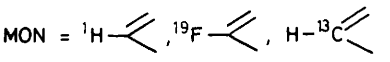
(VI)

CH_3X

(VIII)



(IX)



M^{+} = Li^{+}, Na^{+}, K^{+}, [Na(2.2.1) cryptand]$^{+}$

(1) X = H
(2) X = Ph
(3) X = $CONMe_2$
(4) X = CO_2Me
(5) X = COMe
(6) X = COPh
(9) X = NO_2
(10) X = CN
(11) X = SOMe

(12) X = SO_2Me
(13) X = SOPh
(14) X = SO_2Ph
(16) X = $PO(OEt)_2$
(17) X = $POPh_2$
(19) X = 2-C_5H_4N
(20) X = 3-C_5H_4N
(21) X = 4-C_5H_4N
(22) X = CH=CHPh

Results

N.m.r. Data and Ion Pairing of Carbanions.—Carbanions (VI) were generated in Me_2SO starting from carbon acids (I): solutions of ^{1}H and ^{19}F spectra were 0.1M in substrate, while for ^{13}C experiments they were 0.33M. We needed a two-fold excess of base because with strictly equimolar amounts we obtained poor spectra of carbanions (VI: **10**—**14**) due to apparent fast exchange. Particular care had to be used on generating carbanions (VI-**4**) and (VI-**10**): indeed, for these, relatively slow addition of the basic solution to the substrate led to Claisen-type condensation products. All carbon acids were

---

† See Experimental section for details concerning the numbering of substrates of the present and future publications.

Table 1. $^{1}H_{p}$, $^{19}F_{p}$, and benzenoid ^{13}C shifts of sodium benzyl carbanions $PhCH^{-}X$ (**VI**)

			$^{13}C^{a}$						
Entry	X	Solvent	*ortho*	*meta*	*para*	*ipso*	$^{1}H_{p}{}^{a}$	$^{19}F_{p}{}^{b}$	Ref.
2	Ph	Me_2SO	116.1	127.5	105.7	145.2	5.640		*c*
		Me_2SO + [2.2.1]	116.0	127.3	105.5	144.9			*d*
3	$CONMe_2$	Me_2SO	120.2	127.0	112.3	147.5	6.101		*c*
		Me_2SO + [2.2.1]	119.4	126.4	110.6	148.0			*d*
4	CO_2Me	Me_2SO	120.3	127.1	113.3	146.9	6.189	31.18	*c*
5	COMe	Me_2SO	122.0	126.8	116.1	145.0	6.425	35.34	*c*
		Me_2SO + [2.2.1]	121.5	126.6	115.2	145.7			*e*
6	COPh	Me_2SO	123.5	126.9	117.7	144.6	6.558	37.11	*c*
		Me_2SO + [2.2.1]	122.9	126.6	116.5	145.0			*e*
9	NO_2	Me_2SO	123.9	127.5	123.0	135.7	6.952		*c*
		Me_2SO + [2.2.1]	122.9	127.3	121.5	136.7			*e*
		MeOH	125.5	126.9	125.5	132.1			*f*
10	CN	Me_2SO	115.9	127.6	109.0	148.9	5.859	25.96	*c*
		Me_2SO + [2.2.1]	115.4	127.3	108.3	149.7			*d*
11	SOMe	Me_2SO	115.3	127.6	108.4	148.8	5.851	26.09	*c*
		Me_2SO + [2.2.1]	114.5	127.3	106.7	149.1			*d*
12	SO_2Me	Me_2SO	116.4	127.4	111.0	145.5	6.036		*c*
13	SOPh	Me_2SO	115.9	127.2	110.8	147.7	5.964	28.27	*c*
14	SO_2Ph	Me_2SO	117.5	127.5	112.4	144.3	6.092	29.98	*c*
		Me_2SO + [2.2.1]	117.7	127.3	111.8	144.6			*d*
16	$PO(OEt)_2$	Me_2SO	117.5	127.1	108.4	149.7	5.837	25.15	*c*
		Me_2SO + [2.2.1]	117.2	126.9	107.6	150.4			*d*
17	$POPh_2$	Me_2SO	118.0	128.2	108.7	*g*	5.805	25.69	*c*
19	$2\text{-}C_5H_4N$	Me_2SO	119.8	127.8	110.3	145.0	6.003		*c*
		Me_2SO + [2.2.1]	119.6	126.5	110.0	144.9			*d*
20	$3\text{-}C_5H_4N$	Me_2SO	117.1	127.7	108.2	147.3	5.817		*c*
21	$4\text{-}C_5H_4N$	Me_2SO	120.0	127.1	112.3	143.9	6.14		*c*
		Me_2SO + [2.2.1]	119.6	126.4	111.6	144.1			*d*
22	CH=CHPh	Me_2SO	117.5	127.9	111.2	143.5	5.936		*c*
		Me_2SO + [2.2.1]	117.2	127.5	110.8	145.2			*d*

[a] Relative to TMS. Numbers with four digits for ^{1}H shifts best values from LAOCOON III fittings. [b] Relative to C_6F_6. [c] Using dimsyl:substrate = 2:1 and substrate = 0.33M. [d] Using dimsyl:[2.2.1]:substrate = 2:2.1:1. [e] Using dimsyl:[2.2.1]:substrate = 1:1.1:1. [f] This work, using NaOMe = 2M and substrate = 0.33M. [g] Not determined.

completely deprotonated under these conditions: the only exception was diphenylmethane (**I-2**) for which an equilibrium mixture of 45% in anion (**VI-2**) and 55% in precursor is reached using a two-fold excess of base. Both ^{1}H and ^{13}C n.m.r. spectra show the two species as distinct entities, the rate for their interconversion being sufficiently slow on the n.m.r. time-scale.

While hydrocarbon anions are present in Me_2SO[15] as solvent separated ions, a number of carbanions in which the negative charge is predominantly delocalized onto electronegative atoms[16] show substantial ion pairing. To minimize and possibly eliminate ion pairing we ran the spectra also in the presence of the [2.2.1]cryptand, known to bind strongly and selectively the sodium cation.

^{1}H And ^{19}F monitor shifts and aromatic ^{13}C data for sodium carbanides (**VI**) in Me_2SO are reported in Table 1, together with ^{13}C shifts for a number of anions prepared in the presence of the [2.2.1]cryptand. Shifts of benzylic carbons and protons both in the neutral substrates (**I**) and in the anions (**VI**), and their coupling constants $^{1}J_{CH}$, are collected in Table 2. ^{1}H Parameters obtained by LAOCOON III[17] fitting of the aromatic protons relative to the benzylic moiety of carbanions (**VI**) are reported in Table 3. Our data in Me_2SO and those reported by Gompper in HMPT,[18] using in both cases Na^{+} as counterion, are within 0.1—0.2 p.p.m., and therefore can be considered practically coincident for any subsequent discussion.

Finally the effect of Li^{+}, Na^{+}, and K^{+} counterions on ion-pairing phenomena in Me_2SO has been studied by monitoring the variations of the H_p chemical shifts: results reported in Table 4 show that, even the largest responses of the H-1 monitor to cation variation, are very modest, and sometimes barely detectable.

Correlative Analysis of N.m.r. and Acidity Data.—Table 5 collects intermonitor and interpositional correlations.[14] Excellent correlations are found for C_p *versus* H_p and C_p *versus* F_p: F_p appears to be the most sensitive monitor to variations in X and C_p is *ca.* 13 times more sensitive than H_p. Another interesting correlation is found for C_α *versus* H_α. We consider this correlation non-fortuitous, since it includes substituents that induce in carbanions both a high- and low-field shift of H_α relative to H_α of precursors.

While H_m and H_p are linearly related, C_m and C_p are not. At least for a limited number of substituents, ^{1}H and ^{13}C monitors at the *ortho* position show inverted sensitivities relative to those at the *para* position.

Acidity data for carbon acids $PhCH_2X$ (**I**) and CH_3X (**VIII**) are given in Table 6; intersystem correlations[14] are in Table 7. The chemical shifts of the C_p carbon in carbanions (**VI**) are found to be linearly related to the Me_2SO acidities of carbon acids $PhCH_2X$ (**I**). Data for the CN substituent are badly deviant (Figure 1). Since Me_2SO acidities of the α-substituted toluenes $PhCH_2X$ (**I**) are linearly related to those of substituted methanes CH_3X (**VIII**) (entries 4 and 5), C_p of carbanions (**VI**) are also related to acidities of carbon acids CH_3X (entry 8), data for the $CONMe_2$ and CN substituents being somewhat deviant (entries 9 and 10).

Table 2. ^1H, ^{13}C (p.p.m.), and $^1J_{CH}$/Hz of the benzylic carbon in sodium benzyl carbanions $PhCH^-X$ (VI) and in their precursors $PhCH_2X$ (I)[a]

Entry	X	Solvent	δCH_2	δCH^-	$\Delta\delta(H)^b$	δCH_2	δCH^{-e}	$\Delta\delta(^{13}C)^b$	$^1J_{CH_2}$	$^1J_{CH^-}$	ΔJ	Ref.
2	Ph	Me_2SO	3.92	4.17	0.25	41.25	80.3	39.0	127.2	147.5	20.3	*c*
		Me_2SO + [2.2.1]					80.3	39.0				*d*
3	$CONMe_2$	Me_2SO	3.67	3.97	0.30	37.0	70.2	33.2	125	146.2	21.2	*c*
		Me_2SO + [2.2.1]					69.2	32.2				*d*
4	CO_2Me	Me_2SO	3.61	3.79	0.18	41.3	67.1	25.8	130	151.1	21.1	*c*
5	COMe	Me_2SO	3.72	4.48	0.76	49.5	89.8	40.3	125	148.0	23	*c*
		Me_2SO + [2.2.1]					88.9	39.4				*e*
6	COPh	Me_2SO	4.37	5.35	0.98	44.8	89.8	45.0	127.0	147.7	20.7	*c*
		Me_2SO + [2.2.1]					88.6	43.8				*e*
9	NO_2	Me_2SO	5.71	6.70	0.99	79.3	109.2	29.9	146.0	175.2	29.2	*c*
		Me_2SO + [2.2.1]					107.7	28.4				*e*
		MeOH				78.1	114.7	36.6	147.3	176.4	29.1	*f*
10	CN	Me_2SO	4.00	2.36	−1.64	22.6	33.6	11.0	137.4	150	12.6	*c*
		Me_2SO + [2.2.1]					33.7	11.1				*d*
11	SOMe	Me_2SO	4.11	3.77	−0.34	58.5	71.2	12.7	138.9	170.8	31.9	*c*
		Me_2SO + [2.2.1]		3.93	−0.16		72.8	14.3				*d*
12	SO_2Me	Me_2SO	4.47	3.29	−1.16	59.5	64.1	4.6	138.0	161.0	23	*c*
13	SOPh	Me_2SO	4.24	3.67	−0.57	61.8	68.4	6.6	140.0	166.0	26	*c*
14	SO_2Ph	Me_2SO	4.63	3.49	−1.14	60.8	64.4	3.6	140.0	160.7	20.7	*c*
		Me_2SO + [2.2.1]					64.6	3.8				*d*
16	$PO(OEt)_2$	Me_2SO	3.19	2.10	−1.09	32.4	39.3[g]	6.9	~130.0	149.5	~20	*c*
		Me_2SO + [2.2.1]					40.7	8.3				*d*
17	$POPh_2$	Me_2SO	3.88	2.84	−1.04	*h*	49.7	*h*		147		*c*
19	$2\text{-}C_5H_4N$	Me_2SO	4.06	4.28	0.22	43.9	84.0	40.1	127.7	144.5	16.8	*c*
		Me_2SO + [2.2.1]					83.8	39.9				*d*
20	$3\text{-}C_5N_4N$	Me_2SO	3.94	4.15	0.21	38.2	77.5	39.3	127.0	145.0	18.0	*c*
21	$4\text{-}C_5H_4N$	Me_2SO	3.95	4.27	0.32	40.3	83.6	43.3	128.0	143.6	15.6	*c*
		Me_2SO + [2.2.1]					83.2	42.9				*d*
22	CH=CHPh	Me_2SO	3.56	4.61	1.05	39.5	90.1	50.6	125	144.3	19.3	*c*
		Me_2SO + [2.2.1]					89.9	50.4				*d*

