SOLVENT EFFECTS IN THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF BENZALMALONONITRILES[1]

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ABSTRACT

The nuclear magnetic resonance spectra of a series of substituted benzalmalononitriles were examined in various solvents. The chemical shifts for the olefinic protons are susceptible to large solvent effects which are interpreted as arising from association of a solvent molecule with the olefinic proton (acetone) or a site in its vicinity (benzene). With acetone this leads to a downfield shift from values observed in chloroform. In benzene solution the association produces increased shielding and is present in addition to a second solvation complex, the arrangement of which is governed by the substituent. The difference in behavior of the ethylenic proton in benzalmalononitriles from the formyl proton in benzaldehyde is ascribed to its more highly acidic nature.

INTRODUCTION

In a series of papers (1, 2) Klinck and Stothers reported on studies of the solvent effects in the nuclear magnetic resonance (n.m.r.) spectra of substituted aromatic aldehydes which provided evidence for the occurrence of specific solvent–solute association. In benzene solutions, for example, the observed changes in the chemical shifts of the various protons in the molecule from their values in chloroform solution were interpreted in terms of a molecular complex in which a benzene molecule tends to lie over the electron-deficient portion of the solute, the aromatic rings being parallel to each other. The anisotropy of the benzene then leads to substantially increased shielding of those protons in the vicinity of the center of the solvent ring, and the effect decreases for the more distant protons. Similar "collisional" complexes had been proposed earlier by Hatton and Richards (3) for solutions of amides and other polar compounds in aromatic solvents. These solvents always associate with sites of the solute as far away from an electronegative portion as possible. The observed enhanced shielding by benzene of the formyl and adjacent ring protons in benzaldehydes with electron-withdrawing para-substitutents, and the smaller effect on these protons in the case of electron-donating substituents are thus explained by the association positions of the benzene molecule favored in the respective compounds.

With acetone as solvent the observed differential shifts from chloroform solutions are much smaller and did not allow as definite conclusions for the existence of solute–solvent complexes as with benzene, since part of the shift could be attributed to effects arising from the reaction field of the solvent.

In the present work we have investigated the effect of substituents and solvents on the chemical shift of the protons in benzalmalononitriles which formally resemble the benzaldehydes. The highly electronegative side-chain substituents, however, cause the olefinic protons to be more acidic than the corresponding protons in benzaldehydes. In an interesting synthesis based on this difference in acidity, Bastus (4) obtained acetophone in

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excellent yield by methylation with diazomethane, not directly from benzaldehyde but via benzalmalononitrile and subsequent hydrolysis. It was therefore believed that in the benzalmalononitriles we might encounter more extreme solvent effects with electron-donating solvents. The study of the chemical shifts was simplified by referencing with respect to an internal standard. This eliminated effects due to bulk diamagnetic susceptibility, and the non-specific parts of solvent diamagnetic anisotropy and van der Waals interactions (5).

EXPERIMENTAL

Solutions (10% w/v, about 4–5 mole %) of the compounds in chloroform and acetone were studied at 30°. Deuterated solvents supplied by Merck, Sharp and Dohme of Canada Ltd., Montreal, Que., were used when necessary. In a few examples carbon tetrachloride solutions were also examined, and the spectra of a number of representative compounds were determined in d_6-benzene; 60 Mc/s n.m.r. spectra were recorded with a Varian 4300C spectrometer. The spectra were calibrated by the sideband technique using an electronic counter. The chemical shifts referenced with respect to internal tetramethylsilane are reported as τ values. These are the averages of at least five measurements and have standard deviations of 0.007 p.p.m. or better.

The benzalmalononitriles were obtained by the method of Corson and Stoughton (6) and recrystallized, usually from ethanol. Corrected melting points are given in Table I as well as analytical figures for new compounds.

RESULTS AND DISCUSSION

The chemical shifts of the ethylenic proton in the variously substituted benzalmalononitriles are given as τ values in Table II. This is arranged according to position of the substituent and then in order of increasing values of τ. For reasons to be discussed later the effect of structure on τ will be considered only for chloroform solutions. For the para-substituted compounds there is a qualitative correlation between the expected polarization of the CH bond and the τ value. The latter has a range of 0.45 p.p.m. between the extremes, *p*-nitro- and *p*-dimethylamino-benzalmalononitrile. Quantitatively the correlation between the observed shifts and the Hammett sigma parameters of the substituents as listed by McDaniel and Brown (15) and by Jaffe (16) is, however, not too satisfactory: $\tau = -0.259$ $(\pm 0.035)\ \sigma + 2.303\ (\pm 0.016)$, correlation coefficient $(r) = -0.93$, $n = 10$. The correlation is no better when the meta- and non-ortho-disubstituted compounds are included $(\tau = -0.244\ (\pm 0.036)\ \sigma + 2.322\ (\pm 0.015)$, $r = -0.85$, $n = 20)$. As was suggested for the formyl proton in benzaldehydes (1) the exposed nucleus of the ethylenic proton may be more susceptible to perturbing effects than a fluorine for the shift of which much better correlations with substituent constants have been obtained.

