# Experimental Charge Maps in Di-activated Carbanions: Access to Charge Demands of Primary Electron-withdrawing Functionalities[1]

**Emma Barchiesi, Silvia Bradamante,* Raffaella Ferraccioli, and Giorgio A. Pagani***
*Dipartimento di Chimica Organica e Industriale dell'Università and Centro CNR Speciali Sistemi Organici, Via Golgi 19, 20133, Milano, Italy*

It is found that the $^{13}C$ shifts of C-1 in numerous, 1,1-disubstituted ethylene derivatives, R–CH=$CX_2$ and RCH=CXY, are predictable, relative to the unsubstituted system RCH=$CH_2$ on the basis of additivity of the shielding contributions $A_X$ and $A_Y$. $A_X$ and $A_Y$ are obtained by subtracting the shift of parent ethylene from that of C-1 in monosubstituted ethylenes $CH_2$=CHX or $CH_2$=CHY. This result allows an assessment of the scope of our previously proposed charge–$^{13}C$ relationship, equation (1), which is now applied to numerous carbanions di-activated with both identical and with different 'primary' electron-withdrawing functionalities. It is found that the $^{13}C$ shift of the carbanionic carbon is almost insensitive to the dipolar-aprotic or protic nature of the solvent, $Me_2SO$ or MeOH. The $^1J_{CH}$ coupling constants of the carbanionic carbon provide unequivocal evidence for the trigonal hybridization of the charged carbon in all the carbanions examined, including the sulphonyl-, sulphinyl-, and cyano-stabilized systems. The π-electron density $q_C$ at the carbanionic carbon calculated by using equation (1) for carbanions di-activated with identical groups $^-CHX_2$ provides access to the fraction of negative charge $q_X$ withdrawn by each group X: these values allow a precise prediction of $q_C$ in $^-CHXY$, and thus, of the $^{13}C$ shift of their carbanionic carbon also. The charge demand values $q_X$ constitute a rank of electron-withdrawing capacities of primary functions: COPh,COMe,$CONMe_2$,$CO_2Me$,$SO_2R$,CN, SOPh,$PO(OEt)_2$. The values of $q_X$ as obtained from the $^-CHX_2$ anions are different but are linearly related to the $q_X$ values derived from the previously studied $PhCH^-X$ systems: they are, furthermore, related to the resonance parameters $\sigma_{R^-}$ of functionalities X, in turn obtained from the PhNHX systems.

Di-activated carbon acids $CH_2XY$ with X and Y strong electron-withdrawing ('primary') groups [X,Y = COR, $CO_2R$, $NO_2$, SOR, $SO_2R$, and $PO(OEt)_2$] are useful intermediates in preparative organic chemistry,[2] because of their high acidity. The stabilizing effect of the groups X and Y on the carbanions has been inferred so far only by monitoring (in a given solvent) of the variation of the acidity of the precursor carbon acids.[3] No systematic treatment in terms of charge demands of substituents X and Y has ever been attempted in order to investigate the structural reorganization undergone by the carbon acid on its conversion into the carbanion. The nature of the solvent and of the countercation play an important role in influencing both the ionization constant of the di-activated carbon acids[4] and in governing the regiochemistry of reactions of ambident carbanions with electrophiles.[5] A different distribution of charge in the carbanion on varying the solvent may be one of the factors that could produce different regiochemistry. Knowledge of the distribution of charge in di-activated carbanions will be significant both for establishing a rank of stabilizing effects of the activating groups and for understanding whether the charge distribution dictates the product distribution in reaction with a given electrophile.

$X–CH_2–Y$
**(XV)**

**2,2**: X = Y = Ph
**3,3**: X = Y = $CONMe_2$
**4,4**: X = Y = $CO_2Me$
**5,5**: X = Y = COMe
**6,6**: X = Y = COPh
**10,10**: X = Y = CN
**12,12**: X = Y = $SO_2Me$
(±)-**13,13**: X = Y = SOPh
*meso*-**13,13**: X = Y = SOPh
**14,14**: X = Y = $SO_2Ph$
**16,16**: X = Y = $PO(OEt)_2$

$X–CH^-–Y$
**(XVI)**

**4,5**: X = $CO_2Me$ Y = COMe
**4,6**: X = $CO_2Me$ Y = COMe
**4,13**: X = $CO_2Me$ Y = SOPh
**4,14**: X = $CO_2Me$ Y = $SO_2Ph$
**4,16**: X = $CO_2Me$ Y = $PO(OEt)_2$
**5,14**: X = COMe Y = $SO_2Ph$
**5,16**: X = COMe Y = $PO(OEt)_2$
**6,14**: X = COPh Y = $SO_2Ph$
**39**: X–Y = CO–$(CH_2)_3$–CO

We have shown[6] that the $^{13}C$ shifts of organic ions offer, through equation (1), an easy, experimental, although empirical

$$\delta_{\pm}(^{13}C) = 122.8 + \Sigma A_i - 160(q_C - 1) \qquad (1)$$

access to the π-charge distribution in the ionic species. We undertook a detailed $^{13}C$ NMR study both in $Me_2SO$ and in MeOH of a number of di-activated carbanions to study their structure and the dependence of their NMR parameters upon the nature of the solvent. Several carbon acids di-activated with identical groups $CH_2X_2$ (**XV-2,2**)–(**XV-39**)† were first used to generate the conjugate carbanions $^-CHX_2$ (**XVI-2,2**)–(**XVI-39**): we then extended the study to several other systems (**XVI-4,5**)–(**XVI-6,14**), di-activated by two different groups. In a

---

† The doubly activated carbon acids $CH_2XY$ and their conjugate carbanions $^-CHXY$ have the variable substituents directly bonded to the reacting site: they can be incorporated, therefore, into the body of several other systems containing two contiguous functionalities G and X that we have studied previously.[7] Within such a body of compounds a roman number identifies the active site G and thus the 'family', while an arabic number identifies, whatever the family may be, the substituent X. In the present scheme the methylene disubstituted carbon acids (XV) and their corresponding carbanions are identified by two arabic numbers corresponding to the two substituents X and Y, as previously given.[7]

**Table 1.** Shielding contributions $A_i$ at C-1 in monosubstituted ethylenes.

| Substituent | $A_i$[a] |
|---|---|
| H | 0.00[b] |
| Cl | 3.30[c] |
| Br | −8.80[c] |
| OMe | 30.10[c] |
| Ph | 13.00[d] |
| $CONMe_2$ | 5.88[d] |
| $CO_2Me$ | 6.20[d,e] |
| $CO_2Et$ | 6.00[c] |
| COMe | 14.90[d] |
| COPh | 9.30[d] |
| CHO | 15.80[d] |
| $NO_2$ | 22.80[d] |
| CN | −14.60[d] |
| SOMe | 19.74[d] |
| $SO_2Me$ | 14.60[d] |
| SOPh | 20.18[f] |
| $SO_2Ph$ | 17.46[d] |
| $PO(OEt)_2$ | 3.95[d] |
| $2\text{–}C_6H_4N$ | 13.82[d] |
| $4\text{–}C_6H_4N$ | 12.70[g] |

[a] Positive values mean lowfield displacements. [b] Ethylene, δ(C) 122.8 J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 70. [c] N. Inamoto, S. Mazuda, K. Tori, and J. Nishikawa, *Tetrahedron Lett.*, 1983, **24**, 5265. [d] Reference 7 and references cited therein. [e] Reference 10(*a*) reports $A_i$ = 4.99 ppm. [f] This work. [g] From reference cited in (*b*), p. 250.

forthcoming paper we shall deal with cyanoactivated disubstituted carbon acids $CNCH_2X$ and related anions.[8]

The targets of the investigation were: (*i*) to ascertain whether there are important differences in the charge maps in the two solvents. (*ii*) To obtain evidence concerning the configuration (trigonal or tetrahedral) of the carbanionic carbon, particularly for those systems such as α-sulphinyl and α-sulphonyl carbanions that are reported[9] to be preferentially tetrahedral. Variation of the $^1J_{CH}$ coupling constants for the neutral precursors $CH_2X_2$ and $CH_2XY$ and their corresponding carbanions $^-CHX_2$ and $^-CHXY$ allows the monitoring of the configurational change by using the relationship $0.2\,^1J_{CH} = \Delta(\%s)$ that relates the coupling constant variation to the variation of the component of the s orbital of the involved carbon. (*iii*) To obtain, from the chemical shift of the carbanionic carbon of $^-CHX_2$ and for each functionality X, the charge demands $q_X$,* that is the fraction of the π charge transferred from the carbanionic carbon and delocalized to X. In the case of carbanions $^-CHX_2$ the electron density at the carbanionic carbon would be $q_C = 2 - 2q_X$, because of the equal partitioning of the charge transfer from $CH^-$ to the two functionalities X: the charge term of equation (1) would become $160(2 - 2q_X - 1)$ and equation (1) can be written as equation (2), from which, once known $\delta_\pm(^{13}C)$, $q_X$ can be obtained. A compilation of $q_X$ for a number of primary functionalities would offer the possibility of building up a

$$\delta_\pm(^{13}C) = 122.8 + 2A_X - 160(1 - 2q_X) \qquad (2)$$

relative rank of delocalizing capacities of X. (*iv*) To ascertain whether the charge demands $q_X$, as obtained from $^-CHX_2$, are useful for predicting the charge maps, and hence the chemical shifts of the carbanionic carbon in the unsymmetrically disubstituted systems $^-CHXY$: in this case equation (1) can be rewritten as equation (3). (*v*) To check whether the charge

$$\delta_\pm(^{13}C) = 122.8 + A_X + A_Y - 160(1 - q_X - q_Y) \qquad (3)$$

demands $q_X$ are coherent with the mesomeric $\sigma_R$- constants previously determined[7] for the same functionalities X when interacting with a nitrogen group as in PhNHX.

