Substituent Effects in α-Substituted Carbanions

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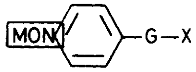
The *para* ^{13}C shifts of benzylcarbanions $PhCH^-X$ (**VI**) in Me_2SO, acidities of toluene carbon acids $PhCH_2X$ (**I**) in Me_2SO, and gas-phase acidities of methane carbon acids CH_3X (**VIII**) are submitted to mono- and bi-parametric substituent treatment using previously defined sets of σ_c^-, σ_{IB}, and σ_{R^-} constants. It is confirmed that these scales are appropriate for describing interactions between contiguous functionalities, as opposed to literature values which account for remote interactions. Gas-phase acidities respond excellently to substituent effect treatment, while solution data show deviations for the SO_2R and CN substituents. Such deviances are accounted for as a manifestation of SSSAR (Stabilization due to Specific Solvent Assisted Resonance) for groups which exhibit extensive charge transfer from the carbanionic carbon to the π-accepting substituent (COR, CO_2R, $CONMe_2$, NO_2, *etc.*). The mesomeric component of substituent effects is about three times more important than the polar–inductive one in governing the acidities of carbon acids in Me_2SO solution and in affecting the chemical shift of the *para* monitor in $PhCH^-X$. Relative to the gas phase, the solvent enhances by a factor of 2 the sensitivity of acidities of carbon acids to the mesomeric components of substituent effects. The sensitivity of the *para* monitor in $PhCH^-X$ to polar–inductive components of substituent effects shows, relative to the neutral precursor $PhCH_2X$ (**I**), a three-fold increase and, relative to the PhNHX family, a two-fold increase. The sensitivity of the *para* monitor in $PhCH^-X$ to mesomeric components of substituent effects shows a three-fold increase relative to the PhNHX family.

Interactions between contiguous functionalities G-X have been described[1] in terms of substituent effects exerted by the substituent X on the involved (reacting) group (or 'cavity'[2]) G. In particular, the PhNHX family (**IV**) was used to define the set of blended σ_c^- empirical constants (σ 'contiguous'); on analogous grounds, using the $PhCH_2X$ and PhNHX families, the σ_{IB} (polar–inductive σ of benzylic type) and σ_{R^-} sets of constants were defined[1] and were anchored to Taft's early σ_I and σ_{RA}^- values.[2] The sets of σ_c^-, σ_{IB}, and σ_{R^-} constants are presented in Table 1.

Both theoretical calculations of substituent effects[3] and the efforts of treating resonance effects in terms of a demand parameter, instead of the four scales currently in use (σ_R°, σ_R^+, σ_{RA}^-, σ_{RBA}) have led to new approaches: the non-linear DSP (NLDSP),[4] the Yukawa–Tsuno equation,[5] the More O'Ferrall quadratic treatment,[6] and other proposals.[7,8] Developments of gas-phase chemistry has suggested[9–11] that the set of σ_{RA}^- constants previously proposed by Taft may be invalid[12] because resonance parameters of substituents have been found to be solvent dependent [Stabilization by Specific Solvent Assisted Resonance (SSSAR)].

To obtain further[13–15] evidence for the general validity of the σ_c^-, σ_{IB}, and σ_{R^-} sets of constants and to provide a quantitative treatment of substituent effects in carbanions, we have applied the above sets in the analysis of: (i) *para* ^{13}C shifts of benzyl carbanions $PhCH^-X$ (**VI**),[15] with reference to their corresponding isoelectronic nitrogen analogues PhNHX (**IV**) and (ii) solution (Me_2SO) as well as gas-phase acidities of methane and toluene carbon acids CH_3X (**VIII**) and $PhCH_2X$ (**I**), respectively. Series (**I**), (**IV**), (**VI**), and (**VIII**) belong to the set of families (**I**)—(**X**) we are currently investigating.

Significant aspects of the effects exerted by contiguous substituents in carbanionic systems are clarified. We show that while most, but not all, substituent effects are coherent in all the families in solution, our proposed sets of σ constants account excellently for gas-phase acidities of methane carbon acids CH_3X (**VIII**). Therefore the sets are relatively insensitive to SSSAR effects and are appropriate for interpreting the role played by the solvent in deprotonation processes of carbon acids. Finally, extrapolations are performed to provide acidities of a number of carbon acids which are too weak to ionize in Me_2SO.



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

H—G—X

(**VIII**) G = CH_2
(**X**) G = O

Results

Our ^{13}C n.m.r. and other's acidity data that have been used in the correlations are collected in Table 2. A relevant intersystem correlation is obtained by plotting C(*p*) of carbanions (**VI**)[5b] *versus* C(*p*) of the isoelectronic family (**IV**) (Figure 1). Analytical fitting parameters for this and other related correlations are in Table 3. For a limited but substantial number of substituents ($n = 8$) the C(*p*) shifts of the two families are linearly related with a high degree of precision (entry 1 of Table 3). The correlation deteriorates somewhat (entry 2) on further considering the NO_2, SOPh, and 2-C_5H_4N substituents. Finally, as previously noted,[15a] the CN, SO_2Me, and SO_2Ph substituents are distinctly deviant. Analogously, effects exerted by substituents X = CN, SOR, SO_2R (R = Me, Ph) on the C(*p*) shift of benzyl anions (**VI**) are not accounted for by σ_c^- constants: the shifts appear too highfield. Comparison of entries 4 and 5 shows that in the Hammett-type analysis the COPh and NO_2 points bring some curvature in the upper part of the straight line: it is

