^{1}H and ^{13}C Nuclear Magnetic Resonance Spectra of Benzylidenemalononitriles: a Method for the Determination of σ^+ Substituent Constants

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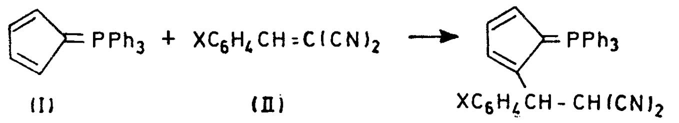
The ^{1}H and ^{13}C n.m.r. spectra of 15 substituted benzylidenemalononitriles (IIa–o) are reported in detail. The ^{1}H chemical shift of the vinylic hydrogen changes by 0.67 p.p.m. over the range of substituents and may be correlated with either σ or σ^+ substituent constants with almost the same degree of confidence (r 0.989 for σ and 0.994 for σ^+). The ^{13}C chemical shift of the β-vinylic carbon is, however, much more sensitive to substituent effects (range of δ = 17.2 p.p.m.) and shows a clear correlation with the σ^+ substituent constants (r 0.996) rather than the corresponding σ values (r 0.968). Three hitherto unreported σ^+ values are derived from the data.

DURING a study of the acid-catalysed nucleophilic addition of cyclopentadienylidenetriphenylphosphorane (I) to a series of substituted benzylidenemalononitriles (II), a linear free energy relationship between the rate of nucleophilic addition and the stability constants (K_π) for π-complex formation between (II) and *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) was established.[1] The nucleophilic addition reactions were third-order [first-order in (I), (II), and acid respectively] and the rate constants, k_3 (= k_{obs}/[I][acid]), showed a Hammett correlation of the Yukawa–Tsuno type[2] (1)



(I) (II)

$$\log k_3 = \rho[\sigma + R(\sigma^+ - \sigma)] \qquad (1)$$

with R = 0.7 and ρ = 2.9 for variation of the substituent X in (II). Furthermore, the K_π values for the molecular

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complexes of TMPD with (II) produced a better correlation with σ^+ than with σ. Since the stabilities of molecular complexes are known to depend to a large extent on dipole–dipole interactions and van der Waals forces [3,4] (*i.e.* ground state properties of donor and acceptor) it was anticipated that substituent induced variations in the n.m.r. spectra of (IIa—o) would also correlate with the σ^+ substituent constants. The object of the work was to test this hypothesis.

RESULTS AND DISCUSSION

The ^1H n.m.r. spectra of (IIa—o), obtained in deuterioacetone at concentrations of 5% or less, are recorded in Table 1. The significant resonance signal is that of the α-(vinylic)proton whose chemical shift varies by only 0.67 p.p.m. over the range of substituents. It has been pointed out [5,6] that in order to ensure that changes in chemical shift are due to *intramolecular* electronic (inductive, resonance, or field) effects rather than intermolecular reactions, one must (*a*) extrapolate to infinite dilution in as inert a solvent as possible and (*b*) include a minimum of ten substituents. In fact, spectra of a number of the benzylidenemalononitriles (IIc, d, f—h, m, n) were obtained at concentrations of 5, 2, and 1% in acetone and no variation of the chemical shift was observed with dilution. Furthermore, the precision of the 15 measurements was better than ±1.0 Hz for each. It was therefore somewhat surprising to find that a clear distinction between a correlation with σ^+ (r 0.994) or σ (r 0.989) was not possible on the basis of ^1H n.m.r. data. It would appear, however, that in this system the data are simply not sensitive enough to allow a choice of the appropriate substituent parameters.

TABLE 1

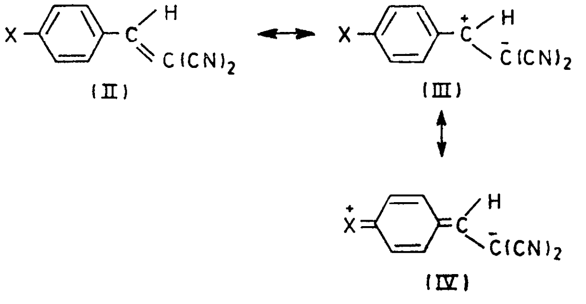
^1H N.m.r. spectra of benzylidenemalononitriles (II) *