Before applying equations (1)–(3) to disubstituted carbanions, and assigning unconditional credit to the charge demands $q_X$, two assessments were, however, needed.

(*a*) In equation (1) it is assumed that the carbanionic carbon is trigonally hybridized and that its $^{13}C$ chemical shift is equal to the shift of ethylene (122.8 ppm) corrected by the shielding effects ($A_i$) of the groups X directly attached to it; the last term $k(q_C - 1)$ is a measure of the effect exerted by the negative charge. Since the numerical values of the shielding effects $A_X$ were obtained as the difference between the C-1 shift in 1-substituted ethylenes $CH_2{=}CHX$ and that of ethylene itself (122.8 ppm), equation (2) can be dependably applied provided that additivity of $A_X$ is verified for the shift of C-1 in 1,1-disubstituted ethylenes $CH_2{=}CX_2$. Despite the numerous studies on di-, tri-, and tetra-substituted ethylenes,[10] it seems that this aspect of shielding additivity has not been considered previously in a simple form. For this reason, the use of equations (1)–(3) needed a preliminary comparison of experimental and calculated values of C-1 shifts of a number of 1,1-disubstituted ethylenes. Unfortunately, many of the simple ethylenes, 1,1-disubstituted with electron-withdrawing groups (X = CN, COMe, $CO_2Me$, COPh) are unstable towards polymerization; for this reason we considered the stable, otherwise 1,1-disubstituted, ethylenes (**1**)–(**5**), the two 1,1-disubstituted-2-ethylethylenes (1,1-disubstituted 1-butenes) (**6**) and (**7**), and several 1,1-disubstituted-2-phenylethylenes (2,2-disubstituted styrenes) (**8**)–(**17**).

R–CH=CXY

(**1**) R = H; X = Y = Cl
(**2**) R = H; X = Y = Br
(**3**) R = H; X = Y = OMe
(**4**) R = H; X = Y = $SO_2Ph$
(**5**) R = H; X = Y = Ph
(**6**) R = Et; X = Y = CN
(**7**) R = Et; X = CN; Y = $CO_2Me$
(**8**) R = Ph; X = Y = $CO_2Et$
(**9**) R = Ph; X = Y = CN
(**10**) R = Ph; X = Y = COMe
(**11**) R = Ph; X = Y = COPh
(**12**) R = Ph; X = Y = $SO_2Ph$
(**13**) R = Ph; X = CN; Y = $CO_2Me$
(**14**) R = Ph; X = COMe; Y = $CO_2Et$
(**15**) R = Ph; X = COPh; Y = CN
(**16**) R = Ph; X = $PO(OEt)_2$; Y = CN
(**17**) R = Ph; X = $PO(OEt)_2$; Y = $CO_2Et$

(*b*) It is required in equations (1)–(3) that the difference $\delta_\pm(^{13}C) - (122.8 + \Sigma A_i)$ is due only to the effect of charge and not to special proximity effects exerted by the substituent X on the paramagnetic component of the carbon shift. As a consequence, in analogy with our previous work,[7] we looked for a correlation between the $^{13}C$ shift of the carbanionic carbon (C-α), and the $^1H$ shift of the proton bonded to (H-α). Indeed, the existence of such a correlation would provide evidence that the substituent affects, in a related way, both the diamagnetic term of the proton shielding and the blend of diamagnetic and paramagnetic terms of the carbon shift, thus disallowing special, specific contributions to the carbon shielding.

## Results

*Additivity of Shielding Effects.*—For compounds (**1**)–(**5**) the computed chemical shift of C-1 was obtained by adding the $A_i$ values[7] reported in Table 1 to the shift of ethylene (122.8 ppm), while for compounds (**6**) and (**7**) the alkenic $CH_2$ shift of butene (112.8 ppm)[11] and for compounds (**8**)–(**17**) the shift of the $CH_2$ of styrene (112.3 ppm)[11] were used. In Table 2 the experimental

---

* Although the $q_X$ values have been previously[7] defined as electron demands, it seems more convenient and accurate to call them charge demands: in this way the $q_X$ values are more clearly associated with the transfer of charge from the carbanionic centre.

**Table 2.** Experimental alkenic $^{13}C$ shifts and calculated C-1 shifts in 1,1-disubstituted ethylenes (**1**)–(**17**).

| Compound | Calc. C-1 | Experimental C-1 | C-2 |
|---|---|---|---|
| (**1**) | 129.40 | 127.10 | 113.30[a] |
| | | 125.90 | 112.10[b] |
| (**2**) | 105.20 | 97.00 | 127.20[c] |
| (**3**) | 183.00 | 161.38 | 54.50[d] |
| | | 167.90 | 54.70[b] |
| (**4**) | 157.72 | 153.63 | 138.07[e] |
| (**5**) | 148.80 | 150.10 | 114.10[f] |
| (**6**) | 83.60 | 89.48 | 170.66[e] |
| (**7**) | 104.40 | 108.84 | 164.66[e] |
| (**8**) | 126.30 | 126.53 | 141.95[e] |
| | | 126.60 | 142.00[g] |
| (**9**) | 83.10 | 82.87 | 159.94[e] |
| | | 87.70 | 160.10[g] |
| (**10**) | 142.10 | 142.70 | 139.43[e] |
| | | 142.90 | 139.70[g] |
| (**11**) | 130.90 | 139.22 | 143.41[e] |
| (**12**) | 147.22 | 144.31 | 151.95[e] |
| (**13**) | 103.90 | 102.53 | 155.30[e] |
| | | 103.20 | 154.90[g] |
| (**14**) | 133.40 | 134.80 | 141.30[g] |
| (**15**) | 107.00 | 110.30 | 155.40[g] |
| (**16**) | 101.65 | 100.80 | 158.60[g] |
| (**17**) | 122.45 | 125.00 | 147.90[g] |

[a] G. Miyajima and K. Takahashi, *J. Phys. Chem.*, 1971, **75**, 331; [b] H.-O. Kalinowski, S. Berger, and S. Braun, 'Carbon-13 NMR Spectroscopy,' Wiley, Chichester, 1984, p. 294. [c] G. Miyajima and K. Takahashi, *J. Phys. Chem.*, 1971, **75**, 3766; [d] E. Taskinen and M. L. Pentikainen, *Tetrahedron*, 1978, **34**, 2365. [e] This work. [f] T. W. Proulx and W. B. Smith, *J. Magn. Reson.*, 1976, **23**, 477; [g] Reference 10(*b*).

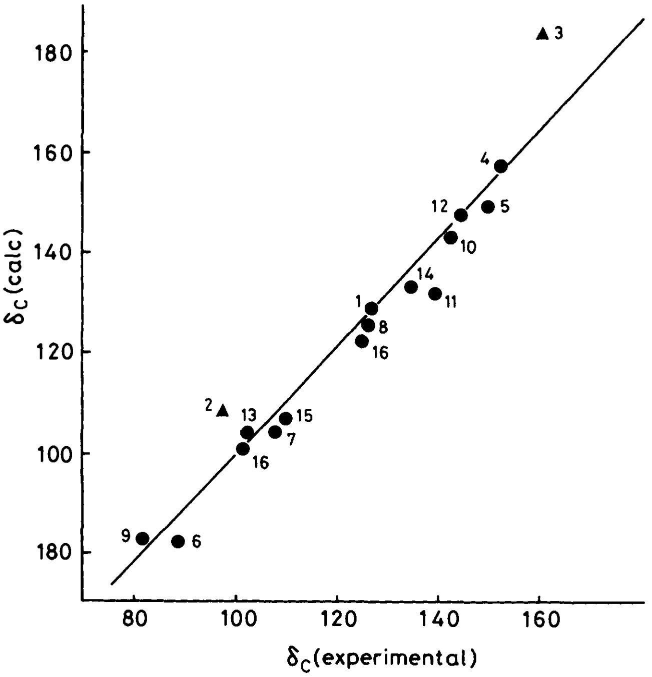


**Figure 1.** Plot of the experimental C-1 shift of 1,1-disubstituted ethylenes (**1**)–(**17**) *vs.* the values calculated by adding the shielding contributions $A_i$ of Table 1 to the methylene $^{13}C$ shift of the related ethylenes $RCH{=}CH_2$. Numbers correspond to the products of Table 2. See the text for the fitting parameter.

chemical shifts of the alkenic carbons of compounds (**1**)–(**17**), together with the computed values for C-1 are reported.