In the ortho-substituted benzalmalononitriles the τ values as shown in Table II are, in the main, little affected by the electronic nature of the substituents, and a quantitative correlation with Hammett's σ_r is very poor $(r = -0.22)$. The electronic effect of the substituent on the τ values of the ethylenic proton is thus less marked in the ortho- than in the meta- and para-substituted compounds. In addition, the resonance occurs at lower field in each of the ortho-substituted compounds than in the parent compound. The similar behavior in benzaldehydes has been adequately discussed by Klinck and Stothers (1) and explained in terms of reduced side chain – ring conjugation resulting from non-coplanarity because of the presence of an ortho substituent. Since, even with the least bulky substituents, the ethylenic proton in ortho-substituted benzalmalononitriles gives peaks which are 0.3 p.p.m. to lower field than those in benzalmalononitrile or the corresponding para-substituted compounds, it is evident that the effects caused by decreased conjugation completely overshadow the opposite effects due to ring current changes. Calculations based on the model of Johnson and Bovey (17) show that, as the side-chain proton goes out of the plane of the ring, its shielding is increased by, at most, 0.11 p.p.m.

Further evidence for the isolation of the side chain from the ring in ortho-substituted compounds is afforded by ultraviolet spectra. The K band for 2-methylbenzalmalononitrile occurs at 312 mμ (ϵ = 16 500) and that for 4-methylbenzalmalononitrile at 323 mμ (ϵ = 25 800). Since the substituent in this case is non-functional, Braude's expression (18) for the extinction coefficient ratio in terms of the out-of-plane angle θ of the side chain may be applied with some confidence, giving $\cos^2 \theta = 0.64$, and $\theta = 37°$. This may be regarded as a measure of the loss of through-conjugation in the ortho compound.

Solvent Effects

Most of the benzalmalononitriles are not soluble enough in interaction-free solvents such as *n*-hexane and, as a compromise, chloroform or deuterated chloroform was chosen as the standard solvent. Chloroform is an acceptor and very likely associates with the cyano groups. It can be seen from Table II that the τ values in carbon tetrachloride are about 0.1 p.p.m. higher than in chloroform. It is therefore inferred that the effect of association of chloroform with the compounds is relatively small. Use of the chloroform values as reference causes no appreciable error when one is discussing the large changes in benzene and it implies minimum values for the effects observed in acetone.

The dilution shift was checked in a few cases. 2-Nitrobenzalmalononitrile showed no change on fourfold dilution of a 3.5 mole % solution in chloroform and a decrease of 0.02 p.p.m. in acetone. The same change was also found on similar dilution of an acetone solution of the 4-nitro compound. It is therefore considered that "infinite dilution" conditions have been sufficiently approached in these experiments.

Before we consider the shifts in Table II in solvents other than chloroform, the effect of the reaction field of the solvent on the highly polar solute will be calculated in the case of 4-methylbenzalmalononitrile (μ = 4.1 D, by addition of group moments). Using the method of Buckingham (19) based on a spherical cavity model, with a calculated value of 1.93×10^{-23} cc for the polarizability of the solute, the contribution to the shielding of a proton is

$$\sigma_R = -0.104\,[(\epsilon - 1)/(2\epsilon + 2.5)]\,\mu \cos\theta \quad \text{p.p.m.}$$

in which ϵ is the solvent dielectric constant and θ the angle that the proton bond axis makes with the dipole μ (in D). The contribution turns out to be much too small to account for the variation of the shift of the olefinic, ortho, and meta protons[2] with solvent shown in Table III. For the solvent change from chloroform to acetone, for example, the calculated shifts caused by the reaction field are only 0.02 p.p.m. downfield on the ethylenic and meta protons and 0.02 p.p.m. upfield on the ortho proton.

The ellipsoidal cavity model of Diehl and Freeman (20) using ellipsoid semi-axes of 6.25, 3.75, and 1.95 Å, a shape factor of 0.144 as calculated by the method of Ross and Sack (21), and a refractive index of 1.5 leads to a contribution

$$\sigma_R = -0.0323\,[(\epsilon - 1)/(\epsilon + 0.378)]\,\mu \cos\theta \quad \text{p.p.m.}$$

This is even smaller than that calculated with the simpler model. Inspection of Table III indicates that the shift of the olefinic proton in fact depends more on the chemical nature of the solvent. In the relatively non-interacting solvents τ is 2.4, in ethers it is 2.1, and in solvents with carbonyl groups τ drops to 1.8.