[a] Proton and carbon shifts are relative to TMS. [b] $\Delta\delta = \delta_{anion} - \delta_{neutral}$. [c] Using dimsyl:substrate = 2:1 with substrate = 0.33M. [d] Using dimsyl:[2.2.1]:substrate = 2:2.1:1 with substrate = 0.33M. [d] Using dimsyl:[2.2.1substrate = 2:2.1:1 with substrate = 0.33M. [e] Using dimsyl:[2.2.1]:substrate = 1:1.1:1 and substrate = 0.33M. [f] Using NaOMe = 2M and substrate = 0.33M. [g] $^1J_{PC}$ = 220.8 Hz. [h] Not determined because of insolubility of the precursor $PhCH_2P(O)Ph_2$.

Table 3. ^1H N.m.r. parameters for $PhCHX^-Na^+$[a]

Entry	X	H_o[b]	H_m[b]	J_{om}	J_{op}	J_{mp}	$J_{oo'}$	$J_{om'}$	$J_{mm'}$	Error
2	Ph	640.63	654.50	8.32	1.12	6.89	1.78	0.27	1.81	0.038
3	$CONMe_2$	724.60	670.88	8.15	1.14	7.05	1.42	0.20	1.67	0.035
4	CO_2Me	715.00	676.62	7.97	1.33	7.06	1.62	0.20	1.67	0.041
5	COMe	751.84	686.47	7.88	1.15	7.13	1.71	0.26	1.56	0.047
6	COPh	780.65	697.01	7.25	1.27	7.24	1.11	0.51	2.21	0.028
9	NO_2	781.22	719.00	7.64	0.98	7.42	1.37	0.56	1.63	0.034
10	CN	628.06	661.27	8.14	1.12	7.07	1.61	0.12	1.44	0.045
11	SOMe	641.38	660.38	7.87	1.27	6.98	1.20	0.41	2.03	0.043
12	SO_2Me	654.06	669.00	7.97	1.23	7.05	1.69	0.42	1.86	0.040
22	CH=CHPh	650.21	664.53	7.93	1.11	6.97	1.25	0.36	2.17	0.046

[a] Best values (in Hz at 100 MHz) from LAOCOON treatment. [b] Chemical shifts.

Charge Maps in Benzyl Carbanions.—We have shown[12] that equation (1) can be used successfully in conjugatively

$$\delta_\pm = \delta_n - k(q_C - 1) \qquad (1)$$

delocalized carbanions and carbenium ions where δ_n = 122.8 + ΣA_i and q = 160 p.p.m. per electron. Table 8 reports the A_i shielding contributions of various groups for C(1) in 1-substituted ethylenes. π Electron density maps in carbanions (VI) have been calculated making use of equation (1) and are reported in Table 9. To obtain the amount of negative charge q_X transferred from the carbanionic carbon to the X substituent, we subtracted from a total of 8π electrons, which is the number of π electrons endowing every $PhCH^-$ fragment, the electron density calculated to reside on the CH^- carbon atom and on the adjacent phenyl group.[12]

Discussion

Structural Reorganization in Carbanions.—(a) *General.* The n.m.r. parameters predicted to be sensitive to the structural reorganization in the carbanions are: (i) the ^1H and ^{13}C shifts of the carbanionic centre, (ii) the chemical shift of the *para* monitor, and (iii) the one-bond coupling constant $^1J_{CH}$ of the carbanionic carbon.

Variations of ^{13}C and ^1H shifts of the carbanionic centre relative to the neutral precursor are *per se* of little structural significance since they are the complex result of a number of

Table 4. Cation effects on proton shifts of $PhCHX^-Y^+$ [a]

Entry	X	CH^-			H_p		
		Y = Li	Y = Na	Y = K	Y = Li	Y = Na	Y = K
2	Ph	431.1	417.4	422.1	565.0	563.9	563.3
3	$CONMe_2$	400.8	397.4		614.6	610.1	
4	CO_2Me	383.1	379.6	378.9	619.8	618.9	615.6
5	COMe	455.0	448.4	446.5	647.5	642.5	636.8
9	NO_2	673.6	669.9	666.3	697.0	695.2	690.4
10	CN		236.1		585.9	585.9	
13	SOPh	370.0	367.6		598.1	596.0	
14	SO_2Ph	350.5	349.0		609.6	609.2	617.2
16	$PO(OEt)_2$	206.4	209.7		585.1	583.7	
19	$2\text{-}C_5H_4N$	433.4	428.0		618.3	600.3	
21	$4\text{-}C_5H_4N$	430.1	427.2		599.7	614.0	

[a] Values in Hz at 100 MHz relative to TMS.

Table 5. Intermonitor and interpositional correlations for $PhCHX^-Na^+$

Entry	*y*	*x*	Slope	Intercept	*r*	*n*	X
1	C_p	H_p	12.85 ± 0.35	33.84 ± 0.11	0.994	17	Ph, $CONMe_2$, CO_2Me, COMe, COPh, NO_2, CN, SOMe, SO_2Me, SOPh, $SO_2PhPO(OEt)_2$, $POPh_2$, $2\text{-}C_5H_4N$, $3\text{-}C_5H_4N$, $4\text{-}C_5H_4N$, CH=CHPh
2	F_p	C_p	1.27 ± 0.04	−112.91 ± 0.13	0.997	9	CO_2Me, COMe, COPh, CN, SOMe, SOPh, SO_2Ph, $PO(OEt)_2$, $POPh_2$
3	H_o	H_p	1.59 ± 0.25	−2.69 ± 0.07	0.955	6	Ph, $CONMe_2$, CO_2Me, COMe, COPh, CH=CHPh
4	H_m	H_p	0.50 ± 0.02	3.67 ± 0.01	0.993	10	As entry 3 + NO_2, CN, SOMe, SO_2Me
5	C_o	C_p	0.56 ± 0.08	56.02 ± 0.34	0.866	17	As entry 1
6			0.60 ± 0.07	52.21 ± 0.25	0.949	10	As entry 3 + $PO(OEt)_2$, $POPh_2$, $2\text{-}C_5H_4N$, $3\text{-}C_5H_4N$
7	C_α	H_α	17.05 ± 1.37	4.96 ± 1.43	0.955	17	As entry 1
8			24.68 ± 1.05	−23.16 ± 0.64	0.990	13	As entry 1 − COPh, NO_2, SO_2Me, $PO(OEt)_2$

Table 6. Me_2SO Acidities of substituted methane and toluene carbon acids

Entry	X	CH_3X	Ref.	$p\text{-}XC_6H_4CH_3$	Ref.	$PhCH_2X$	Ref.
1	Ph	(42)	*a*			32.30	*b*
2	$CONMe_2$	34—35	*c*			26.62	*c*
3	CO_2Et	30—31	*c*			22.71	*c*
4	COMe	26.50	*b,d*			19.80	*b*
5	COPh	24.70	*b*	26.90	*e*	17.70	*f*
9	NO_2	17.20	*b,d*	20.40	*e*	12.52	*f*
10	CN	31.30	*a,b*	30.80	*e*	21.90	*b*
11	SOMe	35.10	*d*			29.10	*b*
12	SO_2Me	31.10	*d*			25.60	*f*
13	SOPh	33.00	*g*			27.20	*d*
14	SO_2Ph	29.04	*a,f*	29.80	*e*	23.40	*f*
	SO_2CF_3	18.76	*g*	24.00	*e*		
16	$PO(OEt)_2$					27.60	*h*
19	$2\text{-}C_5H_4N$					28.18	*h*
20	$3\text{-}C_5H_4N$					30.15	*h*
21	$4\text{-}C_5H_4N$					26.66	*h*

[a] Ref. 6*h* (the number in parentheses refers to an extrapolated value). [b] Ref. 6*a*. [c] Ref. 6*i*. [d] Ref. 6*c*. [e] Ref. 6*e*. [f] Ref. 6*d*. [g] Ref. 6*g*. [h] F. G. Bordwell, unpublished results.

effects (*e.g.* the high-field shift caused by the negative charge, the low-field shift caused by the $sp^3 \rightarrow sp^2$ rehybridization, and the variable displacements induced by the different substituents). The π electron densities of Table 9 are much more informative than the simple and qualitative comparison of chemical shifts, a practice nonetheless extensively followed by others.[19] In our approach we prefer to associate the structural reorganization in solution with the experimental amount of charge residing on the deprotonation site and with the amount of charge transferred to the substituent X and to the phenyl ring. Since we have already demonstrated that the charge maps deduced from equation (1) are dependable, our method is considered to be superior to the alternative of computing charges making reference to fixed model compounds.[20] The linear relationship of C_α *versus* H_α in the carbanions* and the definition itself[12,21] of the A_i values assures that the $(\delta_\pm - \delta_n)$ term, resulting independently of proximity effects, is affected only by charge density variations at the charged carbon. In fact, the linear relationship of C_α *versus* H_α is evidence that the substituent affects in a related way both the diamagnetic term which governs the proton shift, and the blend of diamagnetic and paramagnetic terms (including a charge and an excitation energy component[22]) of carbon shifts. The situation is thus analogous to carbon and proton shifts at the *para*-position, for which charge–shift relationships are widely and firmly accepted.[23] The A_i terms, as defined,[12,21] take care of the shielding of the α-carbon in α-substituted ethylenes by the adjacent substituent X: this already includes the different π bonding interactions between the trigonal carbon and the substituent, and the different excitation energies of the p_π electrons of that carbon. Although the conditions imposed by equation (1) to the treatment of the original, experimental ^{13}C data are rather strict, they appear necessary to avoid the failures that other approaches[24,25] have encountered for charge–shift relationships.