While for the majority of di- and tri-substituted ethylenes the peak assignment is straightforward, a comment is deserved for the discrimination, among quaternary carbons of compounds (**11**)–(**12**), of the *ipso* aromatic carbons from the alkenic carbon C-1. In both cases C-1 and C-2 are unequivocally assigned on the basis of their multiplicity: the three C(*ipso*) carbons are present as triplets with $^3J_{CH}$ 6.7 Hz due to coupling with *meta* protons of the ring. In compound (**11**), C-2 is long-range coupled with the *ortho* hydrogens of the adjacent phenyl ring ($^1J_{CH}$ 156.3; $^3J_{CH}$ 3.2 Hz), while C-1 resonates as a doublet ($^2J_{CH}$ 2.1 Hz). In compound (**12**) the patterns are similar but the values of the coupling constants are slightly different: for C-1, $^2J_{CH}$ 4.2, for C-2, $^1J_{CH}$ 159.5, $^3J_{CH}$ 4.6 Hz.

A good linear relationship (Figure 1) is obtained by plotting the experimental *vs.* the computed C-1 shifts ($n = 17$, $r = 0.973$): once the somewhat deviant points due to compounds (**2**) and (**3**) are excluded, the linearity of the relationship $\delta_{calc} = (1.03 \pm 0.04)\ \delta_{exp} - (5.12 \pm 0.87)$, ($n = 15, r = 0.990$) is highly satisfactory, showing an expected slope of 1. The reason for the deviation of additivity of 1,1-dibromoethene and 1,1-dimethoxyethene is probably due to high steric hindrance caused by these two large substituents: the other compound coming next and barely obeying additivity is β,β-dibenzoylstyrene (**11**), for which the coplanarity of the π system is probably also severely hampered.

*NMR Spectra of the Carbanions.—General.* Data for the neutral precursors (**XV**) are in Tables 3 and 4 while those for the anions are in Tables 5 and 6. Carbanions (**XVI**) were prepared as before[6,7] as 0.33 mol dm$^{-3}$ solutions in $Me_2SO$, using a solution of $Na^+(CH_2OSMe)^-$ (0.66 mol dm$^{-3}$). Spectra of the carbanions in MeOH were obtained by adding a known aliquot of the methanolic solution of the carbon acid to sodium methoxide solutions. This procedure allowed the addition of the carbon acid to a solution of excess base affording clean solutions containing exclusively the deprotonated carbon acid, along with an excess of sodium methoxide. With the reverse addition, instead, we frequently observed either retro-Claisen reactions (β-dicarbonyl compounds) or condensation reactions (malononitrile). In the preparation of the anions in MeOH, a compromise had to be reached among the following variables. (*i*) Sodium methoxide solutions had not to be too concentrated, in order to avoid excessive viscosity and extensive aggregation of the carbanion salt. (*ii*) A lower limit of substrate concentration of 0.33 mol dm$^{-3}$ was needed, to maintain a uniform concentration of the active species in all experiments. (*iii*) Identical base concentrations for all the substrates, to standardize the experimental conditions. We chose to run the spectra in MeOH solutions for which the final concentration of MeONa was 2 mol dm$^{-3}$. According to More O'Ferrall,[12] the $H_-$ value of these solutions is *ca.* 18. The relationship $H_-$ (MeOH) = $pK_a$(MeOH) + log $[^-CHX_2]/[CH_2X_2]$ indicates that $H_- = 18$ would provide, for a carbon acid with a $pK_a$(MeOH) of 16, an ionization ratio of *ca.* 100, that is, more than 99% of the carbon acid would be ionized. Although only a limited number of $pK_a$s are available in MeOH for di-activated carbon acids $CH_2X_2$ and $CH_2XY$, the fact that all the shifts of the anions in MeOH are almost coincident with those in $Me_2SO$ is evidence that in the former solvent the carbon acids are completely ionized.

As reported in Tables 5 and 6 for a number of carbanions in MeOH with X and Y equal to $SO_nR$ ($n$ = 1,2; R = Me,Ph), CN, and $CO_2Me$, the $^1J_{CH}$ vanishes: this must be due to a lifetime of the carbanionic species smaller than $1/^1J_{CH}$, that is, *ca.* 1/150 s$^{-1}$ ~ $6 \times 10^{-3}$ s$^{-1}$. It appears that in observing the $^1J_{CH}$ coupling in the protic solvent, a true enolate structure is

**Table 3.** $^{13}C$ Data for neutral di-activated symmetrical carbon acids $CH_2X_2$.[a]

| X | Solvent | $CH_2$ | $^1J$/Hz | Other groups | | | |
|---|---|---|---|---|---|---|---|
| Ph | $Me_2SO$ | 41.08 | 127.2 | $C_x$ = 141.16 | $C_o$ = 128.60 | $C_m$ = 128.31 | $C_p$ = 125.85 |
| $CONMe_2$ | MeOH | 38.90 | 128.5 | CO = 167.40 | Me = 33.50, 35.91 | | |
| | $Me_2SO$ | 40.29 | 128.6 | CO = 167.03 | Me = 34.71, 37.13 | | |
| $CO_2Me$ | MeOH | 39.55 | 132.6 | CO = 166.72 | Me = 50.75 | | |
| | $Me_2SO$ | 40.69 | 132.5 | CO = 166.86 | Me = 52.03 | | |
| COMe | MeOH | 98.91[b] | 167.0 | CO = 190.86 | Me = 22.48 | | |
| | | 56.42[c] | 128.0 | CO = 202.70 | Me = 28.53 | | |
| | $Me_2SO$ | 100.47[d] | 167.5 | CO = 191.14 | Me = 24.45 | | |
| | | 57.81[e] | 128.5 | CO = 203.24 | Me = 30.65 | | |
| COPh | $Me_2SO$ | 92.26[f] | 166.2 | CO = 185.26 | $C_x$ = 134.67 | $C_o$ = 127.37 | $C_m$ = 128.77<br>$C_p$ = 132.40 |
| CN | MeOH | 6.27 | 144.0 | CN = 111.27 | | | |
| | $Me_2SO$ | 8.40 | 144.2 | CN = 111.88 | | | |
| $SO_2Me$ | $Me_2SO$ | 70.15 | 145.9 | Me = 41.79 | | | |
| ±-SOPh | $Me_2SO$ | 79.38 | 151.3 | $C_x$ = 142.67 | $C_o$ = 124.19 | $C_m$ = 129.21 | $C_p$ = 131.23 |
| *meso*-SOPh | $Me_2SO$ | 76.47 | 150.0 | $C_x$ = 142.82 | $C_o$ = 124.50 | $C_m$ = 129.24 | $C_p$ = 131.22 |
| $SO_2Ph$ | MeOH | 72.08 | 146.2 | $C_x$ = 138.03 | $C_o$ = 127.55 | $C_m$ = 128.08 | $C_p$ = 133.39 |
| | $Me_2SO$ | 71.95 | 146.5 | $C_x$ = 138.92 | $C_o$ = 128.26 | $C_m$ = 129.02 | $C_p$ = 134.32 |
| $PO(OEt)_2$ | $Me_2SO$ | 26.39 | | $CH_2$ = 61.80 | Me = 16.25 | | |
| | $Me_2SO$[g] | 23.74 | | $CH_2$ = 61.61 | Me = 16.07 | | |
| $CO(CH_2)_3CO$ | MeOH | 102.99[f] | 159.2 | C(4) = C(6) = 31.65 | C(5) = 20.69 | CO = 191.86 | |
| | $Me_2SO$ | 103.76[f] | 158.7 | C(4) = C(6) = 32.06 | C(5) = 20.78 | CO = 187.87 | |

[a] Shifts in $Me_2SO$ are referred to external $Me_4Si$; shifts in MeOH are referred to external $Me_4Si$ in $Me_2SO$; $C_x$ is the quaternary carbon of an aromatic ring; [b] Enolic form (30%); [c] Ketonic form (70%); [d] Enolic form (60%); [e] Ketonic form (40%); [f] Enolic form only. [g] T. Bottin-Strzalko, J. Corset, F. Froment, M.-J. Pouet, J. Seyden-Penne, and M.-P. Simmonin, *Phosphorus Sulfur*, 1985, **22**, 217.