X	δ [vinylic-H(s)]	δ (centre aromatic resonance)	δ_A—δ_B †	J_{AB} (= $J_{A'B'}$) (Hz)	δ (X)
p-Me_2N (IIa)	7.88	7.40 (4 H, q)	1.043	9.2	2.52 (6 H, s)
p-HO (IIb)	8.07	7.53 (4 H, q)	0.989	9.0	3.80 (1 H, s)
p-CH_3O (IIc)	8.12	7.62 (4 H, q)	0.873	9.0	4.01 (3 H, s)
p-CH_3 (IId)	8.19	7.70 (4 H, q)	0.471	8.6	2.46 (3 H, s)
p-AcO (IIe)	8.30	7.60 (4 H, q)	0.674	9.0	2.36 (3 H, s)
H (IIf)	8.32	7.66 (5 H, m)			
p-Cl (IIg)	8.33	7.69 (4 H, q)	0.371	8.8	
p-Br (IIh)	8.32	7.89 (4 H, q)	0.100	9.0	
p-$(AcO)_2CH$ (IIi)	8.38	7.91 (4 H, q)	0.295	9.0	7.70 (1 H, d) 2.16 (3 H, s)
p-HO_2C (IIj)	8.44	8.17 (4 H, q)	0.141	8.0	7.46 (1 H, s)
p-CO_2Me (IIk)	8.44	8.16 (4 H, q)	0.072	9.0	3.74 (3 H, s)
p-CN (IIl)	8.47	8.12 (4 H, q)	0.133	9.0	
m-NO_2 (IIm)	8.52	8.36 (4 H, m)			
p-NO_2 (IIn)	8.55	7.89 (4 H, q)	0.120	8.6	
p-$(CN)_2C{=}CH$ (IIo)	8.46	8.23 (4 H, s)			

* s = Singlet; m = multiplet; q = quartet, which in the case of aromatic protons is the typical AA′BB′ pattern for *para*-substitution. † For *para*-substituted compounds only.

By contrast with ^1H chemical shifts, ^{13}C chemical shifts, which primarily reflect substituent effects transmitted through the bonding network of the molecule, are relatively insensitive to magnetic anisotropy effects [7] and to solvent and concentration effects.[8,9] Consequently, ^{13}C chemical shifts have provided considerable information about electronic substituent effects in aromatic derivatives.[9b] Hence it was expected that analysis of the ^{13}C n.m.r. spectra of the benzylidenemalononitriles would help to establish the appropriate choice of substituent parameter more precisely.

Complete analyses of the ^{13}C n.m.r. spectra of the benzylidenemalononitriles appear in Table 2. Assignments were made on the basis of the spectra of model compounds derived either from the literature [10] or by independent measurement. The important chemical shift, however, is that of the β-carbon which varies by over 17 p.p.m. throughout the range of substituents and shows a clear correlation with the σ^+ values (r 0.996) rather than the σ values (r 0.968).



(II) (III) (IV)

The implication of these results is that in essence, substituents on the phenyl rings serve to stabilise (or destabilise) the positive charge on the α-carbon atom

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[formally represented by canonical form (III)] through a resonance interaction such as that represented by (IV). This in itself implies a high degree of planarity between the phenyl ring and the ββ-dicyanovinyl group, a situation which apparently obtains for the *para*-substituted styrenes [11-13] though not for α-substituted styrenes.[14] The observation that the chemical shifts of all the β-carbons are considerably upfield relative to normal olefinic carbons [15] (*i.e.* are closer to the carbanion shift region) provides further evidence in support of this suggestion. The α-carbon is correspondingly deshielded and appears for all the compounds within a very narrow field width of 2.5 p.p.m. (see Table 2).

TABLE 2

^{13}C Chemical shifts of benzylidenemalononitriles (II)

δ [p.p.m. (±0.06) downfield from Me_4Si]

Compound	β	α	C-1 *	C-2 and C-6 *	C-3 and C-5 *	C-4 *	CN †	X
(IIa)	71.0	158.4	121.7	133.7	111.8		122.1	39.2
(IIb)	77.0	159.8	123.8	133.9	116.6	163.6	127.7	—
(IIc)	77.3	159.1	122.9	132.8	114.5	164.3		54.9
(IId)	80.9	160.3	129.1	130.1	130.7	146.0	119.2	25.9
(IIe)	81.9	159.8		132.4	123.1	plus 155.4 and 129.0 §		168.4 (C=O); 20.2 (CH_3)
(IIi)	83.6	160.0		130.9	127.7	plus 141.7, 132.6, and 126.9 §		168.5 (C=O); 88.6 (>CH–); 19.9 (CH_3)
(IIf)	82.6	160.8	128.8	131.7	129.5	134.6		
(IIg)	83.5	159.7	130.3	132.4	130.7	140.2	125.5	
(IIh)	83.2	159.4	130.7	132.7	132.1	118.2	128.5	
(IIk)	84.9	159.5	135.2	130.0	130.5	134.4		165.2 (C=O); 52.0 (CH_3)
(IIl)	86.2	159.0	135.3	130.9	133.1	‡		
(IIm)	86.0	161.1	Unassigned peaks appear at 142.9, 135.5, 130.8, 126.9, and 113.3					
(IIn)	86.9	158.7	137.0	131.7	124.4			
(IIo)	88.2	159.1	‡	⟵116.6⟶		‡	‡	

* Assignments made on the basis of model compounds. † Frequently not observable. ‡ Not detected. § Not assigned.