According to equation (2),[26] the variation of $^1J_{CH}$ between the

$$0.2\Delta{}^1J_{CH} = \Delta(\%s) \qquad (2)$$

neutral precursor and the carbanion should provide information about the extent of configurational rehybridization of the ion: an increase of *ca.* 40 Hz in $^1J_{CH}$ would involve an increase of *ca.* 8% in the *s* character of the carbanionic carbon, corresponding to the change $sp^3 \rightarrow sp^2$. Carbanions (**VI**) show, relative to their neutral precursors (**I**), an increase in $^1J_{CH}$ ranging from 12 to 30 Hz; since there are indications that excess of π negative charge tends to decrease the size of $^1J_{CH}$ in trigonal carbons,[27] we interpret our results as evidence for extensive, if not total, trigonalization of the carbanionic carbon.

(b) *Nitronate and enolate anions.* These species (X = NO_2 and X = COMe, COPh, CO_2Me, and $CONMe_2$) consistently show a small but perceptible upfield shift (0.9—1.5 p.p.m.) of the *para*-carbon upon decomplexation: a similar small upfield shift

---

* It is noteworthy that no correlation whatsoever is found instead for ^{13}C and ^1H in the neutral precursors (**I**)

Table 7. Intersystem correlations[a]

Entry	System A(y)	System B(x)	y	x	Slope	Intercept	r	n	X
1	$PhCH_2X$	$PhCH^-X$	pK_a	C_p	-1.20 ± 0.04	159.51 ± 0.22	0.994	10	Ph, CO_2Me, COMe, COPh, NO_2, SOMe, SOPh, SO_2Me, SO_2Ph, 3-C_5H_4N
2					-1.21 ± 0.06	160.94 ± 0.29	0.985	12	As entry 1 + 2-C_5H_4N + 4-C_5H_4N
3					-1.18 ± 0.07	157.68 ± 0.32	0.977	14	As entry 2 + $CONMe_2$ + $PO(OEt)_2$
4	MeX	$PhCH_2X$	pK_a	pK_a	1.006 ± 0.053	5.82 ± 0.29	0.993	7	COMe, COPh, NO_2, SOMe, SO_2Me, SOPh, SO_2Ph
5					1.003 ± 0.010	6.31 ± 0.51	0.971	8	As entry 4 + CN
6	MeX	p-MeC_6H_4X	pK_a	pK_a	1.32 ± 0.10	-10.10 ± 0.39	0.995	4	COPh, NO_2, CN, SO_2Ph
7					1.42 ± 0.18	-13.12 ± 0.69	0.976	5	As entry 6 + SO_2CF_3
8	MeX	$PhCH^-X$	pK_a	C_p	-1.16 ± 0.08	159.98 ± 0.37	0.989	8	As entry 4 + CO_2Me
9					-1.11 ± 0.10	154.49 ± 0.44	0.973	9	As entry 8 + CN
10					-1.18 ± 0.14	157.63 ± 0.57	0.946	10	As entry 9 + CONMe
11	$PhCH_2X$	$PhCH^-X$	pK_a	q_X	-51.9 ± 8.5	45.06 ± 0.99	0.950	6	Ph, CO_2Me, COMe, COPh, NO_2, 4-C_5H_4N
12					-55.5 ± 8.6	47.77 ± 0.87	0.925	9	As entry 11 + $CONMe_2$, 2-C_5H_4N, 3-C_5H_4N
13					-165.5 ± 19.9	70.15 ± 0.39	0.972	6	Ph, CN, SO_2Me, SOPh, SO_2Ph, $PO(OEt)_2$
14	$ArCH_2X$	$PhCH_2X$	$\rho(pK_a)$	q_{CH}	10.34 ± 1.35	-10.65 ± 0.14	0.983	4	COMe, NO_2, CN, SO_2Me
15	σ_{R-}	$PhCH^-X$	ρ_{R-}	q_X	0.90 ± 0.09	0.03 ± 0.009	0.968	9	Ph, CO_2Me, COMe, COPh, SOPh, $PO(OEt)_2$, 3-C_5H_4N, 4-C_5H_4N
16					0.67 ± 0.11	0.11 ± 0.01	0.874	14	As entry 15 + NO_2, CN, SO_2Me, SO_2Ph, 2-C_5H_4N
17	$PhCH^-X$	$PhCH^-X$	q_X	q_p	-4.61 ± 0.32	5.40 ± 0.008	0.974	13	Ph, $CONMe_2$, CO_2Me, COMe COPh, NO_2, CN, SOMe, SO_2Me, SOPh, SO_2Ph, $PO(OEt)_2$, 4-C_5H_4N

[a] Acidity data are in Me_2SO (ref. 6).

Table 8. Shielding contributions (p.p.m.) of substituents for C(1) in substituted ethylenes

Entry	Substituents	$^{13}C(1)$ shift	A_i	Ref.
1	H	122.80	0.00	*a*
2	Ph	135.80	13.00	*a*
3	$CONMe_2$	128.68	5.88	*b*
4	CO_2Me	129.00	6.20	*c*
5	COMe	137.70	14.90	*c*
6	COPh	132.10	9.30	*d*
7	CHO	138.60	15.80	*c*
9	NO_2	145.60	22.80	*c*
10	CN	108.20	−14.60	*c*
11	SOMe	142.54	19.74	*e*
12	SO_2Me	137.43	14.63	*e*
13	SOPh	145.49	22.69	*b*
14	SO_2Ph	140.26	17.46	*b*
16	$PO(OEt)_2$	126.75	3.95	*b*
19	2-C_5H_4N	136.62	13.82	*b*

[a] Ref. 22. [b] This work. [c] J. Schraml, *Collect. Czech. Chem. Commun.*, 1976, **41**, 3063 and references therein. [d] R. Visser and E. A. D. F. Dahmen, *Anal. Chim. Acta*, 1978, **100**, 271. [e] V. M. Bzhezovskii, G. A. Kalalin, B. A. Trofimov, G. G. Efremova, and N. K. Gusarova, *Izv. Akad. Nauk. SSSR., Ser. Khim.*, 1980, 1007.

Table 9. Experimental π electron densities from equation (1)[a]

X	q_p	$q_{p[221]}$	q_{CH}	$q_{CH[221]}$	q_{Ph}	$q_{Ph[221]}$	q_X	$q_{X[221]}$
Ph	1.126	1.127	1.428	1.428	6.264	6.270	0.308[b]	0.302
$CONMe_2$	1.085	1.086	1.447	1.453	6.135	6.147	0.418	0.400
CO_2Me	1.084		1.468		6.128		0.404	
COMe	1.064	1.070	1.381	1.380	6.110	6.120	0.509	0.500
COPh	1.055	1.062	1.346	1.353	6.091	6.107	0.563	0.540
NO_2	1.040	1.049	1.308	1.318	6.125	6.108	0.567	0.574
NO_2[c]	1.024		1.274		6.088		0.638	
CN	1.115	1.119	1.547	1.549	6.170	6.179	0.283	0.272
SOMe	1.118	1.128	1.527	1.517	6.192	6.213	0.281	0.270
SO_2Me	1.107		1.539		6.192		0.269	
SOPh	1.105		1.563		6.173		0.264	
SO_2Ph	1.101	1.104	1.555	1.558	6.163	6.177	0.282	0.265
$PO(OEt)_2$	1.111	1.117	1.581	1.619	6.163	6.171	0.256	0.210
2-C_5H_4N	1.098		1.410		6.179		0.411	
3-C_5H_4N[d]	1.112		1.440		6.221		0.340	
4-C_5H_4N[d]	1.087		1.407		6.185		0.408	

[a] q_p, q_{CH}, and q_{Ph} refer to the calculated π electron densities present in Me_2SO at the *para* and benzylic positions, and on the whole phenyl ring respectively: $q_{[221]}$ values were calculated using as input in equation (1) shifts obtained in the presence of the [2.2.1]cryptand. [b] Since X = Ph, q_{Ph} should be identical to 6 + q_X; this is not verified because of the discussed imprecision of equation (1) in providing the exact amount of charge delocalized by the phenyl group. A value of $q_X = (0.264 + 0.308):2 = 0.286$ is obtained on averaging q_X and 6-q_{Ph}. [c] In MeOH. [d] Approximate values were obtained using A_{Ph} for $A_{3\text{-}C_5H_4N}$ and $A_{4\text{-}C_5H_5N}$ in equation (1).

is also experienced by the carbanide carbon. Within the series, the nitronate anion (**VI-9**) and the enolate anion (**VI-6**) show the largest shifts: indeed these anions should be better regarded as oxyanions rather than carbanions. Some ion pairing occurs between the hard oxygen anion and the sodium cation in a way strictly analogous to that shown for β-ketoenolates.[16] When the [2.2.1]cryptand disrupts the co-ordination of the oxygen atom with sodium, some of the negative charge is no longer polarized on the oxygen atom by the coulombic interaction of the ion pair and is left therefore to delocalize more freely onto the carbon