**Table 4.** $^{13}C$ data for neutral di-activated non-symmetrical carbon acids $CH_2XY$.[a]

| X,Y | Solvent | $CH_2$ | $^1J$/Hz | Other groups | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $CO_2Me$,COMe | MeOH | 47.79 | 131 | CO = 200.90 | $CO_2$ = 167.27 | Me = 27.83 | Me = 50.34 | | |
| | $Me_2SO$ | 49.33[b] | 131 | CO = 201.32 | $CO_2$ = 167.65 | Me = 29.95 | Me = 51.71 | | |
| | | 88.86[c] | — | CO = 172.55 | $CO_2$ = 167.55 | Me = 20.09 | Me = 51.71 | | |
| $CO_2Et$,COPh | MeOH | 44.34[b] | [d] | CO = 192.53 | $CO_2$ = 167.78 | $C_x$ = 135.22 | $C_o$ = 127.28 | $C_m$ = 127.55 | $C_p$ = 132.55 |
| | | | | $CH_2$ = 60.07 | Me = 12.11 | | | | |
| | | 85.84[c] | 161 | $CH_2$ = 59.15 | Me = 13.34 | | | | |
| | $Me_2SO$ | 45.47[b] | 131 | CO = 193.35 | $CO_2$ = 167.56 | $C_x$ = 135.78 | $C_o$ = 128.31 | $C_m$ = 128.72 | $C_p$ = 133.66 |
| | | | | $CH_2$ = 60.51 | Me = 13.87 | | | | |
| | | 86.90[c] | — | $CH_2$ = 55.90 | Me = 14.44 | | | | |
| $CO_2Et$,SOPh | MeOH | 59.55 | 143 | CO = 164.14 | $C_x$ = 141.54 | $C_o$ = 123.49 | $C_m$ = 128.57 | $C_p$ = 131.05 | |
| | | | | $CH_2$ = 60.91 | Me = 12.26 | | | | |
| | $Me_2SO$ | 60.23 | 143 | CO = 164.90 | $C_x$ = 143.28 | $C_o$ = 124.20 | $C_m$ = 129.15 | $C_p$ = 131.24 | |
| | | | | $CH_2$ = 61.07 | Me = 13.80 | | | | |
| $CO_2Et$,$SO_2Ph$ | MeOH | 59.36 | 141 | CO = 161.81 | $C_x$ = 138.19 | $C_o$ = 126.10 | $C_m$ = 128.10 | $C_p$ = 133.11 | |
| | | | | $CH_2$ = 60.88 | Me = 11.88 | | | | |
| | $Me_2SO$ | 59.75 | 141 | CO = 162.47 | $C_x$ = 138.92 | $C_o$ = 127.97 | $C_m$ = 129.16 | $C_p$ = 134.06 | |
| | | | | $CH_2$ = 61.37 | Me = 13.56 | | | | |
| $CO_2Et$,$PO(OEt)_2$ | $Me_2SO$[e] | 33.25 | 131 | CO = 166.15 | Me = 52.05 | $CH_2$ = 61.95 | Me = 16.05 | | |
| COMe,$SO_2Ph$ | MeOH | 65.52 | 139 | CO = 195.81 | $C_x$ = 138.37 | $C_o$ = 127.00 | $C_m$ = 128.18 | $C_p$ = 133.06 | Me = 29.14 |
| | $Me_2SO$ | 65.97 | 139 | CO = 196.95 | $C_x$ = 139.29 | $C_o$ = 127.71 | $C_m$ = 129.24 | $C_p$ = 133.96 | Me = 31.07 |
| COMe,$PO(OEt)_2$ | $Me_2SO$[f] | 42.30 | 129 | CO = 200.12 | Me = 31.07 | $CH_2$ = 61.72 | Me = 16.09 | | |
| COPh[g],$SO_2Ph$ | $Me_2SO$ | 62.15 | 139 | CO = 188.94 | $C_x$ = 139.47 | $C_{x'}$ = 135.66 | $C_o$ = 127.92 | $C_{o'}$ = 128.62 | $C_m$ = 128.99 |
| | | | | $C_{m'}$ = 129.08 | $C_p$ = 134.05 | $C_{p'}$ = 135.88 | | | |

[a] Shifts in $Me_2SO$ are referred to external $Me_4Si$; shifts in MeOH are referred to external $Me_4Si$ in $Me_2SO$; $C_x$ is the quaternary carbon of an aromatic ring. [b] Ketonic form. [c] Enolic form. [d] Covered by solvent peaks. [e] T. Bottin-Strzalko, J. Corset, F. Froment, M.-J. Pouet, J. Seyden-Penne, and M.-P. Simonnin, *J. Org. Chem.*, 1980, **45**, 1270. [f] T. Bottin-Strzalko, J. Seyden-Penne, M.-J. Pouet, and M.-P. Simonnin, *Org. Magn. Reson.*, 1982, **19**, 69. [g] Identified with primed letters.

necessary, as in the acetylacetone anion, methyl acetoacetate, and the like. Implications of this interesting observation will be discussed later in terms of structural reorganization of the carbanion.

All the symmetrically and unsymmetrically disubstituted carbanions give rise, both in MeOH and in $Me_2SO$, to a single set of resonances: there are two notable exceptions, *viz.* the anion of ethyl phenylsulphonylacetate in MeOH and of ethyl phenylsulphinylacetate both in MeOH and $Me_2SO$. For these species there are two enolate isomers which are non- or slowly-interconverting on the NMR time scale.

The carbanionic carbons flanked by two carbonyl groups display sizeable low-field shifts relative to the methylene of the neutral precursor but a slight upfield shift relative to the alkenic carbon of the tautomeric enol form eventually present in the neutral species. Conversely, methylenes flanked by two sulphonyl or sulphinyl groups experience an upfield shift in the corresponding anions. Small to moderate low-field shifts are

**Table 5.** $^1H$ and $^{13}C$ data of symmetrically di-activated carbanions $^-CHX_2$ sodium salts.[a]

| X | Solvent | $CH^-$ | $CH^-$ | $^1J$/Hz | Other groups | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ph | $Me_2SO$ | 4.17 | 80.30 | 147.5 | $C_x$ = 145.20 | $C_o$ = 116.10 | | $C_m$ = 127.50 | $C_p$ = 105.70 |
| $CONMe_2$ | $Me_2SO$ | 3.80 | 62.51 | 148.8 | CO = 171.56 | Me = 36.60 | | | |
| $CO_2Me$ | MeOH | | 59.68 | *b* | CO = 172.51 | Me = 48.27 | | | |
| | $Me_2SO$ | 3.65 | 60.87 | 157.8 | CO = 170.55 | Me = 47.87 | | | |
| COMe | MeOH | | 97.71 | 151.8 | CO = 189.86 | Me = 26.79 | | | |
| | $Me_2SO$ | 4.90 | 96.56 | 150.7 | CO = 186.17 | Me = 28.97 | | | |
| COPh | $Me_2SO$ | 6.30 | 90.58 | 150.0 | CO = 182.33 | $C_x$ = 143.90 | $C_o$ = 126.30 | $C_m$ = 127.40 | $C_p$ = 128.47 |
| CN | MeOH | | −0.78 | *b* | CN = 130.31 | | | | |
| | $Me_2SO$ | 1.12 | −0.25 | 175.3 | CN = 130.36 | | | | |
| $SO_2Me$ | MeOH | | 62.36 | *b* | Me = 45.74 | | | | |
| | $Me_2SO$ | | 63.94 | 176.6 | Me = 47.14 | | | | |
| (±)-SOPh | $Me_2SO$ | | 77.76 | 171.0 | $C_x$ = 152.00 | $C_o$ = 126.12 | | $C_m = C_p$ = 127.96 | |
| *meso*-SOPh | $Me_2SO$ | 3.80 | 80.84 | 168.2 | $C_x$ = 151.80 | $C_o$ = 125.83 | | $C_m = C_p$ = 127.83 | |
| $SO_2Ph$ | MeOH | | 63.62 | *b* | $C_x$ = 145.57 | $C_o$ = 124.60 | | $C_m$ = 127.80 | $C_p$ = 130.35 |
| | $Me_2SO$ | 3.80 | 63.65 | 175.8 | $C_x$ = 149.63 | $C_o$ = 124.84 | | $C_m$ = 127.40 | $C_p$ = 124.84 |
| $CO(CH_2)_3CO$ | MeOH | | 101.89 | | C(4) = C(6) = 34.34 | C(5) = 21.39 | CO = 196.26 | | |
| | $Me_2SO$ | 4.60 | 101.25 | 149.8 | C(4) = C(6) = 36.26 | C(5) = 22.03 | CO = 191.95 | | |
| $PO(OEt)_2$[c] | $Me_2SO$ | 0.35 | 9.64 | 143.8 | $CH_2$ = 58.48 | Me = 16.42 | | | |

[a] External reference: $Me_2SO$ (39.5 ppm) relative to $Me_4Si$ (0.0 ppm); [b] Under conditions of fast reprotonation; [c] Potassium salt, reference (*g*) of Table 4.