Table 1. Substituent parameters

Substituent	σ_c^- [a]	σ_{IB} [a]	σ_I [b]	σ_I [c,d]	σ_{R^-} [a]	$\sigma_{R(g)}$ [d]
H	0.00	0.00	0.00	0.00	0.00	0.00
Ph	0.47	0.10			0.26	
$CONMe_2$	0.70	0.14			0.40	
CO_2Me	0.74 (0.81)	0.26	0.20	0.17	0.39 (0.45)	0.41
COMe	0.82	0.20	0.20	0.22	0.47	0.43
COPh	0.94 (0.81)	0.21	0.22		0.52 (0.47)	
CHO	0.98	0.26	0.27	0.32	0.49	0.46
$COCF_3$	1.09	0.58			0.42 (0.36)	
NO_2	1.27	0.80	0.65	0.65	0.45	0.41
CN	0.88 (0.99)	0.43	0.56	0.58	0.33 (0.42)	0.23
SOMe	0.73	0.40	0.49	0.36	0.29	(0.23)
SO_2Me	0.99	0.59	0.60	0.58	0.33	0.30
SOPh	0.76	0.46			0.26	
SO_2Ph	1.00	0.62	0.62		0.34	
$PO(OEt)_2$	0.58 (0.68)	0.19			0.29 (0.38)	
$2\text{-}C_5H_4N$	0.55	0.12			0.31	
$3\text{-}C_5H_4N$	0.58	0.15			0.31	
$4\text{-}C_5H_4N$	0.73	0.18			0.45	

[a] From ref. 1. Numbers in parentheses refer to values to be used for the oxygen cavity. [b] From ref. 26. [c] Inherent constants. [d] From ref. 12*a*.

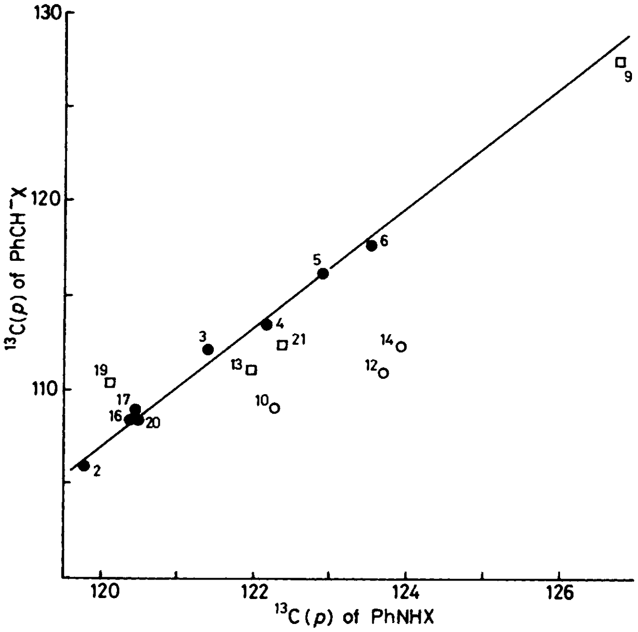


Figure 1. C(*p*) of $PhCH^-X$ as a function of the C(*p*) of PhNHX. With reference to fitting parameters of Table 3 entry 1 pertains to points designated as ●, entry 2 to points ● and □, entry 3 to points ●, □, and ○. Key for Figures 1—6: 2, Ph; 3, $CONMe_2$; 4, CO_2Me; 5, COMe; 6, COPh; 7, CHO; 8, $COCF_3$; 9, NO_2; 10, CN; 11, SOMe; 12, SO_2Me; 13, SOPh; 14, SO_2Ph; 16, $PO(OEt)_2$; 17, $POPh_2$; 19, $2\text{-}C_5H_4N$; 20, $3\text{-}C_5H_4N$; 21, $4\text{-}C_5H_4N$

possible in fact to place these points, together with the COMe point, on the line for entry 5, characterized by a slope which is almost one half that of correlation of entry 4.

In view of the good intersystem correlation between $PhCH_2X$ acidities and C(*p*) of $PhCH^-X$ (VI),[15b] acidities of $PhCH_2X$ for X = CN, SO_2Me, SO_2Ph, SOMe, and SOPh are expected to be unaccounted for by σ_c- constants. Also for $PhCH_2X$ acidities some curvature is present for X = COPh and NO_2 (entry 10).

Entry 11 of Table 3 reports results of correlative analysis of acidities of $PhCH_2X$ carbon acids as if they were disubstituted methane carbon acids, assuming additivity of effects. The constants used are therefore the sum of the constant of the phenyl ring (σ_c^- 0.47) and that due to the variable functionality X. The intercept of entry 8 affords the extrapolated pK_a of toluene (49.46 ± 0.22) and entry 11 provides the extrapolated pK_a of methane (66).