Owing to the low solubilities of the benzylidenemalononitriles, investigations into concentration effects of the ^{13}C chemical shifts were not carried out. Deuterioacetone was found to be the most suitable solvent (deuterium being used to field lock the spectrometer) but even so, *p*-dimethylaminobenzylidenemalononitrile and 1,4-bis-(2,2-dicyanovinyl)benzene were only soluble to the extent of 1%. Other derivatives were soluble to as much as 5%. No changes in the more sensitive ^{1}H n.m.r. shifts were observed over this concentration range and moreover, Nelson *et al.*[9] found that for groups such as *p*-methoxy or *p*-methoxycarbonyl in trifluoroacetic acid as solvent, solute concentrations as high as 10—15% effectively simulated infinite dilution as far as solute perturbation of ^{13}C chemical shifts was concerned. It was assumed, therefore, that concentration effects on the ^{13}C chemical shifts of (II) were negligible.

TABLE 3

Predicted σ⁺ substituent constants based on the ^{13}C chemical shifts of the α-carbons

Linear regression equation:

$$\delta \text{ (p.p.m. from } Me_4Si) = 6.44\sigma^+ + 82.4$$

Substituent	β-Carbon ^{13}C δ (p.p.m. from Me_4Si)	Predicted σ^+ value
p-CO_2Me	81.9	−0.05 (±0.06)
p-$(AcO)_2CH$	83.6	+0.22 (±0.06)
p-$(CN)_2C{=}CH$	88.2	+0.96 (±0.07)

On the basis of the excellent correlation of the β-carbon chemical shifts with the σ^+ parameters, predictions of three, as yet unreported σ^+ values were made and are shown in Table 3. The value for the *p*-dicyanovinyl group may be compared with a value of $\sigma^+ = 0.8$ derived from a plot of ^{13}C chemical shifts of the *para*-carbon of monosubstituted benzenes against σ^+ values.[8,9]

EXPERIMENTAL

Carbon-13 n.m.r. spectra were obtained on a Bruker HFX90 spectrometer, field-locked on deuterium (CD_3COCD_3 as solvent) and linked to a Nicolet Fourier transform system. ^{1}H Spectra (again with CD_3COCD_3 as solvent) were obtained either on the Bruker HFX90 or on a Varian HA100 instrument (PCMU, Harwell). ^{1}H Spectra were referenced internally to tetramethylsilane; ^{13}C spectra were referenced externally to CS_2 and all the chemical shift values were converted to the tetramethylsilane standard (192.8 p.p.m. upfield from CS_2).

The substituted benzylidenemalononitriles were prepared from the corresponding substituted benzaldehyde and malononitrile according to the procedure of Corson and Stoughton.[16] The yields and m.p.s of the products, $XC_6H_4CH{=}C(CN)_2$, were as follows: (IIa), 90%, 179°; (IIb), 86%, 188—189°; (IIc), 85%, 115.5—116.5° (lit.,[16] 115°); (IId), 92%, 136—137° (lit.,[16] 134°); (IIe), 63%, 102—104°; (IIf), 87%, 83.5—84.5° (lit.,[16] 83—84°); (IIg), 83%, 162—163° (lit.,[17] 162—163°); (IIh), 82%, 160—161° (lit.,[16] 160°); (IIj), 90%, 160—165°; (IIk), 75%, 163°; (IIl), 90%, 152—153°; (IIm), 91%, 105—106° (lit.,[17]

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105—106°); (IIn), 91%, 165.5—166° (lit.,[17] 165—166°). New compounds [(IIa, b, e, j—l)] gave satisfactory elemental analyses for C, H, and N.

p-Diacetoxymethylbenzylidenemalononitrile (IIi) was prepared in 60% yield by the oxidation of (IId) with chromium trioxide in acetic anhydride.[18] The product was a crystalline solid, m.p. 147—150° (Found: C, 63.1; H, 4.3; N, 9.6. $C_{15}H_{12}N_2O_4$ requires C, 63.4; H, 4.25; N, 9.85%). 1,4-Dicyanovinylbenzene (IIo) was prepared in 94% yield, m.p. 265—270°, from terephthalaldehyde and malononitrile.[19]

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