**Table 7.** Charge demands of primary organic functionalities in $^-CHX_2$, and $PhCH^-X$, and mesomeric electron demands $\sigma_{R^-}$.

| X | $q_X$ in $^-CHX_2$ | $q_X$ in $PhCH^-X$ | $\sigma_{R^-}$ |
|---|---|---|---|
| Ph | 0.29 | 0.29 | 0.26 |
| $CONMe_2$ | 0.275 | 0.42 | 0.40 |
| $CO_2Me$ | 0.268 | 0.40 | 0.39 |
| COMe | 0.325 | 0.51 | 0.47 |
| COPh | 0.341 | 0.56 | 0.52 |
| CN | 0.207 | 0.28 | 0.33 |
| $SO_2Me$ | 0.225 | 0.27 | 0.33 |
| SOPh | 0.243 *meso* 0.233 (±) | 0.26 | 0.26 |
| $SO_2Ph$ | 0.206 | 0.28 | 0.34 |
| $PO(OEt)_2$ | 0.122 | 0.26 | 0.29 |

caused by the $CH^-$ carbons contiguous to a carbonyl on one side and to sulphinyl, sulphonyl, and diethoxyphosphonyl groups on the other side. It is, therefore, evident that shift displacements between the anion and the neutral cannot be taken as a probe for rehybridization.

Larger $^1J_{CH}$ coupling constants are found for the $CH^-$ carbanionic carbon relative to the couplings of the methylenes in the corresponding neutral systems: the increments range from a minimum of 16.4 Hz for bis(diethoxyphosphonyl)methane to a maximum of 30.9 Hz for malononitrile.

C(α)–H(α) *Relationship*.—As reported in Figure 2, only seven data points of the thirteen available both for C(α) and H(α) shifts of the carbanionic centre provide an excellent straight line: C(α) = 25.28 H(α) − 30.32 ($r$ = 0.997). Inclusion of the point for the diphenylmethyl carbanion does not alter substantially the fitting parameters (slope = 25.78, intercept = −30.58) while affecting somehow the correlation coefficient ($r$ = 0.985). It is worth noting that the *ca.* 25-fold greater sensitivity to substitution displayed by carbon relative to the proton of the carbanionic centre is numerically almost identical with what we have already found in α-substituted benzylcarbanions $PhCH^-X$.[7] The other data points show deviations possibly due to proximity effects operating on proton shifts; among these, three carbanionic centres are contiguous to a benzoyl group and a ring current effect exerted by the phenyl ring as in the conformation shown in Figure 3 is likely to be responsible for the displacement of H(α) to a field lower than expected.

## Discussion

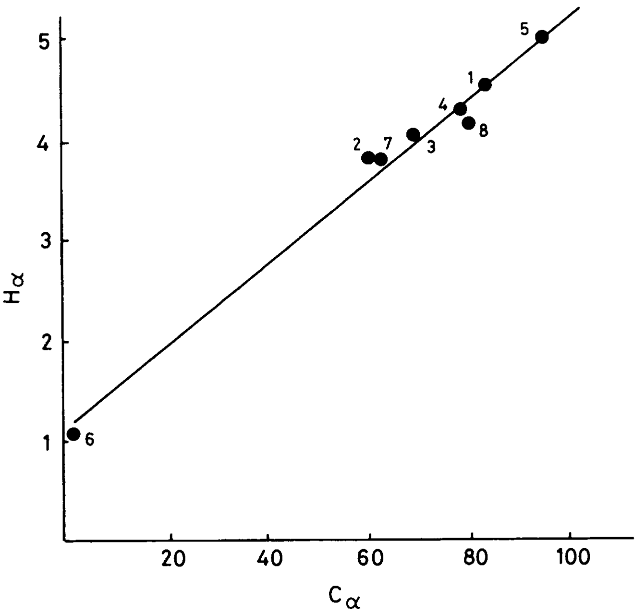
*Solvent Effects*.—Only small differences are recorded for the shifts in the two solvents $Me_2SO$ and MeOH: this is clear evidence from equation (1) that the π-electron density at the carbanionic site is only negligibly affected by the different solvation of the species in the two media. In any case the carbanionic carbon does not appear to be engaged in hydrogen-bonding processes: should these occur, electronegative atoms of the X and Y functionalities would be involved. Indeed, data of Tables 5 and 6 show that the carbonyl $^{13}C$ shifts are relatively more sensitive to the variation of the solvent than the carbanionic carbon. The $^{13}C$ shifts of the carbonyl groups show dichotomous behaviour: the ketone carbonyls (acetyl, benzoyl) show a sizeable (10–15 ppm) upfield shift upon deprotonation of the contiguous methylene, while carbonyls of ester and carboxamido groups show a small but systematic low-field shift. Since carbon shifts of carbonyl groups may depend, in a variable way, on σ- and π-electron densities,[13] no interpretation of these variations in quantitative terms is available. Our findings, however, qualitatively support the idea that neither the acidity increase of acetylacetone by several powers of ten on going from $Me_2SO$ to MeOH,[4a,b] nor the different C/O isomer ratio[5a] of its reactions with electrophiles is governed by the π-electron density along the delocalized system: instead they support the theory, intuitively and elegantly proposed by Kornblum[5c] over 20 years ago, that solvation is primarily responsible for the different behaviour in the two media. Alternatively, when the X and Y groups in di-activated carbanions are reluctant to delocalize the negative charge as in the case of third-row element functionalities [$SO_nR$, $n$ = 1,2, $PO(OEt)_2$, and for CN], the present results indicate that the carbanions are not differently solvated in the two media. In accordance with this, the acidities in protic solvents of malononitrile [$pK_a(H_2O)$ = 11.2][14] and of bis(methylsulphonyl)methane [$pK_a(H_2O)$ = 14][15] are quite close to the values in $Me_2SO$[4b] (11.1 and 14.4 for malononitrile and bis(ethylsulphonyl)methane respectively).

*Structural Reorganization in the Carbanions*.—The $^1J_{CH}$ increase of every carbanionic carbon relative to its precursor is of 20–30 Hz: although the expected variation of $^1J_{CH}$ would be of *ca.* 40 Hz for a complete (Δ%$s$ = 8) pyramidal to trigonal carbon rehybridization, there are literature indications[16] that excess of negative charge tends to decrease the $^1J_{CH}$ values in

**Table 6.** $^{13}C$ and $^{1}H$ data of asymmetrically di-activated carbanions $^{-}CHXY$ sodium salts.[a]

| X, Y | Solvent | C*H*$^-$ | *C*H$^-$ | $^1J$/(Hz) | Other groups | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CO_2Me$, COMe | MeOH | | 81.20 | 157.3 | CO = 186.33 | $CO_2$ = 170.71 | Me = 26.42 | Me[b] | | | |
| | $Me_2SO$ | 4.28 | 79.75 | 154.7 | CO = 185.45 | $CO_2$ = 178.56 | Me = 28.67 | Me = 47.87 | | | |
| $CO_2Et$, COPh | MeOH | | 80.63 | 157.3 | CO = 182.58 | $CO_2$ = 171.14 | $C_x$ = 143.61 | $C_p$ = 127.35 | $C_m$ = 126.59 | $C_o$ = 125.25 | |
| | | | | | $CH_2$ = 56.46 | Me = 13.17 | | | | | |
| | $Me_2SO$ | 4.90 | 78.26 | 154.3 | CO = 180.09 | $CO_2$ = 169.61 | $C_x$ = 144.10 | $C_p$ = 127.97 | $C_m$ = 127.32 | $C_o$ = 125.96 | |
| | | | | | $CH_2$ = 55.88 | Me = 14.88 | | | | | |
| $CO_2Et$, SOPh | MeOH[d] | | 62.63 | *c* | CO = 170.99 | $C_x$ = 146.64 | $C_p$ = 130.10 | $C_m$ = 128.27 | $C_o$ = 123.15 | $CH_2$ = 55.94 | Me = 16.96 |
| | *e* | | 67.60 | | CO = 170.46 | $C_x$ = 146.36 | $C_p$ = 127.76 | $C_m$ = 127.25 | $C_o$ = 124.12 | $CH_2$ = 55.94 | Me = 16.96 |
| | $Me_2SO$[d] | 4.00 | 71.70 | 168.2 | CO = 167.78 | $C_x$ = 152.20 | $C_p$ = 127.20 | $C_m$ = 127.55 | $C_o$ = 125.00 | $CH_2$ = 55.70 | Me = 15.30 |
| | *e* | | 69.72 | 170.0 | CO = 168.98 | $C_x$ = 151.60 | $C_p$ = 127.20 | $C_m$ = 127.55 | $C_o$ = 125.00 | $CH_2$ = 55.70 | Me = 15.30 |
| $CO_2Et$, $SO_2Ph$ | MeOH[f] | | 62.22 | *c* | CO = 169.37 | $C_x$ = 138.71 | $C_p$ = 128.26 | $C_m$ = 127.11 | $C_o$ = 124.22 | $CH_2$ = 48.72 | Me = 16.89 |
| | *g* | | 61.40 | *c* | CO = 166.45 | $C_x$ = 147.43 | $C_p$ = 129.23 | $C_m$ = 127.11 | $C_o$ = 126.83 | $CH_2$ = 48.72 | Me = 16.89 |
| | $Me_2SO$ | 3.80 | 62.42 | 170.5 | CO = 167.25 | $C_x$ = 150.02 | $C_p$ = 129.26 | $C_m$ = 127.84 | $C_o$ = 124.78 | $CH_2$ = 55.29 | Me = 14.98 |
| $CO_2Me$, $PO(OEt)_2$ | $Me_2SO$[h] | | 37.40 | 152.3 | CO = 168.70 | Me = 16.60 | $CH_2$ = 58.20 | Me = 47.40 | | | |
| | | | 36.00 | | CO = 169.30 | Me = 16.60 | $CH_2$ = 58.20 | Me = 47.70 | | | |
| COMe, $SO_2Ph$ | MeOH | | 83.65 | 172.1 | CO = 182.95 | $C_x$ = 146.24 | $C_p$ = 129.73 | $C_m$ = 127.17 | $C_o$ = 124.41 | | |
| | $Me_2SO$ | 4.48 | 84.03 | 170.0 | CO = 181.16 | $C_x$ = 148.76 | $C_p$ = 129.79 | $C_m$ = 127.86 | $C_o$ = 125.03 | | |
| COMe, $PO(OEt)_2$ | $Me_2SO$[i] | | 63.30 | 152.0 | CO = 184.29 | Me = 28.78 | $CH_2$ = 58.75 | Me = 16.33 | | | |
| | | | 64.70 | *j* | CO[j] | Me = 25.78 | $CH_2$ = 58.41 | Me = 16.43 | | | |
| COPh,[k] $SO_2Ph$ | $Me_2SO$ | 5.25 | 83.44 | 169.3 | CO = 176.24 | $C_x$ = 148.33 | $C_{x'}$ = 142.16 | $C_p$ = 129.92 | $C_{p'}$ = 129.51 | $C_m$ = 127.84 | |
| | | | | | $C_{m'}$ = 127.37 | $C_o$ = 125.98 | $C_{o'}$ = 125.15 | | | | |