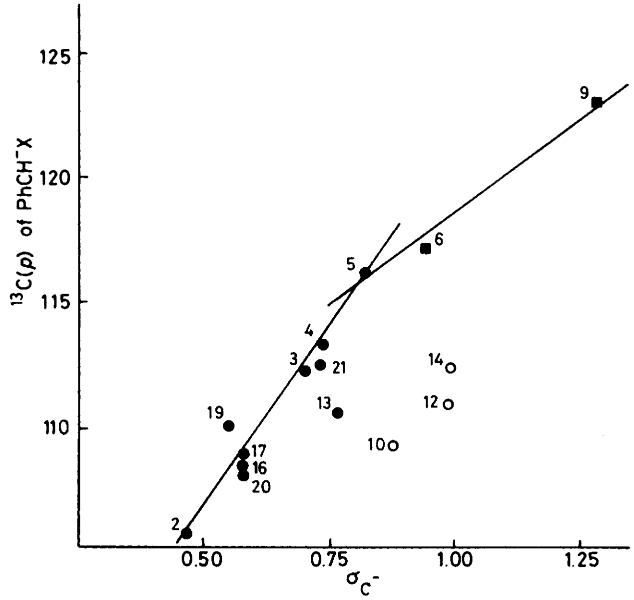


Figure 2. C(*p*) of $PhCH^-X$ as a function of σ_c^-. With reference to fitting parameters of Table 3, entry 1 pertains to points designated as ●, entry 2 to points ■ and number 5 of ●, entry 3 to ● + ■, entry 4 to ●, ■, ○ points. See Figure 1 for key to numbers

The DSP treatment we have used for $^{13}C(p)$ of $PhCH^-X$ and for Me_2SO acidity data of $PhCH_2X$ must be somewhat different from the original equation (1) described by Taft. In fact, we are

$$\delta\Delta P = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

$$\delta P = \rho_{IB}\sigma_{IB} + \rho_{R^-}\sigma_{R^-} + \text{constant} \qquad (2)$$

Table 2. $^{13}C(p)$ Chemical shifts (p.p.m. for PhNHX and $PhCH^-XNa^+$) and acidity data for methane (CH_3X) and toluene ($PhCH_2X$) carbon acids

	$^{13}C(p)$[a]		Acidities		
			CH_3X		$PhCH_2X$
X	PhNHX[b]	$PhCH^-X$[c]	D-EA[d]	Me_2SO[e]	Me_2SO[e]
H	115.51				
Ph	119.51	105.73	65.40		32.30
$CONMe_2$	121.43	112.30	59.90	34—35	26.62
CO_2Me	122.17	113.27	57.40	30—31	22.71
COMe	122.83	116.15	55.20	26.50	19.80
COPh	123.51	117.66	48.90	24.70	17.70
CHO			52.30		
$COCF_3$	124.75		36.70		
NO_2	126.73	122.97	45.10	17.20	12.52
CN	122.25	109.03	58.60	31.30	21.90
SOMe		108.40	59.10	35.10	29.10
SO_2Me	123.70	110.98	53.00	31.10	25.60
SOPh	121.93	110.85		33.00	27.20
SO_2Ph	123.96	112.37	49.10	29.04	23.40
$PO(OEt)_2$	120.40	108.43			27.60[f]
$POPh_2$	120.43	108.73			
$2\text{-}C_5H_4N$	120.19	110.31			28.18[f]
$3\text{-}C_5H_4N$	120.43	108.19			30.15[f]
$4\text{-}C_5H_4N$	122.37	112.57			26.66[f]

[a] In Me_2SO relative to TMS. [b] See ref. 1. [c] See ref. 15*b*. [d] Ref. 9. [e] Taken from F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin, and W. S. Matthews, *J. Am. Chem. Soc.*, 1975, **97**, 3226; 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; F. G. Bordwell and H. E. Fried, *ibid.*, 1981, **46**, 4327. [f] Unpublished results.

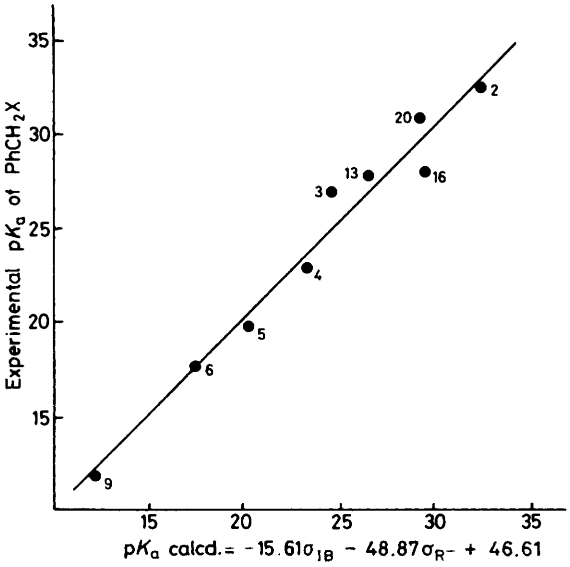


Figure 3. Experimental pK_a values of $PhCH_2X$ as a function of the calculated pK_a values using fitting parameters of entry 4 of Table 4. See Figure 1 for key to numbers