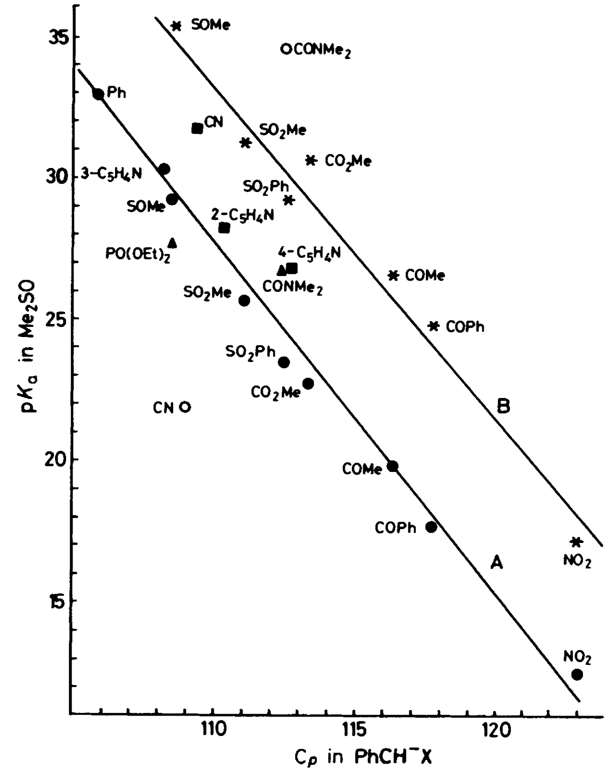
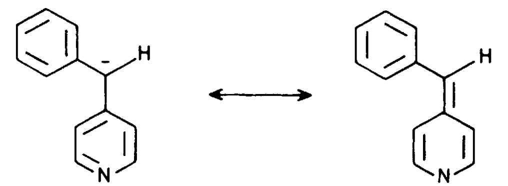


Figure 1. pK_a Values of PhCH$_2$X and CH$_3$X as a function of the $^{13}C_p$ shift of PhCH$^-$X. With reference to fitting parameters of Table 7, entry 1 pertains to points of line A designated as ●, entry 2 to points ● and ■, and entry 3 to points ●, ■, and ▲; for line B entry 8 pertains to points designated as ✱, and entry 9 to points ✱ and ■; for both lines points designated as ○ were not considered in the correlations

skeleton, originating upfield shifts of the carbanionic and *para*-carbons. The variation of the cryptand-induced shift is in qualitative accord with the amount of charge transferred from the carbanionic carbon to the substituent: thus the order is approximately $NO_2 > COPh > COMe > CONMe_2 > CO_2Me$. Within the series, the nitro group is undoubtedly the most powerfully electron withdrawing, since it removes almost $\frac{3}{5}$ of a unit charge from the carbanionic carbon, while the weakest group appears to be the methoxycarbonyl group, which removes only $\frac{2}{5}$ of a unit charge.

Ab initio calculations on methanenitronate anion predict[10a,b] a negative charge transfer in the gas phase from the carbanionic carbon to the nitro group of 0.5 π electron units. Although the analogous charge transfer is not available in Me$_2$SO solution because of the insolubility of sodium methanenitronate in this solvent, a figure of 0.8 electron units can be calculated using equation (1) from the spectrum in MeOH.[28] For the sodium phenylmethanenitronate (**VI-9**) it is possible to obtain the charge distribution, and hence the charge transfer both in Me$_2$SO and in MeOH. Although a small increase in the charge transfer is qualitatively evident on going from Me$_2$SO to MeOH, the difference is so small (0.56 *versus* 0.58 electron units, from Table 9) that is numerically within the limits of error of the method. It seems logical that such a small difference in charge transfer is valid not only for phenylmethanenitronate, but also for methanenitronate in Me$_2$SO and MeOH: then one would anticipate that in Me$_2$SO the charge transfer would be *ca.* 0.75—0.80 electron units, an amount appreciably different from that calculated in the gas phase (0.50 electron units); the difference of 0.25 electron units is well beyond the limits of error of the empirical estimate. It is concluded then that the charge transfer from the carbanionic carbon to the nitro group is greatly assisted by the solvent. The interaction of the polar electronegative nitro group with the dipolar Me$_2$SO solvent helps in dispersing the negative charge, spreading it over a larger cavity:[29] through hydrogen bonding, the protic MeOH solvent will further help the polarization of the negative charge onto the oxygen atoms of the nitro group.



(VI-21) (VI-21a)

The ^{13}C shifts of enolates (**VI-3**) and (**VI-6**) in Me$_2$SO and in the presence of the cryptand are very close and sometimes coincident with those in HMPT:[18] both of them are, however, considerably different from the shifts obtained in ethereal solvents, even in the presence of crown ethers or of variable amounts of HMPT.[19,30] The fact that the carbanionic carbon in all these other cases is present at lower field indicates some ion pairing of the cation with the oxygen atom of the enolates giving rise to an interaction which is not fully disrupted by the ethereal oxygens or by the complexant. The recently described[31] ^{13}C n.m.r. parameters of the anion of ethyl phenylacetate, different from ours, appear due to incomplete carbanion formation.

One-bond couplings $^1J_{CH}$ of the carbanionic carbon strongly support a trigonal configuration at this site for the solvent-separated or free ions, a conclusion in accord with proton results obtained for tighter ion pairs.[32,33]

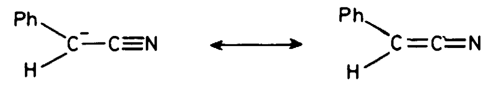
(c) *Phenyl- and pyridyl-methyl Carbanions.* No appreciable variations are observed on the addition of the cryptand to 1,3-diphenylallyl (**VI-22**), diphenylmethyl (**VI-2**), and phenyl-(4-pyridyl)methyl (**VI-21**) anions. These species therefore are not associated with the sodium counterion in Me$_2$SO and should be considered as solvent-separated or free ions. This is in accord with Hogen-Esch and Smid's results from u.v. and visible spectroscopy for fluoradenide[15e] and fluorenide anions,[15a–c] O'Brien's n.m.r.[34,35a,b] and Buncel's u.v.[35c,d] results for diphenylmethyl carbanions, and Edlund's[36] and Grutzner's[37] results for indenyl anions. A small, but significant lowfield shift (0.1 p.p.m.) is found for H$_\alpha$ of the lithium salt of diphenylmethyl carbanion (**VI-2**). It is possible that, although almost complete, dissociation of the lithium salt is partially hampered by the comparatively stronger interaction of the carbanion with this small and unpolarizable cation.

The presence of five different carbon resonances for the pyridine moiety of phenyl-(4-pyridyl)methyl carbanion (**VI-21**) is clear evidence for slow rotation at room temperature of the pyridine ring along the $C_{4'}$–C_α bond,* thus supporting a substantial contribution of the canonical structure (**VI-21a**).

(d) *Phenylacetonitrile anion.* The ^1H n.m.r. data for this species previously reported by Das and Wilkie[38] are not in accord with ours and appear to be due to the un-ionized substrate. α-Cyanocarbanions [*e.g.* (**VI-10a**)] are commonly believed to be stabilized by charge transfer to the nitrogen atom: the importance of the resonance contributor (**VI-10b**) has

---

* δ(C-2′,-6′) = 146, 149 p.p.m.; δ(C-3′,-5′) = 107, 113 p.p.m.; details concerning the assignment of carbon resonances of the pyridine ring will be reported elsewhere.



(VI-10a) (VI-10b)

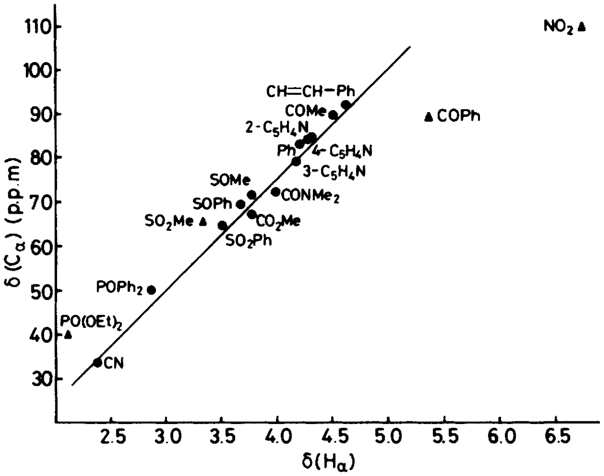


Figure 2. The $^{13}C_{\alpha}$ chemical shift as a function of $^{1}H_{\alpha}$ chemical shift in $PhCH^{-}$ X. With reference to fitting parameters of Table 5, entry 8 pertains to points designed as ●, entry 7 to points designed ● and ▲

further gained credence from Cram's proposal of a conducted tour mechanism.[39] Such a belief is put forward even in textbooks.[40] Our own results, based on ion-pairing phenomena and on charge maps, indicate that there is a very limited charge transfer from carbon to nitrogen: the contribution of the keteneimine structure (**VI-10b**) to the phenylacetonitrile anion appears to be minor.

(i) The cyanocarbanion shows very small upfield shifts upon decomplexation with the [2.2.1]cryptand. If indeed the canonical formula (**VI-10b**) did contribute substantially, one would expect that the hard, negatively charged nitrogen atom of the keteneimine structure should co-ordinate strongly with the sodium counterion: keteneimine nitroanions would also be expected to exhibit strong hydrogen-bonding phenomena with protic solvents. Neither case is confirmed by experiment. It can be shown,[41] in fact, that the chemical shifts of malonitrile anion salt are constant in MeOH and in Me_2SO; pK_a values of malononitrile in H_2O[42] and in Me_2SO[6c] are nearly identical.

(ii) Charge maps of Table 9 indicate a high π charge density at the benzylic carbon. This result may appear surprising: however, if it is recalled that the shifts of the benzylic carbon and proton in (**VI-10**) nicely fit the line of Figure 2, and that the cyano group in acrylonitrile induces, relative to unsubstituted ethylene, downfield shifts of *all* protons,[43] then the upfield shift of the benzylic proton in (**VI-10**), and thus that of the corresponding ^{13}C, cannot be due to any special effect of the cyano functionality or to any special bonding situation at this site, but must be due unequivocally to an excess of π negative charge.

In *N*-substituted keteneimines the high-field shift of the sp^2 carbon,[44] analogous to that of allenes,[44,45] ketenes,[45,46] and diazoalkanes,[47] has been ascribed[48] to partial charge transfer from nitrogen to carbon; this consideration on neutral molecules enforces the idea that in anion (**VI-10**) the negative charge on the benzylic carbon does not delocalize extensively on the nitrogen atom.

The conclusion that the negative charge in phenylacetonitrile anion resides predominantly on the benzylic carbon and is only partly transferred to the nitrile nitrogen does not suggest by any means that the carbanionic carbon does not 'conjugate' with the adjacent nitrile *sp* carbon,[49] as the absence of mesomerism between limit valence-bond structures (**VI-10a**) and (**VI-10b**) would imply. This ambiguity originates because of the limitations inherent in the valence-bond representation which necessarily, but equivocally, associates conjugation with charge transfer (**VI-10a**)⟷(**VI-10b**). The overall picture of cyanocarbanions we give is in accord with ideas and results of other workers. (i) Long[50] has concluded from protonation-rate studies that cyanocarbanions show negligible structural reorganization relative to other carbanions. (ii) In contrast with carbonyl-stabilized carbanions, cyanocarbanions show high selectivity for carbon relative to nitrogen toward electrophiles.[1b,51] (iii) Hopkinson's theoretical study[10a,b] supports strong conjugation of the planar carbanionic carbon with the adjacent cyano group in acetonitrile anion, but a very limited charge transfer from carbon to nitrogen (0.12 electron units).