[a] External reference: $Me_2SO$ (39.5 ppm) relative to $Me_4Si$ (0.0 ppm). [b] Covered by solvent. [c] Under fast exchange. [d] *E* form: 45% MeOH, 30% $Me_2SO$. [e] *Z* form 55% MeOH, 70% $Me_2SO$. [f] *E* form: 45%. [g] *Z* form: 55%. [h] Potassium as counter-ion, reference (*f*) of Table 4. [i] Reference (*e*) of Table 4. [j] Not observed. [k] Identified with primed letters.



1: X = $SO_2Ph$ Y = COMe
2: X = $SO_2Ph$ Y = $CO_2Et$
3: X = SOPh Y = $CO_2Et$
4: X = COMe Y = $CO_2Me$
5: X = Y = COMe
6: X = Y = CN
7: X = Y = $CONMe_2$
8: X = Y = Ph

**Figure 2.** Plot of $^{13}C$ shift of the carbanionic carbon C(α) *vs.* the $^1H$ shift of the proton attached to, H(α).

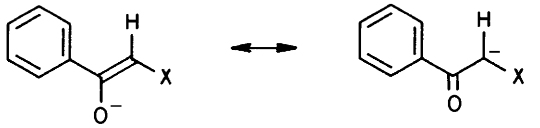


**Figure 3.** Possible spatial arrangement of the enolate of α-benzoylcarbanions.

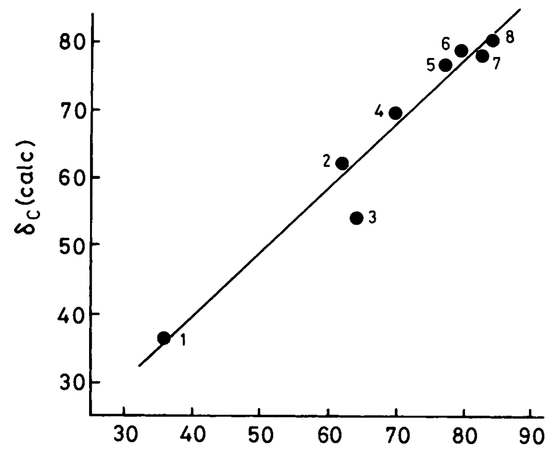
**Table 8.** Comparison of experimental and calculated $^{13}C$ shifts of the carbanionic carbon in $^-CHXY$ as given by equation (3).

| X, Y | Calc | Experimental |
|---|---|---|
| $CO_2Me$, COMe | 78.78 | 79.75 |
| $CO_2Et$, COPh | 75.74 | 78.26 |
| $CO_2Et$, SOPh | 70.14 | 71.70; 69.72 |
| $CO_2Et$, $SO_2Ph$ | 62.30 | 62.42 |
| $CO_2Me$, $PO(OEt)_2$ | 35.35 | 37.40; 36.00 |
| COMe, $SO_2Ph$ | 80.12 | 84.03 |
| COMe, $PO(OEt)_2$ | 53.17 | 63.30; 64.70 |
| COPh, $SO_2Ph$ | 77.02 | 83.44 |

trigonal carbons. To support this point further, it is convenient to compare the coupling constants of the alkenic carbon of the enol forms of (**XV–5,5**), (**XV–6,6**), and (**39**) (Table 3) with those of the corresponding anions (**XVI**): it is immediately evident that the presence of the charge on the same trigonal carbon decreases the $^1J_{CH}$ coupling of 10–17 Hz. This is not confined to oxo-carbanions since the same trend is observed in nitro-anions[17] such as those derived from benzaldehyde phenylhydrazones ($^1J_{CH}$ 5 Hz). Taking this into account, an increase of $^1J_{CH}$ of *ca.* 20 Hz on going from any neutral to the corresponding anion should be considered evidence for a trigonal configuration of the carbanionic carbon. This consideration leads to the important conclusion that carbanions stabilized by groups containing oxidized third-row elements (sulphinyl, sulphonyl, phosphonyl) are trigonal.[9c] This contrasts sharply with Cram's earlier proposal[9b] for a tetrahedral arrangement in the anion of bis(methylsulphonyl)methane. Since $^{13}C$ shifts of sulphonyl and sulphinyl stabilized carbanions are insensitive to the nature of the solvent, it must be concluded that any alleged specific solvation plays an irrelevant role in determining the configuration of the anions. All this raises doubts concerning isotope exchange reactions at chiral centres adjacent to sulphonyl and sulphinyl functionalities, previously interpreted with the intermediacy of tetrahedral carbanions. In this context the short lifetime, on the NMR time scale, of disulphonyl and dicyano carbanions in the protic solvent MeOH is interesting because it points to the fact that these anions, although trigonal, reprotonate extremely quickly: indeed most of the negative charge formed upon deprotonation resides on the carbanionic carbon. The proposal of Hibbert[18] that these anions undergo 'negligible structural reorganization' relative to their precursors should be looked at with the above discussion in mind.

While anions of β-dicarbonyl compounds have been thoroughly investigated[19] in protic solvents and evidence for geometrical isomers has been obtained only at low temperature,[20] so far we do not know whether the single set of resonances of the anions of β-keto sulphones are due to the presence of one isomer only or whether a rapid interconversion of the *E* and *Z* isomers is occurring. Unfortunately, the high freezing point of $Me_2SO$ prevents any low temperature investigation of the anions. In this frame it is peculiar that the phenylsulphonyl and phenylsulphinyl groups contiguous to the ethoxycarbonyl moiety induce a sufficiently high barrier in the interconversion of the *Z* and *E* isomers. Further experimental results are needed before understanding the factors governing the stability and structure of such anions.