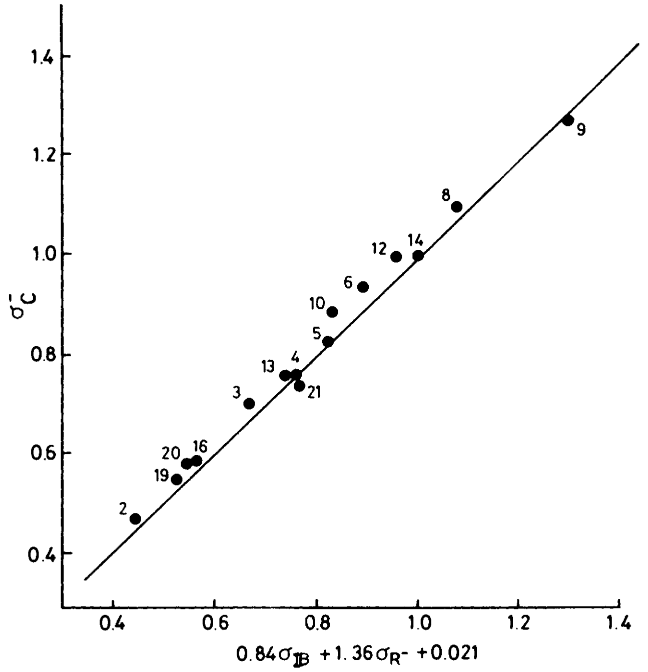


Figure 4. Experimental σ_c^- values as a function of the blend of polar-inductive (σ_{IB}) and mesomeric (σ_{R^-}) components of substituent effects. See Figure 1 for key to numbers

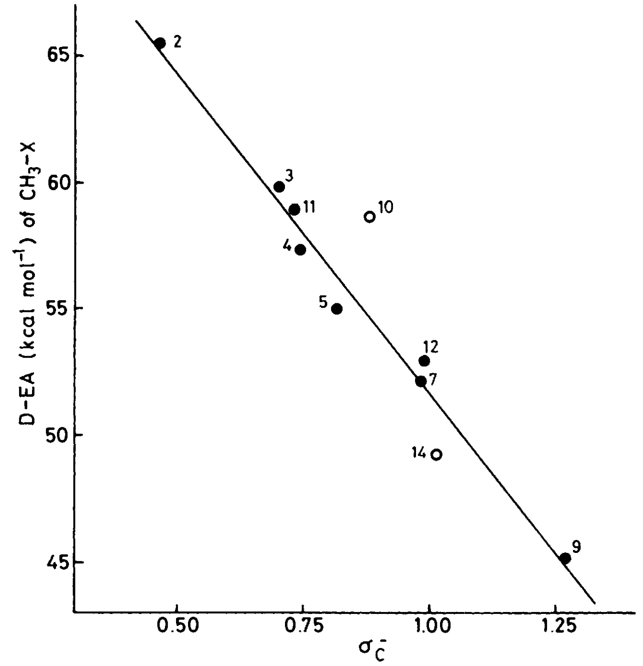


Figure 5. D-EA values for methane carbon acids CH_3X as a function of σ_c^-: with reference to fitting parameters of Table 3, entry 13 pertains to points designated as ●, entry 15 to points ● + ○. See Figure 1 for key to numbers

forced to use equation (2) because neither the C(*p*) of (VI-1) nor the pK_a of toluene (I-1) are obtainable in Me_2SO.

The DSP treatment of $^{13}C(p)$ data for carbanions (VI) reveals that, while data for X = CN, SOR, SO_2R are still unaccounted for at a satisfactory level (entry 3 of Table 5), data for X = NO_2 and COPh, are reasonably consistent with other points of the regression (entry 1 of Table 4). Me_2SO acidity data for $PhCH_2X$ carbon acids show almost the same relative sensitivities as C(*p*) of carbanions (VI) for polar inductive (ρ_I) and resonance (ρ_R) effects of substituents, although with a lower degree of precision.

Entries 8—11 of Table 4 report the treatment of gas-phase acidities of methane carbon acids CH_3X (VIII) for which values of (D-EA) are expressed in kcal mol^{-1}. To allow a comparison of

Table 3. Intersystem and Hammett-type correlations

Entry	System	y	x	slope (ρ)	intercept	*r*	*n*	X
1	$PhCH^-X$–PhNHX	C(*p*) in $PhCH^-X$	C(*p*) in PhNHX	3.02 ± 0.12	−255.13 ± 0.15	0.995	8	Ph, $CONMe_2$, CO_2Me, COMe, COPh, $PO(OEt)_2$, $POPh_2$, 3-C_5H_4N
2				2.36 ± 0.19	−175.48 ± 0.36	0.969	12	as entry 1 + NO_2, SOPh, 2-C_5H_4N, 4-C_5H_4N
3				1.99 ± 0.33	−130.47 ± 0.59	0.860	15	as entry 2 + CN, SO_2Me, SO_2Ph
4	$PhCH^-X$	C(*p*)	σ_c^-	29.62 ± 1.20	91.42 ± 0.13	0.995	8	Ph, $CONMe_2$, CO_2Me, COMe, $PO(OEt)_2$, $POPh_2$, 3-C_5H_4N, 4-C_5H_4N
5				15.35 ± 0.74	103.42 ± 0.14	0.999	3	COMe, COPh, NO_2
6				21.33 ± 1.58	97.06 ± 0.33	0.974	11	as entry 4 + 2-C_5H_4N, COPh, NO_2
7				15.60 ± 3.25	100.02 ± 0.67	0.788	15	as entry 6 + CN, SOPh, SO_2Me, SO_2Ph
8	$PhCH_2X$	$pK_a(Me_2SO)$	σ_c^-	−36.50 ± 1.85	49.46 ± 0.22	0.995	6	Ph, CO_2Me, COMe, $PO(OEt)_2$, 2-C_5H_4N, 3-C_5H_4N
9				−34.53 ± 3.97	48.59 ± 0.45	0.968	7	as entry 8 + $CONMe_2$
10				−25.87 ± 2.29	42.98 ± 0.56	0.977	8	as entry 8 + COPh, NO_2
11			$\Sigma\sigma_c^-$	−36.50 ± 1.85	66.62 ± 0.22	0.995	6	as entry 8
12		*b*	σ_c^-	−49.72 ± 2.55	67.56 ± 0.31	0.995	6	as entry 8
13	MeX	D-EA[b]	σ_c^-	−24.99 ± 1.23	76.85 ± 0.28	0.993	8	Ph, $CONMe_2$, CO_2Me, COMe, CHO, NO_2, SOMe, SO_2Me
14				−24.64 ± 2.37	76.98 ± 0.50	0.969	9	as entry 13 + CN
15				−25.71 ± 2.69	77.57 ± 0.56	0.959	10	as entry 14 + SO_2Ph
16				−31.72 ± 5.90	81.43 ± 1.18	0.862	12	as entry 15 + COPh, $COCF_3$