Finally, the increase of $^{1}J_{CH}$ in carbanion (**VI-10**) relative to the precursor (**I-10**) is the smallest observed for the whole series of carbanions (**VI**): its actual size is considerably smaller than that of ethylene (^{1}J 156 Hz), of C(1) of acrylonitrile (^{1}J 179 Hz), or that of allenes (^{1}J 165 Hz). Although excess of π negative charge tends to decrease the size of $^{1}J_{CH}$ in trigonal carbon atoms,[27] we interpret this result as a circumstantial indication of incomplete $sp^3 \longrightarrow sp^2$ rehybridization: this may find support in the relatively small energy difference (6 kcal mol^{-1}) computed to separate trigonal and pyramidal acetonitrile anion. Absence of a strong preference for the trigonal *versus* the pyramidal configuration in α-cyanocarbanions is also the result of a limited basis set computation.[52]

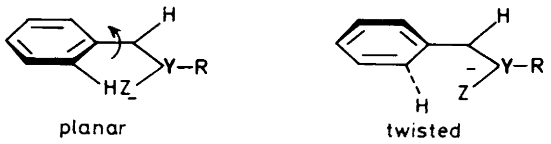
(e) *Sulphonyl-, sulphinyl-, and phosphonyl-stabilized benzyl anions.* Sulphonyl carbanions have been studied in great detail by more than one research group:[53,54] addition of the [2.2.1]-cryptand to the Me_2SO solution induces only negligible upfield shifts both at C_{α} and C_p. This is evidence for the slight tendency of these anions to ion pair with the sodium countercation in this solvent: appreciable shifts are observed though in solvents of lower ionizing and co-ordinating capacities. The absence of any involvement of sulphonyl oxygens in co-ordinative processes is in line with the absence of hydrogen-bonding phenomena as evidenced by the invariance of ^{13}C shifts in non-hydrogen-bond donor and hydrogen-bond donor solvents of disulphonylmethane anions[41] and of the pK_a values of the neutral precursor C–H acids.[6c,55] The high negative charge density residing on carbon disfavours the hypothesis of a large structural reorganization in the anion: this is in accord with Bell's[56] conclusions derived from reprotonation rates of sulphonyl carbanions.

The presence of the [2.2.1]cryptand induces a downfield shift on ^{-}CH but an upfield shift of the *para*-carbon both for sulphinyl- and phosphonyl-stabilized carbanions. This has been interpreted[53,57–59] as evidence for co-ordination of the sulphinyl or phosphonyl oxygen with the countercation. In all cases the $^{1}J_{CH}$ is unequivocally in favour of extensive trigonalization of the carbanion, as noted by others.[53,57]

It is evident from the charge maps of Table 9 that in all these sulphonyl-, sulphinyl-, and phosphonyl-stabilized carbanions the negative charge is reluctant to delocalize other than onto the adjacent phenyl ring: such a high π negative charge density is retained on the carbanionic carbon because of effects that are different from purely polar–inductive–electrostatic which might be thought to intervene between the negatively charged carbon and the (partially) positive sulphur or phosphorus atoms. In fact, the polar–inductive σ_{IB} constant is high for the sulphonyl group [$(\sigma_{IB})_{SO_2Me}$ 0.59 and $(\sigma_{IB})_{SO_2Ph}$ 0.62], considerably more modest for SOPh (σ_{IB} 0.46), but unquestionably not relevant for the PO(OEt)$_2$ group (σ_{IB} 0.19). In contrast, the amount of negative charge on the α carbon is PO(OEt)$_2$ > SOPh > SO$_2$Ph. Furthermore, if the high π electron density on the carbanionic carbons of anions **(VI-11)**—**(VI-17)** were stabilized exclusively by coloumbic attractive forces with the adjacent positively charged site, one would expect that stabilities of anions **(VI-11)**—**(VI-17)** should be similar to that of the nitrogen ylide PhCH$^-$-N$^+$Me$_3$ arising by deprotonation of a benzyltrimethylammonium halide **(I-33)**. Since we find that this salt is not deprotonated by a two-fold excess of sodium dimsyl in Me$_2$SO, the pK_α of this carbon acid must be placed around or above 35. This is a clear indication that sulphonyl, sulphinyl, and phosphonyl carbanions are stabilized by some sort of bonding between the carbanionic carbon and the heteroatom. In a recent re-examination of the question of *p–d* π conjugation, Wolfe and his co-workers concluded[10d,g] that incorporation of *d* orbitals in the computations was necessary to obtain realistic carbon–sulphur bond lengths and structures compatible with experiment: our results suggest that the largest stabilization is achieved when the carbanionic carbon has available a great deal of π electron density to enter into localized π bonding with the appropriate vacant orbital of the adjacent third-row element.

Structure–Acidity Relationships.—The linear relationship of Figure 1 indicates that the variation of free energy changes associated with the deprotonation of carbon acids **(I)** is dominated by the same factors that govern the transfer and delocalization of charge in carbanions **(VI)**. The importance and generality of the relationship of Figure 1 is illustrated by the fact that it holds for substituents (*e.g.* SO$_2$R, SOR) whose effects are not accounted for by any of the sets of empirical constants σ_{c^-} and $\sigma_{IB}, \sigma_{R^-}$.[60] The only seriously deviant point is for the cyano group: phenylacetonitrile **(I-10)** is far more acidic than would be predicted both from the shift of any of the *para*-monitors ^{1}H, ^{13}C, and ^{19}F in the conjugate carbanion **(VI-10)** and from the very precise linear relationship of unit slope of acidities of substituted toluenes **(I)** and substituted methanes **(VIII)** (Table 7, entry 4).

On one side the high-field resonance of the *para*-monitor in phenylacetonitrile anion **(VI-10)** is indicative of high negative charge density on that carbon, suggesting that the cyano group is a rather modest electron-withdrawing function; in contrast with this, the CN group in phenylacetonitrile acidifies the adjacent methylene more than a methoxycarbonyl group and almost as much as an acetyl group, in accord with a strongly electron-withdrawing nature. The discrepancy is accommodated if it is accepted that the larger transfer of negative charge from the carbanionic carbon to the *para*-position is evidence for extended planarity of this carbanion, in contrast with all the other benzyl anions **(VI)** which would present some twisting of the phenyl ring. This distortion, necessary in benzyl anions **(VI)** to relieve the non-bonding interactions of the *ortho* hydrogens with atoms or groups α to the carbanionic carbon, is unnecessary with the cylindrical cyano group because of its very modest steric requirements. It is clear that under these circumstances the negative charge transfer from the carbanionic carbon to the phenyl ring is somewhat hampered in all benzyl anions **(VI)**, except phenylacetonitrile anion: as a result, the intrinsic stabilization of all the benzyl carbanions will be weaker relative to the case of full conjugation, as in phenylacetonitrile anion, and will be associated with a generalized lower acidity of the precursors. Phenylacetonitrile anion is unique in the series of benzyl anions **(VI)**, showing greater charge transfer to the phenyl group (*para* monitor upfield), and thanks to this, greater stability, and hence greater acidity of the precursor. Strong support for the evidence that our results provide for the twisting of the phenyl ring in a α-substituted benzyl anions **(VI)** is offered by a survey of the crystal structures of a number of 1,1-disubstituted 2-phenylethylenes. The phenyl ring appears coplanar or nearly so whenever the substituent *cis* to it on the olefinic double bond is a cyano group:[61] in contrast, a variety of other groups *cis* to the phenyl induce a sizeable twisting of the phenyl ring.[62]



(VI-3) Y = C, Z = O, R = NMe$_2$
(VI-4) Y = C, Z = O, R = OMe
(VI-5) Y = C, Z = O, R = Me
(VI-6) Y = C, Z = O, R = Ph
(VI-10) Y = N, Z = R = O

The twisting of the phenyl group is also important for interpreting why the empirically calculated amount of negative charge residing on the benzylic carbon of diphenylmethyl carbanion **(VI-2)** is substantially greater (0.42 π electron units) than that predicted by LCAO calculations (0.32 π electron units).[2] Indeed in 1,1-diphenylethene,[63] in the crystal state, the two phenyl rings are twisted of 37 and 50°, respectively. If delocalization of the negative charge into the benzene rings is prevented to some extent in **(VI-2)**, then the π charge density on the carbanionic carbon will be higher than predicted for a planar arrangement. The results in solution contrast with the model assumed by theory: we already discussed[12] the analogous discrepancy found for the triphenylcarbenium ion.

α-Substituted toluenes PhCH$_2$X **(I)** and *p*-substituted toluenes *p*-XC$_6$H$_4$CH$_3$ are respectively iso-Hammett and Hammett phenyl homologues of methane carbon acids CH$_3$X.[14] The linear relationship of Figure 1 linking C_p of carbanions **(VI)** and the pK_a values of α-substituted toluenes **(I)** is clear evidence for the success of the phenylogy principle[14b] for these substrates as well as for the oxygen acids XOH and its homologues *p*-XC$_6$H$_4$OH and PhOX **(III)**. The acidity correlations in Table 7 further demonstrate that the fall-off factor between parent methane carbon acids CH$_3$X and their phenyl homologues *p*-substituted toluenes is close to unity, and is therefore considerably different from the fall-off factor of 6 obtained for oxygen acids and *p*-substituted phenols.