To pinpoint the interactions in acetone and benzene solutions it is necessary to determine, as well, the solvent dependence of the shift of the aromatic protons in the benzalmalononitrile molecule. The shifts can be readily deduced only for the para-substituted

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[2] *Here and subsequently ortho and meta refer to the ring position relative to the* —CR = C(CN)$_2$ *substituent.*

TABLE I

Melting points and analyses

Aromatic substituent	Melting point		Calcd. %			Found %			
	Obs.	Lit.	C	H	N	C	H	N	Ref.
			Benzalmalononitriles						
None	83.4– 84.0	83.5– 84							6
4-NO$_2$	161.0–161.4	159 –160							7
4-COOMe	163.0–163.8		67.71	3.79	13.30	67.94 67.62	4.02 3.84	13.00 13.18	
4-F	126.8–127.2		69.82	2.93	16.26	69.77 69.63	3.12 3.13	16.01 16.00	
4-Cl	161.0–162.0	162 –163							7
4-Br	161.8–162.5		51.53	2.16	12.02	51.36 51.63	3.34 2.53	11.94 11.73	
4-Me	134.0–135.0	134							8
4-OMe	113.6–114.2	114.5–115							6
4-OEt	138.0–138.4		72.71	5.08	14.13	72.66 72.43	5.08 4.93	13.76 13.55	
4-NMe$_2$	180.7–181.2	178							8
2-COOMe	85.0– 86.0		67.91	3.79	13.30	67.83	3.71	13.16	
2-NO$_2$	138.8–139.2	143							9
2-OEt	79.0– 80.0	80							9
2-OnPr	60.0– 60.6		73.55	5.70	13.20	73.75 73.62	5.74 5.83	12.94 13.04	
2-OiPr	102.4–102.8		73.55	5.70	13.20	73.70 73.61	5.83 5.83	13.09 12.86	
2-OnBu	69.8– 70.3		74.31	6.24	12.38	74.26 73.98	6.35 6.19	11.83 11.88	
2-OMe	84.0– 85.0	84 – 84.5							6
2-Cl	95.2– 95.8	95 – 96							6
2-Br	90.5– 91.0	90 – 90.5							7 10

TABLE I (*Concluded*)

Melting points and analyses

Aromatic substituent	Melting point		Calcd. %			Found %			Ref.
	Obs.	Lit.	C	H	N	C	H	N	
			Benzalmalononitriles						
2-F	118.4–118.8	119							
2-Me	106.0–106.6	104 –106							7
3-NO_2	106.6–107.0	104.5–105				69.88	3.09	15.90	6
3-F	93.0– 93.4		69.82	2.93	16.26	69.85	3.10	15.84	
						71.57	4.34	15.20	
3-OMe	105.6–106.2		71.72	4.38	15.21	71.39	4.34	14.97	
3-Cl	115.5–116.0	116 –117				72.34	5.06	14.02	7
3-OEt	82.0– 82.6		72.71	5.08	14.13	72.37	5.16	13.96	
3-Br	110.0–110.8	109.5–110							7
2-OMe 5-OMe	107.4–108.2	110							11
2-Cl 5-NO_2	121.8–122.2	119 –120							7
2-Cl 4-Cl	150.0–151.0	150				50.14	2.74	—	8
2-OMe 5-Br	137.0–139.0		50.21	2.67		50.08	2.73	—	
						67.40	4.73	12.82	
2-OMe 4-OMe	142.2–142.6	144	67.28	4.70	13.08	67.15	4.77	12.89	12
2-Cl 6-Cl	88.0– 89.0	89– 90				53.76	2.09	12.46	7
3-Cl 4-Cl	151.0–151.6		53.83	1.80	12.56	53.99	2.17	12.55	
3-OMe 4-OMe	145.0–145.6	144							8
3-OEt 4-OEt	105.0–106.0	106							9
3,4-OCH_2O—	198.4–198.8	199 –200							6
2,3 $(CH)_4$	168.0–169.0	170 –171.5							7
3,4 $(CH)_4$	140.2–140.8	141							9
			1,1-Dicyano-2-phenyl-1-propenes						
4-Cl	95 – 96	96							13
4-Me	98 – 99	97							13
4-OMe	80 – 81	73 – 74	72.71	5.09	14.13	72.71	5.22	14.29	14

TABLE II

The τ values (p.p.m.) of the ethylenic proton in benzalmalononitriles in various solvents