[a] $\Sigma\sigma_c^- = (\sigma_c^-)_X + (\sigma_c^-)_{Ph}$. [b] pK_a kcal mol^{-1}.

Table 4. Fitting parameters for the DSP treatment of data using σ_{IB} and σ_{R^-} values

Entry	System	*y*	ρ_I	ρ_R	intercept	*b*[a]	*r*[b]	*n*	X
1	$PhCH^-X$	C(*p*)	13.34 ± 0.53	41.31 ± 1.30	93.71 ± 0.48	1.00 ± 0.02	0.999	8	Ph, $CONMe_2$, CO_2Me,[c] COMe, COPh, NO_2, $PO(OEt)_2$,[d] 3-C_5H_4N
2			13.49 ± 1.62	37.31 ± 3.62	95.20 ± 1.37	1.00 ± 0.06	0.982	11	as entry 1 + 2-C_5H_4N, 4-C_5H_4N, SOPh
3			8.94 ± 2.24	42.36 ± 6.05	93.90 ± 2.35	0.999 ± 0.12	0.927	14	as entry 2 + CN, SO_2Me, SO_2Ph
4	$PhCH_2X$	$pK_a(Me_2SO)$	−15.61 ± 2.46	−48.87 ± 5.98	46.61 ± 2.20	1.00 ± 0.07	0.986	8	as entry 1
5		*e*	−15.49 ± 2.73	−47.22 ± 6.52	59.58 ± 3.97	1.00 ± 0.08	0.982	8	as entry 1
6		*e*	−13.80 ± 2.91	−46.11 ± 7.36	59.59 ± 4.88	1.00 ± 0.12	0.912	14	as entry 1 + SOMe, SO_2Me, SOPh, SO_2Ph, 2-C_5H_4N, 4-C_5H_4N
7	$PhCH_2X$	*f*	−21.59 ± 3.21	−73.50 ± 8.56	67.27 ± 3.24	1.00 ± 0.07	0.987	8	as entry 1
8	CH_3X	D-EA[f]	−18.70 ± 1.00	−41.48 ± 2.85	78.32 ± 1.13	1.00 ± 0.04	0.996	8	Ph, $CONMe_2$, CO_2Me, COMe, CHO, SOMe, SO_2Me, NO_2
9			−18.27 ± 1.47	−43.43 ± 4.11	79.13 ± 1.63	1.00 ± 0.05	0.990	9	as entry 8 + CN
10			−20.26 ± 2.26	−40.78 ± 6.92	78.50 ± 2.68	1.00 ± 0.09	0.972	10	as entry 9 + SO_2Ph
11			−23.93 ± 5.68	−53.66 ± 15.41	83.52 ± 6.64	1.00 ± 0.18	0.870	12	as entry 10 + COPh, $COCF_3$
12	$\sigma_c{}^-$	$\sigma_c{}^-$	0.84 ± 0.03	1.36 ± 0.06	0.02 ± 0.02	1.00 ± 0.02	0.996	16	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, $COCF_3$, CN, NO_2, SOPh, SO_2Me, SO_2Ph, $PO(OEt)_2$, 2-C_5H_4N, 3-C_5H_4N, 4-C_5H_4N
13	PhNHX	C(*p*)	6.97 ± 0.09	12.64 ± 0.22	117.08 ± 0.08	1.00 ± 0.01	0.999	8	as entry 1

[a,b] *r* is the correlation coefficient of the relationship $Y_{\text{exptl.}} = bY_{\text{calc.}}$ + constant, where $Y_{\text{calc.}}$ are the values calculated using ρ_{IB} and ρ_R in the same row. [c] Using σ_{R^-} 0.39. [d] Using σ_{R-} 0.29. [e] Using $\Sigma\sigma_{IB} = (\sigma_{IB})_X + (\sigma_{IB})_{Ph}$ and $\Sigma\sigma_{R^-} = (\sigma_R{}^-)_X + (\sigma_R{}^-)_{Ph}$. [f] Acidities in kcal mol^{-1}.

gas-phase acidities of CH_3X with Me_2SO acidities of $PhCH_2X$, entry 7 reports the treatment of $PhCH_2X$ acidities expressed in kcal mol^{-1}.