Acidities of Carbon Acids, Carbanion Electron Density (q_{CH}), *and Substituent Electron Demands* (q_X).—Two different lines are necessary to fit the plot of acidities of carbon acids **(I)** *versus* the electron demand q_X (lines A and B of Figure 3). They are evidence for the existence of two different mechanisms that provide stabilization to the conjugate carbanions and reflect the different situations between the carbanionic carbon and the adjacent group X. For carbon acids fitting line A, stabilization of carbanions is primarily provided by extensive charge delocalization on the adjacent π system (C=C, C=O, aryl, *etc.*) For carbon acids fitting line B, stabilization of the carbanion must be associated with a strong π interaction of the carbanion with the adjacent C≡N and the third-row element functionalities, with limited charge transfer: in the light of the foregoing discussion, this stabilization is not primarily provided by inductive mechanisms but instead by the strength of the localized π bonding which requires in all cases a high negative charge density to reside on the carbanionic carbon. As expected, the goodness of the fit for line A is only modest because acidities of carbon acids **(I)** are not dominated exclusively by the mesomeric electron withdrawal of groups X:

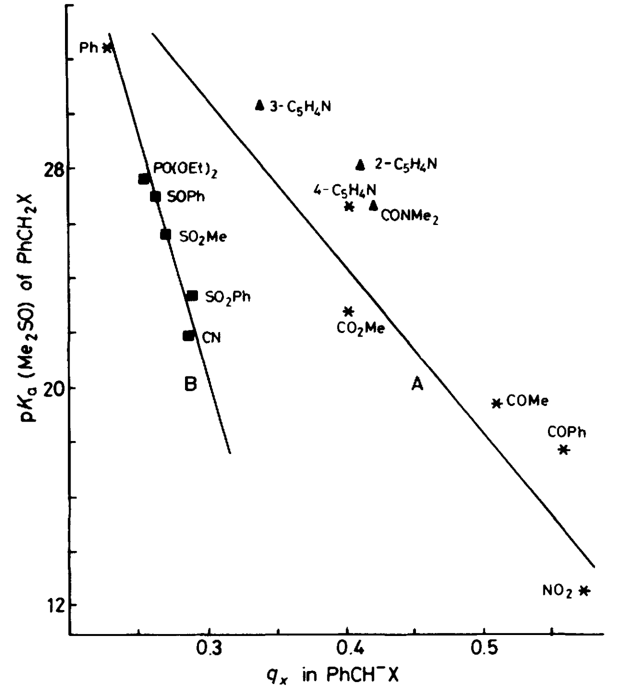


Figure 3. pK_a Values of $PhCH_2X$ as a function of q_X. Fittings of the lines are reported in Table 7

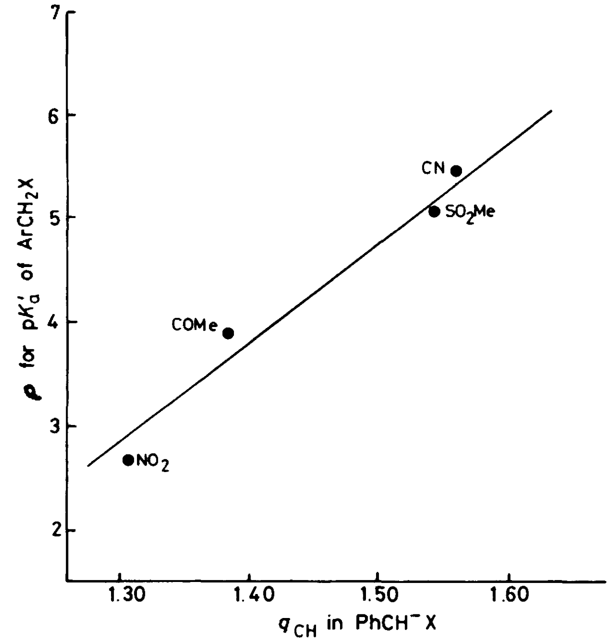


Figure 4. The sensitivity ρ of Me_2SO acidities of $ArCH_2X$ to substituents on the aryl ring as a function of q_{CH} in $PhCH^-X$

since however this mechanism is approximately three times as important as polar-inductive mechanisms,[60] the plot is almost linear.

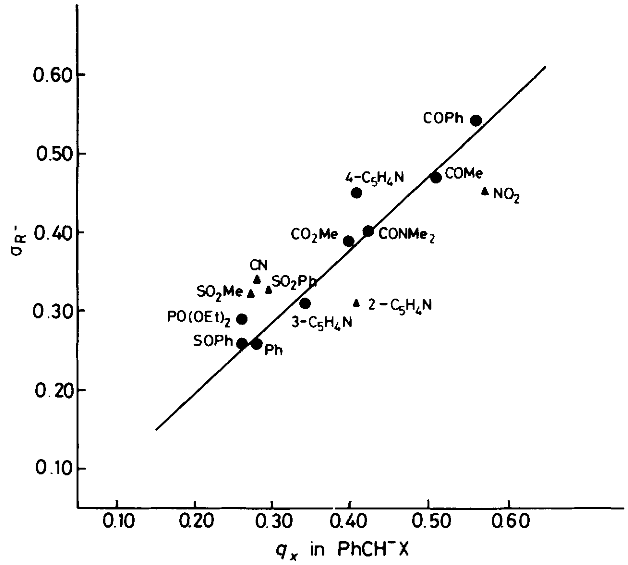


Figure 5. The σ_{R^-} values as a function of q_X in $PhCH^-X$. With reference to the fitting parameters of Table 7 entry 14 pertains to points designated as ●, entry 15 to points ● and ▲

Our prediction[14a] that the high sensitivity to aryl substituents of the benzylic proton of $ArCH^-Ph$, $ArCH^-CN$, $ArCH^-SO_2Me$, $ArCH^-SO_2Ph$ was due to a high electron density at the carbanionic carbon is now nicely fulfilled by the electron density maps of Table 9. Furthermore, we can now correlate quantitatively the π electron density at the carbanionic carbon of (VI), q_{CH}, with Bordwell's acidity sensitivities[6f] of $ArCH_2X$ to aryl substituents. The significance of the linear plot (Figure 4) is clear: an increasingly greater electron density on the carbanionic carbon corresponds to an increasingly more intense and favourable interaction of this centre with the aryl ring. As a consequence, substituents thereon will have a greater influence.

Benzyl carbanions (VI) are a special case of disubstituted carbanions in which the two substituents, the phenyl ring, and the functionality X, compete in delocalizing the negative charge from the carbanionic carbon. The electron demand of groups X, the q_X values obtained for such systems, therefore, is not a fixed, invariable quantity but is a relative measure of the ability of the various groups X to delocalize the negative charge. They are expected therefore to be linearly related to the corresponding σ_{R^-} values anchored to the mesomeric interaction of the contiguous functionalities X and NH in PhNHX (IV).[14] The above expectation is nicely fulfilled for Ph, PhSO, 3-pyridyl, CO_2Me, $CONMe_2$, COMe, and COPh substituents (Figure 5), but points for the 2-pyridyl and NO_2 substituents fall below the line, and the CN and SO_2Me groups fall above.

Finally, increasingly larger transfers of charge from the carbanionic carbon to the group X should leave increasingly smaller electron densities on the phenyl group in carbanions (VI). Due to the approximations already discussed[12] in evaluating the π charge delocalized by the phenyl ring, the electron density at the *para* position q_p can be used as a significant alternative. The above expectation is also experimentally fulfilled as shown in Figure 6 where q_p is plotted against q_X.

Conclusions

^1H and ^{13}C n.m.r. data for benzyl carbanions (VI), obtained in Me_2SO solution, allow a unified treatment of the substituent-induced structural reorganizations in the anions and pK_a variations in Me_2SO.

A detailed examination of the n.m.r. parameters allows an

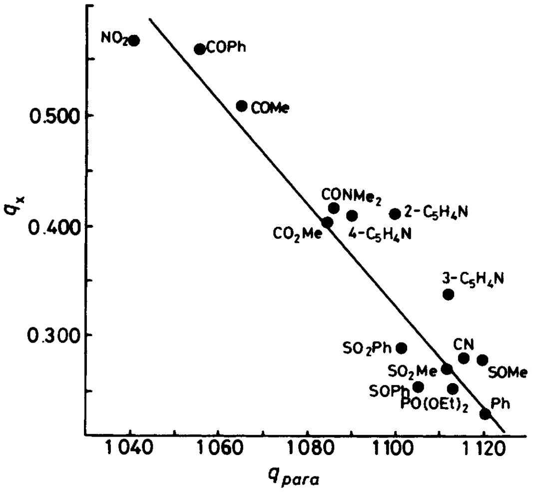


Figure 6. The q_{para} values as a function of q_X in $PhCH^-X$. Fitting parameters are in Table 7

Table 10. Analytical data for the *p*-fluorophenyl-tagged carbon acids (**I**)

Compound	Yield (%)	Solvent	M.p. (°C) [B.p. (mmHg)]	Found(%) (Required)	
p-$FC_6H_4CH_2CO_2Me$	80		[100 (0.5)]	64.4 (64.7)	5.2 (5.4)
p-$FC_6H_4CH_2SOCH_3$	60	Light petroleum	68	56.1 (55.8)	5.1 (5.3)
p-$FC_6H_4CH_2SPh$	73	MeOH–H_2O	44	71.7 (71.5)	5.0 (5.1)
p-$FC_6H_4CH_2SOPh$	81	EtOH	142—143	66.4 (66.6)	4.7 (4.7)
p-$FC_6H_4CH_2SO_2Ph$	85	EtOH	160—161	62.7 (62.4)	4.3 (4.4)
p-$FC_6H_4CH_2PO(OC_2H_5)_2$	60		[135—140 (2.5)]	53.5 (53.7)	6.6 (6.5)
p-$FC_6H_4CH_2POPh_2$	88	EtOH	208—210	73.3 (73.5)	5.2 (5.2)

experimental mapping of the charge densities in the anions and a structural description of these species in solution: it is found that the solvent greatly assists charge delocalization.

Stabilized carbanions fall into two different classes: one in which the formation of the *p*–π bond allows an extensive transfer of the negative charge from the carbanionic carbon to the substituents, the other in which it is evident that most of the negative charge is confined to the carbanionic carbon. This supports the idea of π-bonding (as in the case of cyano-stabilized carbanions) and of *p*–*d* π bonding, whose stability is not primarily associated with delocalization. Mesomeric effects exerted by activating groups are therefore described in terms of substituent electron demands: these experimental quantities are shown to govern in a related way not only the bonding situation and the charge distribution in the anions but also the acidity of the precursor acids $PhCH_2X$ and their sensitivity to remote aryl substitution. The violation of the reactivity–selectivity principle found for different families of activated arylmethyl carbon acids $ArCH_2X$ [14a] is thus accounted for by structural considerations.