*Charge Demands* $q_X$, *Shift Predictivity, and Saturation Phenomena.*—The proven additivity of shielding effects of substituents at the same trigonal carbon, the proven trigonal configuration of $^-CHX_2$ and $^-CHXY$ anions, the circumstantial evidence that the term $\delta_{\pm}(^{13}C) - (122.8 + \Sigma A_i)$ is solely due to charge effects, all provide unconditional support to the determination of charge demands $q_X$ through equation (2). The $q_X$ values for $^-CHX_2$, those previously obtained from benzylcarbanions $PhCH^-X$ (**VI**)[7] (here designated $q_X{}^{Ph}$), and the mesomeric electron demands $\sigma_{R^-}$[7] are collected altogether in Table 7. The $q_X$ values can be used to predict, through equation (3), the chemical shift of the carbanionic carbon in $^-CHXY$. Table 8 compares the computed and the experimental values, while Figure 4 reports the relative plot. It can be seen that the linearity is highly satisfactory ($\delta_{exp} = 1.005\ \delta_{calcd} + 2.807$, $r = 0.975$, $n = 8$; exclusion of the (**5,16**) point leads to $\delta_{exp} = 1.075\ \delta_{calcd} - 3.001$, $r = 0.993$, $n = 7$). Despite the good predictive power that the $q_X$ values can offer, they should not be considered a constant of each group X. This result is quite evident on comparing their numerical values with those of $q_X^{Ph}$: the $q_X$ are considerably smaller. The plot of Figure 5 shows, however, that the charge demands do not vary at random: the slope of the line $q_X^{Ph} = 2.216\ q_X - 0.205$ ($n = 8$, $r = 0.996$) indicates that each group X is twice as powerful in dissipating (or withdrawing) the negative charge from the carbanionic carbon in $PhCH^-X$ than in $^-CHX_2$. As already pointed out,[21] we believe this is a manifestation of a saturation phenomenon: the partitioning of the charge between the X and Y groups is mutually conditional. Also, the apparent deviation of the Ph and $PO(OEt)_2$ groups in the plot of Figure 5 should be interpreted in terms of saturation effects once it is considered they are among the weakest groups in transferring the charge. In



| X | Y |
|---|---|
| 1: $CO_2Me$ | $PO(OEt)_2$ |
| 2: $CO_2Me$ | $SO_2Me$ |
| 3: COMe | $PO(OEt)_2$ |
| 4: $CO_2Me$ | SOPh |
| 5: $CO_2Me$ | COPh |
| 6: $CO_2Me$ | COMe |
| 7: COPh | $SO_2Ph$ |
| 8: COMe | $SO_2Ph$ |

**Figure 4.** Plot of the experimental carbanionic $^{13}C$ shift of $^-CHXY$ *vs* the values calculated by equation (3).

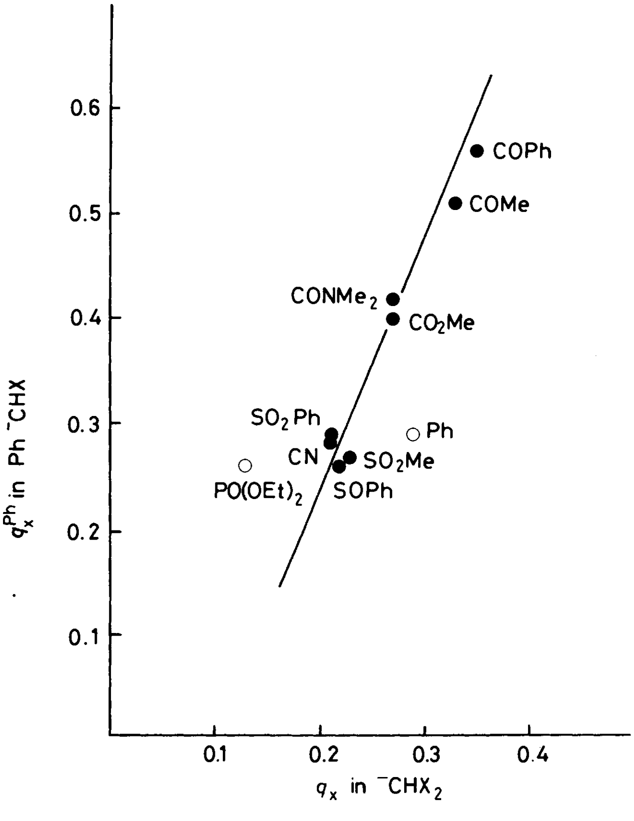


**Figure 5.** Plot of $q_x$ values obtained from $^-CHX_2$ systems *vs.* $q_x^{Ph}$ values obtained from $PhCH^-X$.

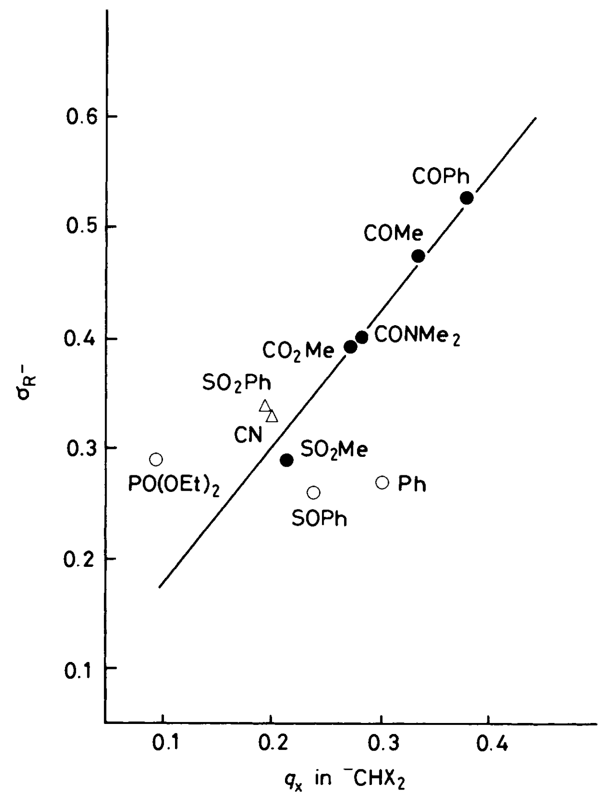


**Figure 6.** Plot of $q_X$ values *vs.* $\sigma_{R^-}$ of the same groups.

any case, the weak charge demands of the SOR, $SO_2R$, and cyano functionalities are again reproduced here for $^-CHX_2$ carbanions, in addition to $PhCH^-X$ systems.[7] All the considerations we have put forward previously[7] concerning the bonding and charge transfer in carbanions activated by the above groups are confirmed by the present results.

The charge demands $q_X$ have been obtained choosing as a monitor the $-CH^-$– group, an entity contiguous to X; the $\sigma_{R^-}$ constants have been obtained in PhNHX systems[7] choosing a remote monitor [$^{13}C(p)$]. The plot of Figure 6 shows excellent linearity for five substituents: $\sigma_{R^-} = 1.572q_X - 0.029$ ($r$ = 0.992) while inclusion of the CN and $SO_2Ph$ substituents disrupts the fit somewhat (slope = 1.321, intercept 0.050, $r$ = 0.977). Although Ph, SOPh, and $PO(OEt)_2$ show considerable scatter from the line, apparently unaccounted for so far, it is rewarding to note that the two approaches, choosing either a contiguous or a remote monitor, provide comparable quantitative answers.

## Experimental

*Materials.*—Diphenylmethane, acetylacetone, methyl acetoacetate, methyl malonate, malononitrile, dibenzoylmethane, cyclohexane-1,3-dione, bis(diethylphosphonyl)methane, and ethyl benzoylacetate, were all commercial products (Fluka or Aldrich). The following products were prepared according to known procedures: bis(phenylsulphonyl)methane,[22] (*N*,*N*-dimethyl)malondiamide,[23] diethyl benzylidenemalonate,[24] benzylidenemalononitrile,[25] methyl benzylidenecyanoacetate,[26] benzylideneacetylacetone,[27] benzylidenedibenzoylmethane,[28] benzylidenebis(phenylsulphonyl)methane,[29] propylidenemalononitrile,[30] methyl propylidenecyanoacetate,[31] ethyl phenylsulphinylacetate,[32] ethyl phenylsulphonylacetate,[33] phenylsulphonylacetone,[34] and phenylsulphonylacetophenone.[35] 1,1-Bis(phenylsulphonyl)ethylene[36] was kindly provided by Professor O. De Lucchi, University of Sassari.

*Bis(methylsulphonyl)methane*.—A solution of $KMnO_4$ (3.16 g, 20 mmol) in $H_2O$ (400 $cm^3$), acidified with $H_2SO_4$ (0.53 $cm^3$) was slowly added to a mechanically stirred solution of methyl methylthiomethyl sulphoxide (1.24 g, 10 mmol, Fluka) in benzene (50 $cm^3$), maintaining the temperature at 20–25 °C. The reaction was monitored by TLC: when the starting sulphoxide disappeared, excess $NaHSO_3$ was added to reduce the excess of permanganate. Care was taken to keep the aqueous solution acidic by the addition of dil. $H_2SO_4$. Manganese dioxide was removed by filtration, the layers were separated and the aqueous phase evaporated to dryness. The solid residue was treated in refluxing ethanol (2 × 25 $cm^3$), the mixture was filtered hot and the solution evaporated to dryness. The residue (1 g, 58%) was the pure compound, m.p. 143 °C (lit.,[37] 143 °C).

