9, 873-97-2; $(ArO)_3P$ (Ar = p-MeC_6H_4), 620-42-8; $(ArO)_3P$ (Ar = m-MeC_6H_4), 620-38-2; $(ArO)_3P$ (Ar = p-ClC_6H_4), 5679-61-8; $(ArO)_3P$ (Ar = p-t-BuC_6H_4), 4235-89-6; $(ArO)_3P$ (Ar = p-$MeOC_6H_4$), 19909-81-0; $(ArO)_3P$ (Ar = Ph), 101-02-0; methanol, 67-56-1; benzyl alcohol, 100-51-6; pentaerythritol, 115-77-5; neopentyl glycol, 126-30-7; phosphorus trichloride, 7719-12-2; p-methylphenol, 106-44-5; m-methylphenol, 108-39-4; p-chlorophenol, 106-48-9; p-*tert*-butylphenol, 98-54-4; p-methoxyphenol, 150-76-5; phenol, 108-95-2.

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A Convenient Determination of σ^+ Values

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The empirical σ^+ parameters devised by Brown and Okamoto[1] to account for the effect of substituents in aromatic electrophilic substitution reactions possess a much greater generality. For instance, Streitwieser et al.[2] have recently demonstrated their applicability to gas-phase protonation of benzenes.

We report here an easy and straightforward method for measurement of previously unavailable σ^+ values, from NMR chemical shifts in meta- or para-substituted benzylidene malononitriles[3] $XC_6H_4CH{=}C(CN)_2$. These are prepared according to standard procedures.[4] The singlet resonance for the olefinic proton is readily identified in the ^1H NMR spectrum. Relationship 1

$$\sigma^+ = 3.57\delta_H - 29.6 \qquad \text{(para substituents)} \quad (1)$$

holds for 5% w/v acetone-d_6 solutions,[5] with a correlation coefficient of 0.989 (11 points) (Figure 1). The σ^+ parameters are thus determined to ±0.3 at the 99% confidence level (three standard deviations). Use of the ^{13}C chemical shift for the cyano-bearing carbon, with a distinctive chemical shift of 80 ± 10 ppm,

$$\sigma^+ = 0.16\delta_C - 13.4 \qquad \text{(para substituents)} \quad (2)$$

leads to better accuracy also for deuteriochloroform solutions (25% w/v) with a correlation coefficient of 0.998 (seven points, including the substituents in the recommended[6] basis set) (Figure 2). Equation 2 is both more *sensitive* and more *accurate* than previous correlations between ^{13}C chemical shifts and σ^+ parameters (Table I). Another advantage of our approach is the possibility of evaluating σ^+ for a meta substituent, since in acetone-d_6 solution a *single* relationship holds

Table I. Comparison with Published Correlations Between σ^+ and ^{13}C Chemical Shifts

Compd	Slope	Standard deviation	Ref
Triaryl carbocations	−0.06	0.23	7
Benzenes	0.12	0.19	8
Benzylidenemalononitriles	0.16	0.04	This work

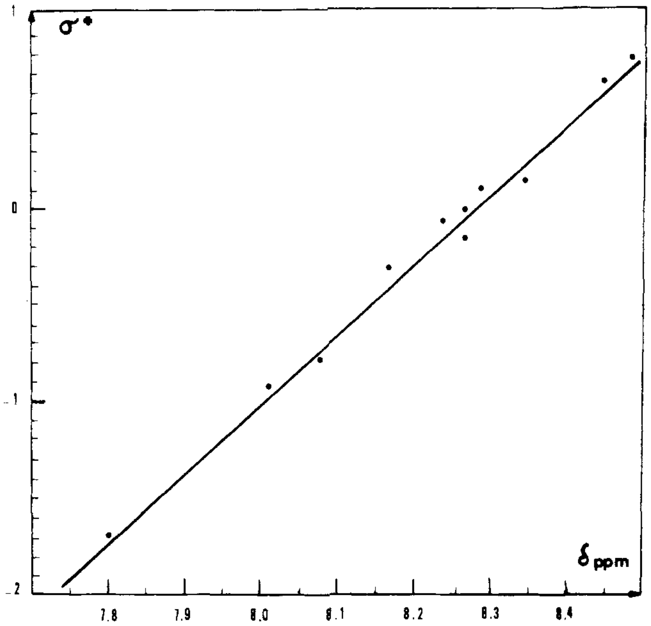

Figure 1. ^1H chemical shift for the olefinic proton vs. σ^+ in acetone-d_6 solution: $\sigma^+ = 3.574\delta - 29.579$.