Experimental

Numbering of Substrates.—For the sake of clarity and conciseness compounds with a variable substituent X are identified by a roman and arabic number, the former characterizing the 'family' to which the compound belongs, the latter the substituent X; substituents which have been considered so far are listed in Table 1 of ref. 14*c* and their number is retained throughout this and future papers. The sequence of families for which results have already been obtained but which are still unpublished or only in preliminary communications, is the following: PhN^-X (**VII**);[11,64a,b] NH_2X (**XI**), NH^-X;[64a,b] Ph_2C^-X;[64c] Ph_2NX;[64d,e] $2,6$-$Me_2C_6H_3NHX$, $2,6$-$Me_2C_6H_3N(Me)X$, and $2,6$-$Me_2C_6H_3N^-X$.[64e]

Materials.—Diphenylmethane, methyl phenylacetate, phenylacetone, deoxybenzoin, phenylacetonitrile, diethyl benzylphosphonate, 2-benzylpyridine, and 4-benzylpyridine, were commercial products (Fluka or Ega Chemie). *NN*-dimethylphenylacetamide,[65] *p*-fluorobenzyl methyl ketone,[66] *p*-fluorobenzyl phenyl ketone,[67] phenylnitromethane,[68] *p*-fluorophenylacetonitrile,[66] benzyl methyl sulphoxide,[69] benzyl methyl sulphone,[70] benzyl phenyl sulphoxide,[71] benzyl phenyl sulphone,[71] benzyldiphenylphosphine oxide,[72] 3-benzylpyridine,[73] and 1,3-diphenylpropene [74] were prepared according to known procedures. Physical and analytical data of the *p*-fluorophenyl-tagged carbon acids (**I**) are reported in Table 10: *p*-fluorobenzyl chloride (Fluka) was the commercially available precursor material for their preparation. Methyl *p*-fluorophenylacetate was obtained from methanol and *p*-fluorophenylacetyl chloride, in turn prepared *via* the corresponding nitrile and acid.[66] *p*-Fluorobenzyl methyl sulphoxide and *p*-fluorobenzyl phenyl sulphoxide were obtained by $NaIO_4$ oxidation of the corresponding *p*-fluorobenzyl methyl sulphide (obtained in a crude state) and *p*-fluorobenzyl phenyl sulphide, according to a reported general procedure.[75] *p*-Fluorobenzyl phenyl sulphone was obtained by oxidation [76] of the corresponding sulphide. Diethyl *p*-fluorobenzylphosphonate and *p*-fluorobenzyldiphenylphosphine oxide were obtained similarly to their *p*-H analogues.

N.m.r. Measurements.—The preparation of the dimsyl solution for n.m.r. experiments and the preparation of the sodium salts of the anions in the n.m.r. tubes has been described previously;[12] an analogous procedure was used to prepare the lithium and potassium salts starting from lithium and potassium hydride to obtain the corresponding dimsyl solutions. The general procedure already described was also followed for the preparation of the carbanions, the cations of which are complexed with the [2.2.1]cryptand: weighed amounts of the starting carbon acid and of the [2.2.1]cryptand were placed in the n.m.r. tube and the required amount of the dimsyl solution of known titre was added. ^1H And ^{19}F spectra of the anions were recorded on an HA-94-100D Varian spectrometer using 0.1M sample solutions (5 mm o.d. tubes). ^1H Shifts were measured relative to 3-(trimethylsilyl)propanesulphonic acid sodium salt (TPS) as internal reference and then converted relative to TMS using the relationship: $\delta_{TPS} - \delta_{TMS} = 0.009$ p.p.m.: the Me_2SO solvent provided the internal proton lock. ^{19}F Shifts were measured relative to trifluoroacetic acid (neat) as external standard and then converted into shifts relative to hexafluorobenzene using the relationship: $\delta_{C_6F_6} = \delta_{CF_3CO_2H} + 84.4$ p.p.m.. ^{13}C Spectra were obtained either on an XL-100-15 or an XL-100-12 WG Varian instruments operating at 25.18 MHz and using 0.33M sample solutions (12 mm o.d. tubes). An external lock was used on the XL-100-15 instrument; the deuterium lock required by the XL-100 WH instrument was provided by neat $[^2H_6]Me_2SO$ contained in an internal 5 mm tube coaxial with the 12 mm tube containing the solution of the anion. ^{13}C Shifts were measured relative to TPS as internal reference and then converted into shifts relative to TMS using the relationship $\delta_{TPS} - \delta_{TMS} = 1.63$ p.p.m. TPS was unstable in dimsyl solutions containing the [2.2.1]cryptand when a two-fold excess of base was used: in these cases ^{13}C shifts were measured relative to the peak of Me_2SO of the dimsyl solution and then converted into shifts relative to TPS using the shift of Me_2SO in the dimsyl solution relative to TPS, which was found to be constant through the whole series of anions. ^{13}C Spectra were obtained with 16 K data points collected over a spectral width of 5 000 Hz, resulting in a resolution of 0.025 p.p.m. The reproducibility of the ^{13}C shifts obtained with external and internal deuterium lock was evaluated by comparing a few spectra obtained with the two instruments and was found to be in the order of 0.05 p.p.m. Assignments of aromatic carbons are based on proton coupled spectra.

Acknowledgements

We are indebted to Professor F. G. Bordwell, Northwestern University, Evanston, for making available results prior to publication and for helpful discussions.

References

1 (*a*) D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1966; (*b*) J. C. Stowell, 'Carbanions in Organic Synthesis,' Wiley, New York, 1979.

2 'Comprehensive Carbanion Chemistry,' eds. E. Buncel and T. Durst, Elsevier, New York, 1980, vols. 1 and 2.

3 G. Scorrano and V. Lucchini, *J. Org. Chem.*, 1979, **44**, 1726.

4 A. Streitweiser, Jr, E. Juaristi, and L. L. Nebenzahl, ref. 2, vol. 1, ch. 7.

5 C. D. Ritchie in 'Solute-Solvent Interactions,' eds. J. R. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969.

6 (*a*) F. G. Bordwell, J. E. Bartmess, J. E. Drucker, Z. Margolin, and W. S. Matthews, *J. Am. Chem. Soc.*, 1975, **97**, 3226; (*b*) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *ibid.*, p. 7006; (*c*) F. G. Bordwell, *Pure Appl. Chem.*, 1977, **49**, 963; (*d*) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, 1977, **42**, 321; (*e*) F. G. Bordwell, D. Algrim, and N. R. Vanier, *ibid.*, p. 1817; (*f*) D. Algrim, J. E. Bares, J. C. Branca, and F. G. Bordwell, *ibid.*, 1978, **43**, 5024; (*g*) F. G. Bordwell, J. C. Branca, C. R. Johnson, and N. R. Vanier, *ibid.*, 1980, **45**, 3884; (*h*) F. G. Bordwell, G. E. Drucker, and H. E. Fried, *ibid.*, 1981, **46**, 632; (*i*) F. G. Bordwell and H. E. Fried, *ibid.*, p. 4327.

7 B. Juan, J. Schwarz, and R. Breslow, *J. Am. Chem. Soc.*, 1980, **102**, 5741 and references therein.

8 (*a*) E. M. Arnett, D. E. Johnston, and L. E. Small, *J. Am. Chem. Soc.*, 1975, **97**, 5598; (*b*) J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *ibid.*, 1979, **101**, 6046; (*c*) *ibid.*, p. 6056; (*d*) J. Bromilow, J. L. M. Abboud, C. B. Lebrilla, R. W. Taft, G. Scorrano, and V. Lucchini, *ibid.*, 1981, **103**, 5448.

9 (*a*) M. J. Pellerite and J. I. Brauman in ref. 2. vol. 1, ch. 2; J. B. Cumming and P. Kebarle, *J. Am. Chem. Soc.*, (*b*) 1977, **99**, 5818; (*c*) 1978, **100**, 1835.

10 (*a*) A. C. Hopkinson, M. H. Lien, K. Yates, P. G. Mezey, and I. G. Csizmadia, *J. Chem. Phys.*, 1977, **67**, 517; (*b*) A. C. Hopkinson and M. H. Lien, *Int. J. Quantum Chem.*, 1980, **18**, 1371; (*c*) P. G. Mezey, A. J. Kresge, and I. G. Csizmadia, *Can. J. Chem.*, 1976, **54**, 2526; (*d*) S. Wolfe, H. B. Schlegel, I. G. Csizmadia, and F. Bernardi, *ibid.*, 1975, **53**, 3365; (*e*) A. Pross and L. Radom, *Tetrahedron*, 1980, **36**, 673; (*f*) A. Pross, D. J. De Frees, B. A. Levi, S. K. Pollack, L. Radom, and W. J. Here, *J. Org. Chem.*, 1981, **46**, 1693; (*g*) S. Wolfe, A. Stolow, and L. A. LaJohn, *Tetrahedron Lett.*, 1983, **24**, 4071.

11 Preliminary communication, S. Bradamante, F. Gianni, and G. A. Pagani, *J. Chem. Soc., Chem. Commun.*, 1976, 478.

12 S. Bradamante and C. A. Pagani, *J. Org. Chem.*, 1984, **49**, 2863.

13 (*a*) L. Greifenstein and G. A. Pagani, *J. Org. Chem.*, 1981, **46**, 3336; (*b*) S. Bradamante, A. Marchesini, and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2*, 1973, 568; S. Bradamante, A. Mangia, and G. A. Pagani, (*c*) *J. Chem. Soc. B*, 1971, 545; (*d*) *Tetrahedron Lett.*, 1970, 3381.

14 S. Bradamante and G. A. Pagani, *J. Org. Chem.*, 1979, **44**, (*a*) 4735; (*b*) p. 4737; (*c*) 1980, **45**, 105; (*d*) p. 114; (*e*) S. Bradamante, S. Colombo, G. A. Pagani, and S. Roelens, *Gazz. Chim. Ital.*, 1981, **111**, 357.

15 T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, (*a*) 1965, **87**, 669; (*b*) 1966, **88**, 307; (*c*) 1967, **89**, 2764; (*d*) H. J. Parker, *Q. Rep. Sulfur Chem.*, 1968, **3**, 185; (*e*) T. E. Hogen-Esch, *J. Am. Chem. Soc.*, 1973, **95**, 639.

16 (*a*) V. M. De Palma and E. M. Arnett, *J. Am. Chem. Soc.*, 1978, **100**, 3514 and references therein; (*b*) M. Raban and D. P. Haritos, *ibid.*, 1979, **101**, 5178 and references therein; (*c*) C. Cambillau, G. Bram, J. Corset, C. Riche, and C. Pascard Billy, *Tetrahedron*, 1978, **34**, 2675; (*d*) C. Cambillau, O. Bram, J. Corset, and C. Riche, *Nouv. J. Chim.*, 1979, **3**, 9; (*e*) P. Szczecinski, *Roczniki Chem.*, 1977, **51**, 2029; (*f*) G. Illuminati, L. Mandolini, and B. Masci, *J. Am. Chem. Soc.*, 1983, **105**, 555.

17 A. A. Bothner-By and S. Castellano, 'Computer Programs for Chemistry,' ed. D. F. De Tar, Benjamin, New York, 1968, p. 10.