*Periodate Oxidation of Formaldehyde Di(phenylthio)acetal: Isolation of* (±) *and* meso-*Bis(phenylsulphinyl)methane, Phenylsulphinyl(phenylthio)methane, and Phenylsulphonyl(phenylthio)methane*.—A solution of formaldehyde di(phenylthio)acetal[22] (2 g, 8.6 mmol) in MeOH (40 $cm^3$) was slowly added to a magnetically stirred suspension of $NaIO_4$ (5.5 g, 26 mmol) in the same solvent (32 $cm^3$). After two days the mixture was filtered and the solution evaporated to dryness: the residue was taken up in methylene chloride, the solution was filtered and evaporated to dryness. The residue was chromatographed (silica gel 63 g, $CH_2Cl_2$:AcOEt = 9:1 as the eluant at first, gradually decreased to a ratio of 4:1 and finally pure AcOEt): the first eluate was mainly the starting bis-sulphide, then, in the order, phenylsulphinyl(phenylthio)methane as an oil[38] (500 mg, 25%) (Found: C, 62.7; H, 4.8. $C_{13}H_{20}OS_2$ requires C, 62.4; H, 4.8%), $\delta_H$ (90 MHz, $CDCl_3$) 4.08, 4.18 (2 H, $J_{AB}$ 15, C$H_2$), 7.20–7.79 (10 H, m, aromatic); phenylsulphonyl(phenylthio)methane[39] (80 mg, 4%), $\delta_H$ (90 MHz, $CDCl_3$) 4.42 (2 H, s, $CH_2$), 7.47–7.84 (8 H, m, aromatic), 7.94–8.17 (2 H, m, *ortho* protons in the $PhSO_2$ fragment) and finally a mixture of (±)- and *meso*-bis(phenylsulphinyl)methane (900 mg, 45%). The mixture was separated according to the Jarvis procedure[40] to give the (±)-isomer (330 mg, 37%) m.p. 189 °C (lit.,[40] m.p. 188–190 °C) and the *meso* isomer (135 mg, 15%) m.p. 113–115 °C (lit.,[40] m.p. 118–119 °C). As reported the *meso* compound presented the methylene at the $^1H$ NMR analysis as a singlet while the (±)-isomer presented it as an AB system.

## References

1 G. A. Pagani and S. Bradamante, presented in part at the Symposium on the Chemistry of Carbanions, Durham, July 1984; preliminary communication: E. Barchiesi, S. Bradamante, R. Ferraccioli, and G. A. Pagani, *J. Chem. Soc., Chem. Commun.*, 1987, 1548.

2 (*a*) J. C. Stowell, 'Carbanions in Organic Synthesis,' Wiley, New York, 1979; (*b*) 'Comprehensive Carbanion Chemistry,' eds. E. Buncel and T. Durst, Elsevier, New York, 1980, vols. 1 and 2.

3 A. Streitwieser, Jr., E. Juaristi, and L. L. Nebenzahl in 'Comprehensive Carbanion Chemistry,' vol. 1, ch. 7; H. F. Ebel, 'Die Acidität der CH-Säuren,' Thieme Verlag, Stuttgart, 1969.

4 (*a*) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Corforth, J. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, 1975, **97**, 7006; (*b*) F. G. Bordwell, *Pure Appl. Chem.*, 1977, **49**, 963; (*c*) C. D. Ritchie in 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, M. Dekker, New York, 1969, ch. 4.

5 (*a*) H. Stetter in Houbel-Weyl 'Methoden der Organische Chemie,' ed. E. Müller, Thieme Verlag, Stuttgart, 1976, vol. 7/2*b*, p. 1423; (*b*) O. A. Reutov, I. P. Beletskaya, and A. L. Kurto, 'Ambident Anions,' Consultant Bureau, New York, 1983; (*c*) N. Kornblum, R. Seltzer, and P. Haberfield, *J. Am. Chem. Soc.*, 1963, **85**, 1148; (*d*) L. M. Jackman and B. C. Lange, *Tetrahedron*, 1977, **33**, 2737.

6 S. Bradamante and G. Pagani, *J. Org. Chem.*, 1984, **49**, 2863.

7 S. Bradamante, F. Gianni, and G. Pagani, *J. Chem. Soc., Chem. Commun.*, 1976, 478; S. Bradamante and G. Pagani, *J. Org. Chem.*, 1980, **45**, 105 and 114; S. Bradamante and G. Pagani, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1035, 1047, and 1055; E. Barchiesi, S. Bradamante, C. Carfagna, R. Ferraccioli, and G. A. Pagani, *ibid.*, 1987, 1009.

8 E. Barchiesi, S. Bradamante, and G. A. Pagani, to be submitted.

9 (*a*) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Lett.*, 1962, 515; (*b*) D. J. Cram in 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 78; see also, (*c*) A. Berlin, S. Bradamante, R. Ferraccioli, and G. Pagani, *J. Chem. Soc., Chem. Commun.*, 1986, 1191.

10 (*a*) M. Barfield, T. Gotoh, and H. K. Hall, Jr., *Magn. Reson. Chem.*, 1985, **23**, 705; (*b*) C. N. Robinson, C. D. Slater, J. S. Covington III, C. R. Chang, L. S. Dewey, J. M. Franceschini, J. L. Fritzsche, J. E. Hamilton, C. C. Irving, Jr., J. M. Morris, D. W. Norris, L. E. Rodman, V. I. Smith, G. E. Stablein, and F. C. Ward, *J. Magn. Reson.*, 1980, **24**, 293; (*c*) N. Inamoto, S. Masuda, K. Tori, and J. Nishikawa, *Tetrahedron Lett.*, 1983, **24**, 5265.

11 G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972.

12 R. A. More O'Ferrall and J. H. Ridal, *J. Chem. Soc.*, 1963, 5030.

13 S. Fliszàr, 'Charge Distributions and Chemical Effects,' Springer–Verlag, New York, 1983, p. 50.

14 R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 1953, **75**, 2439; R. H. Boyd and C. H. Wang, *ibid.*, 1965, **87**, 430.

15 G. Schwarzenbach and E. Felder, *Helv. Chim. Acta.*, 1944, **27**, 1701.

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

17 E. Barchiesi, S. Bradamante, C. Carfagna, and R. Ferraccioli, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1565.

18 F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1289.

19 H.-H. Vogt and R. Gompper, *Chem. Ber.*, 1981, **114**, 2884; E. M. Arnett and V. M. De Palma, *J. Am. Chem. Soc.*, 1976, **98**, 7447; V. M. De Palma and E. M. Arnett, *ibid.*, 1978, **100**, 3514; M. Raban, E. A. Noe, and G. Yamamoto, *ibid.*, 1977, **99**, 6527; S. Ki Yooka and K. Suzuki, *Chem. Lett.*, 1975, 793.

20 M. Raban and D. Haritos, *J. Am. Chem. Soc.*, 1979, **101**, 5178.

21 S. Bradamante and G. A. Pagani, *Pure Appl. Chem.*, 1989, **61**, 709.

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

23 H. Bredereck and K. Bredereck, *Chem. Ber.*, 1961, **94**, 2278.

24 C. F. H. Allen and F. W. Spangler, *Org. Synth.*, 1945, **25**, 42.

25 B. B. Corson and R. W. Stoughton, *J. Am. Chem. Soc.*, 1928, **50**, 2825.

26 J. J. Carrick, *J. Prakt. Chem.*, 1892, **45**, 501.

27 C. M. Atkinson and R. E. Rodway, *J. Chem. Soc.*, 1959, 6.

28 E. F. Pratt and E. Werble, *J. Am. Chem. Soc.*, 1950, **72**, 4638.

29 H. Stetter and B. Riberi, *Monatsh. Chem.*, 1972, **103**, 1262.

30 (*a*) F. S. Prout, *J. Org. Chem.*, 1953, **18**, 928; (*b*) J. J. Baldwin, A. W. Raab, and G. S. Ponticello, *J. Org. Chem.*, 1978, **43**, 2529.

31 K. Shiraishi, A. Ichihara, and S. Sakamura, *Agric. Biol. Chem.*, 1977, **41**, 2497.

32 (*a*) R. Pummerer, *Chem. Ber.*, 1910, **43**, 1401; (*b*) S. R. Wilson, L. R. Phillips, Y. Pelister, and J. C. Huffman, *J. Am. Chem. Soc.*, 1979, **101**, 7373.

33 F. Lamar, *J. Am. Chem. Soc.*, 1952, **74**, 394.

34 G. Beck and D. Günther, *Chem. Ber.*, 1973, **106**, 2758.

35 R. T. Ameil and P. J. Marek, *J. Org. Chem.*, 1973, **38**, 3513.

36 O. De Lucchi, L. Pasquato, and G. Modena, *Tetrahedron Lett.*, 1984, **25**, 3647.

37 H. J. Backer, *Recl. Trav. Chim.*, 1946, **65**, 53.

38 K. Ogura and G. Tsuchihashi, *Bull. Chem. Soc. Jpn*, 1972, **45**, 2203.

39 F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, 1968, **33**, 1182.

40 (*a*) B. B. Jarvis and H. E. Fried, *J. Org. Chem.*, 1975, **40**, 1278; (*b*) J. L. Greene, Jr. and P. B. Shevlin, *J. Chem. Soc., Chem. Commun.*, 1971, 1092.

*Paper* 9/02387I
*Received* 6*th June* 1989
*Accepted* 2*nd August* 1989