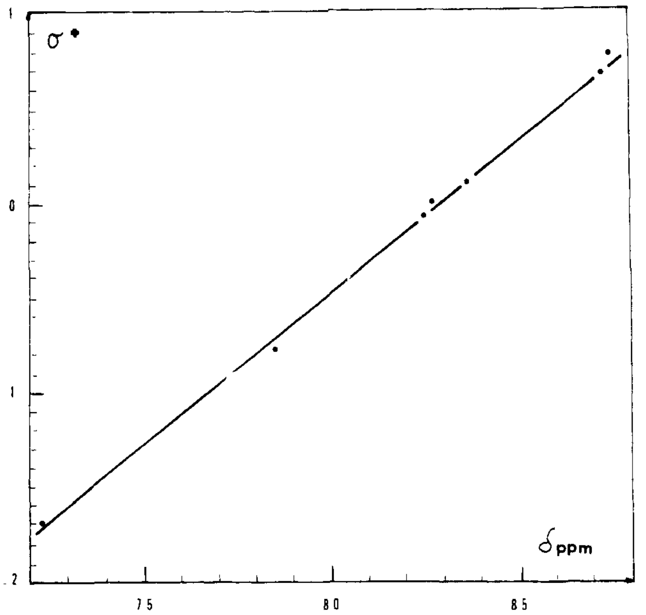

Figure 2. ^{13}C chemical shift for the cyano-bearing cation vs. σ^+ in chloroform-d solution: $\sigma^+ = 0.162\delta - 13.415$

$$\sigma^+ = 0.18\delta_C - 14.8 \qquad \text{(meta and para substituents)} \quad (3)$$

with a correlation coefficient of 0.993 (nine points) (Figure 3). This last relationship (3) yields σ^+ values to ±0.08 at the 99% confidence level.

As an application, we have used this method to determine unknown σ^+ values (Table II). Our values of σ^+ for the mesylate and tosylate groups, viz., 0.15 and 0.16, respectively, are of interest since they complement the σ_p, σ_I, and σ^* values just determined, using acidities or ^{19}F chemical shifts, by Stang and Anderson.[9] The σ^+ value for the dicyanomethylidene $HC{=}C(CN)_2$ substituent points to a powerful acceptor, in the same class as the cyano or nitro groups.

In summary, benzylidene malononitriles display strong polarization of the exocyclic double bond putting positive

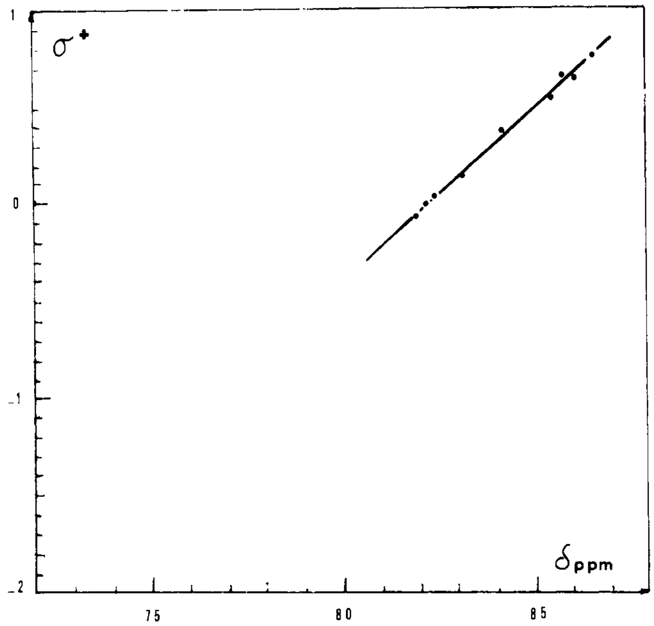

Figure 3. ^{13}C chemical shift for the cyano-bearing cation vs. σ^+ in acetone-d_6 solution: $\sigma^+ = 0.180\delta - 14.812$.

Table II. Sample Values of σ^+ Parameters

Para substituent	Nucleus probe	$\sigma^+(\pm 3\sigma)$
CH═C(CN)$_2$	C-4[8]	$0.8^2 \pm 0.5$
CH═C(CN)$_2$ (acetone-d_6)	olef H δ 8.43	$0.5^5 \pm 0.3$
OCH$_2$C$_6$H$_5$ (acetone-d_6)	olef H δ 8.09	$-0.6^6 \pm 0.3$
OSO$_2$CH$_3$ (acetone-d_6)	olef H δ 8.32	$0.1^6 \pm 0.3$
OSO$_2$CH$_3$ (acetone-d_6)	C-8 δ 83.11	$0.1^5 \pm 0.1$
OSO$_2$C$_6$H$_4$CH$_3$(p) (acetone-d_6)	olef H δ 8.26	$-0.0^6 \pm 0.3$
OSO$_2$C$_6$H$_4$CH$_3$(p) (acetone-d_6)	C-8 δ 83.18	$0.1^6 \pm 0.1$

charge on the α carbon.[11] The empirical finding that either H-7 or C-8[12] have resonances extremely sensitive to σ^+ values for the meta or para ring substituent affords an easy, if not extremely accurate, determination of this important parameter.