In conclusion, results clearly indicate that for Me_2SO solution data the effects of some substituents are incoherent in the two isoelectronic series PhNHX (IV) and $PhCH^-X$ (VI). Discrepancies are found at two quantitative levels: deviations for the NO_2, COPh, 2-C_5H_4N, and SOPh substituents are relatively small and vanish on going from monoparametric (Hammett-type) to biparametric (DSP) treatments, while deviations are substantial and permanent, whatever the treatment (mono- or bi-parametric) for SO_2Me, SO_2Ph, and CN substituents. It is important to note that in contrast with Me_2SO solution data, in the gas-phase these last groups respond correctly (with some limitations for the SO_2Ph group) both to monoparametric and to DSP treatments.

Table 5. Extrapolation of acidities and shifts inaccessible in Me_2SO

Quantity	Source	Extrapolated value	Other exptl. values	Ref.
$^{13}C(p)$ in $PhCH_2^-$	entry 1, Table 3[a]	93.7	95.7	*b*
	entry 1, Table 4, intercept	93.7	95.6	*c*
	entry 4, Table 3	91.4		
pK_a of $PhCH_3$	entry 8, Table 3	49.0	41.2	*d*
	entry 10, Table 3	43.0	44—45	*e*
	entry 4, Table 4	46.6	42	*f*
	g	47.0		
pK_a of CH_4	entry 12, Table 3	66.6	60—62	*e*
	entry 5 Table 4	59.6	59.7	*e*
			55	*f*

[a] Using for C(*p*) of $PhNH_2$ the value of 115.5 p.p.m. [b] See ref. 19. [c] See ref. 20. [d] See ref. 21. [e] See ref. 22. [f] See ref. 23. [g] From the relationship pK_a = (-1.19 ± 0.04) C(*p*) + (158.54 ± 0.22) and using for C(*p*) the value of 93.7 as obtained in entries 1 and 2 of this Table.

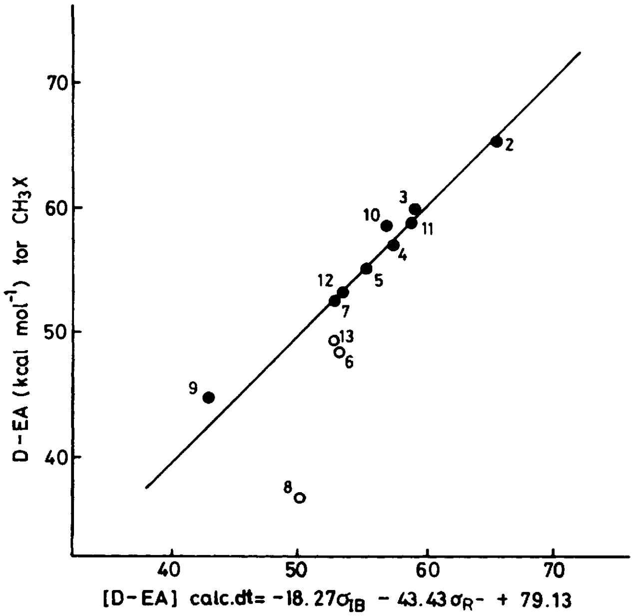


Figure 6. Experimental D-EA values for methane carbon acids CH_3X as a function of calculated values using fitting parameters of entry 8 of Table 4. See Figure 1 for key to numbers

Discussion

Mono- versus Bi-parametric Treatment.—The high ratio of resonance to polar-inductive sensitivities for C(*p*) of $PhCH^-X$ (ρ_R/ρ_I 3.13) and for Me_2SO acidities of $PhCH_2X$ (ρ_R/ρ_I 3.10) as opposed to the low ratio for C(*p*) of PhNHX (ρ_R/ρ_I 1.81) and for σ_c^- (ρ_R/ρ_I 1.62), explains why the COPh and NO_2 substituents deviate in intersystem ($PhCH^-X$ *versus* PhNHX) and in Hammett-type (σ_c^-) correlations. It is concluded, and confirmed, that monoparametric approaches are successful only if the monitor responds to substituent effects with a ratio of polar–inductive to resonance contributions analogous to that of the reference parameter, that is in our case the C(*p*) of PhNHX and the σ_c^- for intersystem and Hammett-type relationships, respectively.

The DSP treatments show that polar–inductive effects of substituents are sizeably more pronounced in the polarizable $PhCH^-X$ system than in PhNHX: this supports the importance of π polarization components in the polar–inductive effects.[16–18] The increase of the sensitivity of monitors to resonance components of substituent effects in $PhCH^-X$ (**VI**) relative to PhNHX (**IV**) is undoubtedly associated with the higher negative charge density at C(*p*) in (**VI**) than in (**IV**).

The Effect of the Solvent on Resonance Parameters.—As shown before, the behaviour of the SO_2Me, SO_2Ph, and CN groups for C(*p*) of the $PhCH^-X$ family and for the acidities of $PhCH_2X$ and MeX in Me_2SO cannot be accounted for either by mono- or bi-parametric relationships: instead, in the gas-phase, either σ_c^- or better the σ_{IB}, σ_{R^-} sets are quite successful. The comparison between the solution and gas-phase results would be quite illuminating for an understanding of the reasons of this different behaviour. However, this is difficult because of the limited number of available acidities in Me_2SO for CH_3X, once the SO_2Me, SO_2Ph, and CN substituents are excluded. The difficulty is circumvented as follows. Thanks to the excellent linear relationship of slope 1 between the Me_2SO acidities of toluene carbon acids $PhCH_2X$ (**I**) and methane carbon acids CH_3X (**VIII**),[15b] we shall use the $PhCH_2X$ family as a reference family for Me_2SO acidity data. The effect of the solvent on acidities will be evaluated therefore on comparing toluene carbon acids $PhCH_2X$ in Me_2SO with methane carbon acids CH_3X in the gas phase.