18 H.-H. Vogt and R. Gompper, *Chem. Ber.*, 1981, **114**, 2884.

19 H. O. House, A. U. Prabhu, and W. V. Phillips, *J. Org. Chem.*, 1976, **41**, 1209.

20 J. B. Lambert and S. M. Wharry, *J. Am. Chem. Soc.*, 1982, **104**, 5857.

21 F. W. Wherli and T. Wirthlin, 'Interpretation of Carbon-13 NMR Spectra,' Heyden, London, 1976, p. 42.

22 J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, 1972, ch. 4.

23 (*a*) D. G. Farnum, *Adv. Phys. Org. Chem.*, 1975, **11**, 123; (*b*) G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magn. Reson.*, 1975, **7**, 2; (*c*) T. M. Tribble and J. G. Traynham, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 4; (*d*) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731; (*e*) B. P. Dailey, *ibid.*, 1964, **41**, 2796; (*f*) G. E. Maciel and J. J. Natterstad, *ibid.*, p. 2427; (*g*) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, 1972, **94**, 3098.

24 (*a*) M. Bauendi and J. B. Grutzner, Communication 192, 185th ACS Meeting, Seattle, 1983; (*b*) N. R. Nowicki and J. B. Grutzner, Communication 193, 185th ACS Meeting, Seattle, 1983.

25 (*a*) H. Baumann and H. Olsen, *Helv. Chim. Acta*, 1980, **63**, 2202; (*b*) M. Witanowski, L. Stefaniak, W. Sicinska, and G. A. Webb, *J. Mol. Struct.*, 1980, **64**, 15.

26 (*a*) L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 1969, 2nd edn., p. 345; (*b*) V. S. Gil and C. F. G. C. Geraldes in 'NMR Spectroscopy of Nuclei other than Protons,' eds. T. Axenrod and C. A. Webb, Wiley-Interscience, New York, 1974, p. 219.

27 H. McNab, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1287.

28 R. W. Bowman, B. T. Golding, and W. P. Watson, *J. Chem. Soc., Perkin Trans. 2*, 1980, 731.

29 Ref. 4*b*, p. 232.

30 (*a*) H. O. House, R. A. Auerbach, M. Gall, and N. P. Peet, *J. Org. Chem.*, 1973, **38**, 514; (*b*) L. M. Jackman and B. C. Lange, *Tetrahedron*, 1977, **33**, 2737.

31 S.-I. Kiyooka and K. Suzuki, *Bull. Soc. Chem. Jpn.*, 1981, **54**, 623.

32 M. W. Rathke and A. Lindert, *J. Am. Chem. Soc.*, 1971, **93**, 2318.

33 R. P. Woodbury and M. W. Rathke, *J. Org. Chem.*, 1977, **42**, 1688.

34 (*a*) D. H. O'Brien, A. J. Hart, and C. R. Russell, *J. Am. Chem. Soc.*, 1975, **97**, 4410; (*b*) K. Takahashi, Y. Kondo, R. Asami, and Y. Inane, *Org. Magn. Reson.*, 1974, **6**, 580.

35 D. H. O'Brien, C. R. Russell, and A. J. Hart, (*a*) *J. Am. Chem. Soc.*, 1976, **98**, 7427; (*b*) 1979, **101**, 633; E. Buncel and B. Menon, (*c*) *J. Chem. Soc., Chem. Commun.*, 1978, 758; (*d*) *J. Org. Chem.*, 1979, **44**, 317.

36 U. Edlund, *Org. Magn. Reson.*, (*a*) 1977, **9**, 593; (*b*) 1979, **12**, 661.

37 J. B. Grutzner, J. M. Lanlor, and L. M. Jackman, *J. Am. Chem. Soc.*, 1972, **94**, 2306.

38 R. Das and C. A. Wilkie, *J. Am. Chem. Soc.*, 1972, **94**, 4555.

39 (*a*) Ref. 1*a*, pp. 101, 189; (*b*) D. J. Cram and L. Gosser, *J. Am. Chem. Soc.*, 1964, **86**, 2950.

40 (*a*) J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry,' Benjamin, New York, 1965, p. 369; (*b*) A. Streitwieser, Jr., and C. H. Heathcock, 'Introduction to Organic Chemistry,' MacMillan, New York, 1976, p. 469.

41 A. Berlin, S. Bradamante, R. Ferraccioli, and G. A. Pagani, 1984, unpublished results.

42 (*a*) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 1953, **75**, 2439; (*b*) K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261.

43 G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, 1961, **83**, 2045.

44 W. Runge, *Org. Magn. Reson.*, 1980, **14**, 25.

45 (*a*) W. Runge and J. Firl, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 907, 913; (*b*) J. Firl and W. Runge, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 668.

46 C. Collier and G. A. Webb, *Org. Magn. Reson.*, 1979, **12**, 659.

47 (*a*) J. Firl, W. Runge, and W. Hartmann, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 270; (*b*) P. L. Lichter, P. R. Srinvasan, A. B. Smith III, R. K. Dieter, C. T. Demy, and J. M. Schulman, *J. Chem. Soc., Chem. Commun.*, 1977, 366.

48 K. Eberl and J. D. Roberts, *Org. Magn. Reson.*, 1981, **17**, 180.

49 See (*a*) I. N. Juchnovski and I. G. Binev, *J. Organomet. Chem.*, 1975, **99**, 1; (*b*) I. N. Juchovski, V. B. Radomirska, I. G. Binev, and E. A. Grekova, *ibid.*, 1977, **128**, 139.

50 (*a*) E. A. Walters and F. A. Long, *J. Am. Chem. Soc.*, 1969, **91**, 3733; (*b*) F. Hibbert and F. A. Long, *ibid.*, 1972, **94**, 2647.

51 See, however, D. S. Watt, *J. Org. Chem.*, 1974, **39**, 2799.

52 J. B. Moffat, *J. Chem. Soc., Chem. Commun.*, 1980, 1108.

53 (*a*) R. Lett, G. Chassaing, and A. Marquet, *J. Organomet. Chem.*, 1976, **111**, C17; (*b*) G. Chassaing and A. Marquet, *Tetrahedron*, 1978, **34**, 1899.

54 S.-I. Nishi and M. Matsuda, *J. Am. Chem. Soc.*, 1979, **101**, 4632.

55 (*a*) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Lett.*, 1962, 515; (*b*) W. Walter and H. L. Wiedemann, *Justus Liebigs Ann. Chem.*, 1965, **685**, 29.

56 R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 1971, 652.

57 (*a*) T. Bottin-Strzalko, J. Seyden-Penne, and M.-P. Simonnin, *J. Chem. Soc., Chem. Commun.*, 1976, 905; (*b*) T. Bottin-Strzalko, J. Seyden-Penne, M.-J. Ponet, and M.-P. Simonnin, *J. Org. Chem.*, 1978, **43**, 4346; (*c*) T. Bottin-Strzalko, J. Corset, F. Froment, M.-J. Ponet, J. Seyden-Penne, and M.-P. Simonnin, *ibid.*, 1980, **45**, 1270; (*d*) T. Bottin-Strzalko, J. Seyden-Penne, M.-J. Ponet, and M.-P. Simonnin, *Org. Magn. Reson.*, 1982, **19**, 69.

58 J. F. Biellmann and J. J. Vicens, *Tetrahedron Lett.*, 1974, 2915.

59 Y. Yamamoto and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1980, 239.

60 S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2*, following paper.

61 (*a*) P. Auvray and F. Genet, *Acta Crystallogr.*, 1971, **B27**, 2424; (*b*) H. Nakanishi, K. Ueno, and Y. Sasada, *ibid.*, 1976, **B32**, 1616; (*c*) H. Nakanishi and Y. Sasada, *ibid.*, 1978, **B34**, 332; (*d*) Y. Delugeard, *Cryst. Struct. Commun.*, 1975, **4**, 289.

62 (*a*) E. Foresti Serantoni, L. Riva di Sanseverino, and G. Rosini, *J. Chem. Soc. B*, 1971, 2372; (*b*) O. Pieroni, G. Montagnoli, A. Fissi, S. Merlino, and F. Ciardelli, *J. Am. Chem. Soc.*, 1975, **97**, 6820; (*c*) M. L. M. Pennings, D. N. Reinhoudt, S. Harkema, and G. J. Van Hummel, *ibid.*, 1980, **102**, 7571; (*d*) M. Cotrait, D. Sy, and M. Ptak, *Acta Crystallogr.*, 1975, **B31**, 1869; (*e*) V. Zabel, W. H. Watson, B. K. Cassels, and D. A. Langs, *Cryst. Struct. Commun.*, 1980, **9**, 461.

63 G. Casalone, A. Gavezzotti, C. Mariani, A. Mugnoli, and M. Simonetta, *Acta Crystallogr.*, 1970, **B26**, 1.

64 S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1055; (*b*) S. Bradamante and G. A. Pagani, Communication presented at the VIth IUPAC Conference on Physical Organic Chemistry, Louvain La Neuve, 1982; *Bull. Soc. Chim. Belges*, 1982, **91**, 379; (*c*) E. Configliacchi, Thesis, University of Milano, 1980; (*d*) A. Ludergnani, Thesis, University of Milano, 1981; (*e*) Presented at the 2nd Euchem Conference on Correlation Analysis in Organic Chemistry, Hull, 1982.

65 M. Saunders and R. W. Murray, *Tetrahedron*, 1960, **11**, 1.

66 C. M. Suter and A. W. Weston, *J. Am. Chem. Soc.*, 1941, **63**, 602.

67 A. Fischer, B. A. Grigor, J. Packer, and J. Vaughan, *J. Am. Chem. Soc.*, 1961, **83**, 4208.

68 N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, 1956, **78**, 1498.

69 S. Hunig and O. Boes, *Justus Liebigs Ann. Chem.*, 1953, **579**, 23.

70 E. Fromm and J. De Seivas Palma, *Ber. Dtsch. Chem. Ges.*, 1906, **39**, 3308.

71 R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Am. Chem. Soc.*, 1930, **52**, 2060.

72 A. Kretzkamp and S. Schindler, *Arch. Pharm.*, 1960, **239**, 296.

73 D. Jerchel, S. Noetzel, and K. Thomas, *Chem. Ber.*, 1960, **93**, 2966.

74 R. J. Bushby and G. J. Ferber, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1683.

75 N. G. Leonard and R. A. W. Johnson, *J. Org. Chem.*, 1962, **27**, 282.

76 B. C. Saunders, G. J. Stacey, F. Wild, and G. E. Wilding, *J. Chem. Soc.*, 1948, 699.

Received 30*th May* 1985; *Paper* 5/917