Since this note was submitted for publication, Posner and Hall have reported[13] an analogous method for determination of σ^+. Their results, although differing somewhat in the solvents used and in the substituent investigated, are complementary to ours.

Experimental Section

^1H NMR spectra were obtained on a Varian T-60 spectrometer, using tetramethylsilane as internal reference, whereas ^{13}C NMR spectra were determined on a Bruker HFX-90 spectrometer, field locked on deuterium (chloroform-d or acetone-d_6) and linked to a Nicolet Fourier transform system. The solvent peak (77.5 ppm) was used as reference for chloroform-d solutions, and a trace of internal methylene chloride (54.0 ppm) served as standard for acetone-d_6 solutions.

The substituted benzylidenemalononitriles were prepared from the corresponding substituted benzaldehyde and malononitrile according to the standard procedure of Corson and Stoughton,[4] except for the p-SO$_3$CH$_3$ and the p-SO$_3$C$_6$H$_4$CH$_3$(p) derivatives, which were prepared by reaction between p-hydroxybenzylidenemalononitrile and the corresponding sulfonyl chloride in pyridine solution. All ^1H and ^{13}C NMR spectra were fully compatible with the correct benzylidenemalononitrile structures.

All the compounds were crystallized to constant melting points, in excellent agreement with data in the literature.[3,4] The following values (uncorrected) have not been previously reported (substituent, mp): p-C$_6$H$_5$, 142–143 °C; m-CN, 147–148 °C; p-SO$_3$CH$_3$, 117.5 °C; p-SO$_3$C$_6$H$_4$CH$_3$(p), 150.5–151 °C; p-CH═C(CN)$_2$, 274.5–275 °C.

^1H Chemical Shift Data for the Olefinic Proton in Acetone-d_6 Solution [substituent, δ (ppm), σ^+]: p-N(CH$_3$)$_2$, 7.80, −1.70; p-OH, 8.01, −0.92; p-OMe, 8.08, −0.78; p-Me, 8.17, −0.31; p-C$_6$H$_5$, 8.27, −0.17; p-F, 8.24, −0.07; p-H, 8.27, 0.00; p-Cl, 8.29, 0.11; p-Br, 8.35, 0.15; p-CN, 8.45, 0.66; p-NO$_2$, 8.49, 0.79.

^{13}C Chemical Shift for the Cyano-Bearing Carbon in Chloroform-d Solution[14] [substituent, δ (ppm), σ^+]: p-N(CH$_3$)$_2$, 72.21, −1.70; p-OMe, 78.45, −0.78; p-F, 82.47, −0.07; p-H, 82.67, 0.00; p-Cl, 83.55, 0.11; p-CN, 87.24, 0.66; p-NO$_2$, 87.47, 0.79.

^{13}C Chemical Shift for the Cyano-Bearing Carbon in Acetone-d_6 Solution[14] [substituent, δ (ppm), σ^+]: p-F, 81.88, −0.07; p-H, 82.21, 0.00; m-OMe, 82.46, 0.05; p-Br, 83.14, 0.15; m-Cl, 84.19, 0.40; m-CN, 85.46, 0.56; p-CN, 86.04, 0.66; m-NO$_2$, 85.72, 0.67; p-NO$_2$, 86.61, 0.79.

Acknowledgments. We thank the Fonds de la Recherche Fondamentale Collective for their help in purchasing the Bruker HFX-90 spectrometer used in this study, and Professor Peter Stang (University of Utah) for suggesting application of the method to the mesylate and tosylate groups.

Registry No.—XC$_6$H$_4$CH═C(CN)$_2$ (X = p-Ph), 26089-09-8; (X = m-CN), 60595-33-7; (X = p-SO$_3$CH$_3$), 60595-34-8; (X = p-SO$_3$C$_6$H$_4$CH$_3$(p)), 60595-35-9; (X = p-H═C(CN)$_2$), 17239-69-9; (X = p-NMe$_2$), 2826-28-0; (X = p-OH), 3785-90-8; (X = p-OMe), 2826-26-8; (X = p-Me), 2826-25-7; (X = p-F), 2826-22-4; (X = p-H), 2700-22-3; (X = p-Cl), 1867-38-5; (X = p-Br), 2826-24-6; (X = p-NO$_2$), 2700-23-4; (X = m-OMe), 2972-72-7; (X = m-Cl), 2972-73-8; (X = p-CN), 36937-92-5; (X = m-NO$_2$), 2826-32-6.

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An Improved Preparation of Phenolic [1.1.1.1]Metacyclophanes

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Phenolic [1.1.1.1.]metacyclophanes (I) represent a very interesting and little studied class of compounds. For example, the cuplike structure[1] and strong complexing ability[1,2] of these macrocycles permit these molecules to act as unique models for enzyme–substrate complexes.[3] The macrocyclic structure