In addition to the dichotomous behaviour of the CN, SO_2Me, and SO_2Ph substituents in the gas and in the condensed phases, results in solution further appear to be contradictory. C(*p*) shifts for benzyl carbanions substituted with the SO_2Me, SO_2Ph, and CN groups are all present at higher field than predicted: these groups behave therefore as if they were less electron-withdrawing than expected on the basis of the effects they exert in PhNHX. However, if Me_2SO pK_a values are considered, while entry 4 of Table 4 would predict $PhCH_2SO_2Me$ and $PhCH_2SO_2Ph$ to be *more* acidic than actually found, $PhCH_2CN$ would be anticipated to be *less* acidic than experimentally found.

To clarify the complex interplay of the various effects it is helpful to consider first the influence of the solvent on the polar–inductive and resonance components of substituent effects. Comparison of entries 7 and 8 of Table 4 clearly indicates that the influence of the solvent on the polar–inductive component is only modest. There is no doubt that the solvent manifests its influence primarily on the mesomeric component: although the influence could be, in principle, both a bulk and a specific effect, we believe that the second is the most important one. The fact that the σ_c^- and σ_{IB}, σ_{R^-} sets of empirical constants, despite their being derived and anchored to substituent effects observed in Me_2SO solution for the PhNX family, are valid also in the gas phase, is a clear demonstration that these constants are devoid of any effect due to specific interactions of the solvent with the substituent groups. The reason why the system they have been derived from and anchored on shows substituent effects which are uncontaminated by specific interactions of the solvent with the substituents can be understood on considering that in PhNHX the extent of charge transfer from the NH group to the substituent X is only modest. In addition to the possible, presumably relatively small, bulk effect of the solvent, the σ_{IB} and σ_{R^-} constants account essentially for the intrinsic effects exerted by the substituents on the adjacent functionality.

Specific solvation of a substituent primarily occurs when the solvent (or more generally the environment, to include counterions) interacts specifically with a charged group or atom in a family of molecules: we have shown that the role of the solvent is exerted in stabilizing an exalted charge transfer from the carbanionic carbon to the electron-withdrawing group X.[15b] In the case of methanenitronate anion $^-CH_2NO_2$ charge transfer from C^- to oxygen is *ca.* 1.5 times more intense in solution than in the gas phase, as evaluated by *ab initio* computations. This phenomenon is nothing else than Taft's recently described SSSAR effect (Stabilization by Specific Solvent Assisted Resonance). In conjugate anions of substituted methane and toluene carbon acids that exhibit a sizeable charge transfer from the carbanionic carbon to the electron-withdrawing group, the substituent is likely to undergo specific interactions with the environment. As a consequence the correlation in Me_2SO solution is valid only for a limited number of substituents and is restricted to the groups of the carbonyl and nitro families. Those substituents that have a different ($2\text{-}C_5H_4N$, $4\text{-}C_5H_4N$) or no specific solvent-assisted resonance stabilization (SOR, SO_2R, and CN) will show deviations in correlative analysis. In this case the deviations have a highly meaningful and heuristic value because they are a clear indication of different delocalization of charge.

The SSSAR effect is not incorporated in our σ_{R^-} parameter: as a result the increased resonance stabilization, assisted by the solvent and operating for those groups of entries 1—7 in Table 4, will show up in the numerical value of ρ_R: the sensitivity of ρ_R of such entries therefore is somewhat artificially increased. Account must be taken of this when mesomeric effects are compared through the values of ρ_R in solution and in the gas phase.

Taft has analysed substituent effects for gas-phase acidities of methane carbon acids in terms of a newly defined $\sigma^-_{R(g)}$ scale,[12] *i.e.*, resonance components of substituent effects as determined for phenols in the gas phase. Numerical values of $\sigma^-_{R(g)}$ are usually decreased relative to the values of σ_{R^-} (see Table 1): the sensitivity ρ of Taft's analysis is considerably higher than ours (ρ_R 87 kcal/$\sigma^-_{R(g)}$ *versus* $\rho_R = 41.5$ kcal/$\sigma^-_{R(\text{solution})}$) but obviously any comparison is meaningless. Indeed, using Taft's $\sigma^-_{R(g)}$ scale, it is difficult to evaluate the effect provided by the solvent in stabilizing the carbanion. Despite all this, the ratio of mesomeric to polar–inductive components of substituent effects in methane carbon acids in the gas phase is similar in our (ρ_{R^-}/ρ_{IB} 2) and in Taft's treatment ($\rho_{R(g)}/\rho_I$ 2.50).

In accord with these considerations it is possible now to interpret the apparently contradictory results of substituent effects in the condensed phase for benzyl carbanions and for the acidity of toluene carbon acids. Carbanions substituted with carbonyl and nitro groups show considerable charge transfer from the carbanionic carbon to the substituent, and are thus strongly affected by specific solvation. Instead, in $PhCH^-CN$, $PhCH^-SO_2Me$, and $PhCH^-SO_2Ph$ the very modest charge transfer from carbon to the substituent leaves most of the charge on the carbanionic carbon: such carbanions centres are soft and thus almost unsuitable to sustain interactions with the solvent. In these cases extra resonance stabilization assisted by the solvent cannot be one of the components affecting acidity of the carbon acid: consequently, $PhCH_2SO_2Me$, $PhCH_2SO_2Ph$, and (to a lesser extent) $PhCH_2SOMe$ are carbon acids less acidic than predicted from the plane defined by the DSP treatment of entry 4. In $PhCH^-CN$ however a further phenomenon is operating: the intrinsic stabilization of the anion is increased, relative to all the other systems, thanks to the almost full coplanarity of the whole molecule: this feature is not promoted by any other substituent so far considered in benzyl anions. Correlations do not take into account variable steric inhibition of resonance: therefore they predict $PhCH_2CN$ to be less acidic than actually found. Coming to consider now the C(*p*) shifts, we can expect that in $PhCH^-SO_2Me$, $PhCH^-SO_2Ph$, $PhCH^-CN$ the negative charge has a greater chance to transfer from the carbanionic carbon to the *para* position of the phenyl ring, because of the large negative charge density at the carbanionic carbon. This process generates upfield shifts of the C(*p*) resonance, which will be inconsistent relative to those of all the other members of the series (COR, NO_2, *etc.*).

Since in the gas phase no solvent effects are operating on COR and NO_2 substituents, these groups can stabilize the carbanion by intrinsic factors only, just as well as the CN and SO_2Me (and SO_2Ph) groups: inconsistency of acidities originating from selected solvent stabilization thus vanishes. In the gas phase, however, different phenomena may become important, and among them the most relevant is polarizability. Indeed, in the gas phase the considerably different acidifying effect of the SO_2Me and the SO_2Ph groups cannot be accounted for by electronic considerations. The polarizability of the hydrocarbon moiety of the SO_2Ph and COPh is believed to be responsible for the somewhat deviant behaviour of these substituents in the gas phase: analogous reasoning applies to the $COCF_3$ group.

Extrapolations.—Table 5 reports the extrapolated values for C(*p*) in $PhCH_2^-$, the pK_a values of toluene and of methane in Me_2SO. These values are experimentally inaccessible in Me_2SO since toluene is a weaker acid than Me_2SO (pK_a 35.1). The extrapolated value for C(*p*) in $PhCH_2^-$, whatever the source, either by mono- or bi-parametric treatments, is astonishingly close to the experimental values determined in THF for $PhCH_2^-K^+$.[19,20]

This is clear evidence that both sets of σ_c^- and of σ_{IB}, σ_{R^-} values work quite well, offering extrapolated values which are presumably very close to the experimental ones: also, it indicates that the procedure we have followed in disregarding a number of points considered to be deviant is justified and that therefore the choice of 'well behaved' substituents is not casual but real. A wider range is obtained for the extrapolated pK_a of toluene using mono- or bi-parametric treatment. In view of the limitations previously discussed inherent in Hammett-type relationships it appears that the value of 49 is too high. It should be noted that the true value should not be too distant from such a value: in fact using the same set of substituents and expressing the pK_a in kcal mol^{-1} units, the extrapolated acidity of toluene is quite close to that obtained in the gas phase (67.5 from entry 12 of Table 3 *versus* 65.4).[9] Conversely, the value of 43, obtained by including the COPh and NO_2 points, already ascertained to be responsible for a decrease of the slope of the line, seems too low. In conclusion, the value of *ca.* 47, originating either from the C(*p*)–pK_a relationship[15b] or from a DSP treatment of data, seems the most appropriate.

The extrapolated values of the pK_a of methane range from 60 to 66. While the upper value seems too high because of the limitations associated with the monoparametric treatment, the lower value is very close to that predicted by Breslow.[22] The value of 55 proposed by Bordwell[23] is somewhat lower: it is possible that his extrapolation method, starting from bis-activated and moving to mono-activated methane carbon acids, suffers from the inevitable neglect of saturation effects.

Conclusions

The σ_c^-, σ_{IB}, σ_{R^-} sets of substituent parameters previously obtained and anchored to the $PhCH_2X$ and PhNHX families are appropriate also for describing interactions between the carbanion cavity and contiguous substituents. These parameter sets are independent of the SSSAR effect: consequently they correctly predict acidities of carbon acids in the gas-phase. Inconsistencies found instead in solution originated from SSSAR phenomena which vary with the substituent. The significance of SSSAR phenomena is dependent upon the extent of charge transfer from the carbanion carbon to the substituent. The practice of inferring properties and characteristics of substituted carbanions from those of their nitrogen isoelectronic analogues is unwarranted for a number of substituents. As a consequence, the analogy of simple unsubstituted carbanions with isoelectronic amines[24] may not be safely extended to substituted carbanions.[25]

Acidity of substituted carbon acids is dominated, both in the gas phase and in Me_2SO, by the mesomeric demand of the substituent: the mesomeric term is further exalted in solution relative to the gas phase thanks to SSSAR phenomena. Careful empirical choice of 'well behaved' substituents provides the acccess to extrapolated n.m.r. parameters for the benzyl anion in Me_2SO and to acidities of toluene and methane in the same solvent: the good agreement of the values with the experimental data obtained under different conditions provides definitive support to the heuristic value of correlative analysis for investigating interactions intervening between contiguous functionalities.

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