Aromatic substituent	τ in $CHCl_3$	$\Delta\tau$*		
		CCl_4	Acetone	C_6D_6
None	2.23	0.07	−0.49	1.15
4-NO_2	2.13		−0.65	1.74
4-COOMe	2.15		−0.55	
4-F	2.23	0.11	−0.53	1.33
4-Cl	2.28		−0.57	1.44
4-Br	2.28		−0.58	
4-Me	2.30		−0.49	1.11
4-OMe	2.36		−0.47	1.01
4-OEt	2.37		−0.45	
4-NMe_2	2.58		−0.39	0.75
2-COOMe	1.28		−0.17	0.68
2-NO_2	1.56		−0.38	1.29
2-OEt	1.70	0.15	−0.13	
2-OnPr	1.70		−0.15	
2-OiPr	1.71		−0.14	
2-OnBu	1.71		−0.14	
2-OMe	1.73	0.13	−0.10	0.60
2-Cl	1.75		−0.27	0.87
2-Br	1.80		−0.26	
2-F	1.91		−0.31	
2-Me	1.91	0.09	−0.44	

Aromatic substituent	τ in $CHCl_3$	$\Delta\tau$*	
		Acetone	C_6D_6
3-NO_2	2.04	−0.56	1.66
3-F	2.24	−0.58	
3-OMe	2.27	−0.50	
3-Cl	2.28	−0.59	
3-OEt	2.29	−0.51	
3-Br	2.30	−0.61	
2-OMe 5-OMe	1.74	−0.08	
2-Cl 5-NO_2	1.76	−0.38	
2-Cl 4-Cl	1.82	−0.30	
2-OMe 5-Br	1.84	−0.18	
2-OMe 4-OMe	1.85	−0.06	
2-Cl 6-Cl	2.08	−0.57	1.21
3-Cl 4-Cl	2.32	−0.64	
3-OMe 4-OMe	2.36	−0.42	
3-OEt 4-OEt	2.39	−0.42	
3,4-OCH_2O	2.41	−0.53	
2,3 $(CH)_4$	1.38	−0.50	
3,4 $(CH)_4$	2.18	−0.54	
$CH_3CH{:}C(CN)_2$	2.57	−0.34	1.47

*$\Delta\tau = \tau$ (in solvent) $-$ τ (in chloroform).

TABLE III

The τ values in various solvents of the olefinic and aromatic protons in 4-methylbenzalmalononitrile

Solvent	ϵ	Olefinic	Aromatic	
			Ortho	Meta
Cyclohexene	2.22	2.45	2.25	2.77
p-Dioxane	2.21	2.09	2.19	2.64
Ether	4.33	2.08	2.14	2.66
Chloroform	4.80	2.30	2.20	2.69
Methyl acetate	6.68	1.87	2.07	2.57
Acetone	20.7	1.81	2.08	2.57

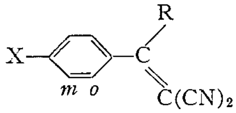
compounds from the pseudo-AB-like part of the A_2B_2 spectrum (22). Analysis of these spectra also yield values for the sums of the ortho and para coupling constants of 8.5–9.3 c.p.s., which are almost independent of substituent and solvent.

Acetone Solutions

Table IV shows the results for para-substituted benzalmalononitriles and some 1,1-dicyano-2-phenyl-1-propenes. It is apparent that the chemical shift of the aromatic protons of para-substituted benzalmalononitriles is generally decreased in changing from chloroform to acetone solutions and by about the same amount (0.1–0.2 p.p.m.) as for benzaldehydes (2). The propylidene methyl and substituent protons are very little affected by this solvent change, but there is a larger effect on the olefinic proton shift. A large effect on the ethylenic proton shift is also noted in the meta-substituted compounds in Table II. When ortho substituents are present this "solvent shift" is much reduced in most of the examples and is then of the same order as that observed for the formyl proton in benzaldehyde. In the disubstituted benzalmalononitriles without an ortho substituent

TABLE IV

The τ values in chloroform and changes in these values in acetone solutions for the system



		Chloroform solution				Acetone solution			
X	R	τ_R	τ_o	τ_m	τ_X	$\Delta\tau_R$	$\Delta\tau_o$	$\Delta\tau_m$	$\Delta\tau_X$
H	H	2.23				−0.49			
NO_2	H	2.13	1.93	1.62		−0.65	−0.19	−0.06	
COOMe	H	2.15	2.03	1.82		−0.55	−0.18	+0.04	
F	H	2.23	2.03	2.77		−0.53	−0.16	−0.18	
Cl	H	2.28	2.15	2.49		−0.57	−0.18	−0.14	
Cl	CH_3	7.38	2.48	2.48		−0.06	−0.19	−0.08	
Br	H	2.28	2.28	2.28		−0.58	−0.23	−0.10	
Me	H	2.30	2.20	2.69	7.55	−0.49	−0.12	−0.12	0.01
Me	CH_3	7.39	2.52	2.71	7.58	−0.04	−0.12	−0.07	0.01
OMe	H	2.36	2.10	2.99	6.09	−0.47	−0.13	−0.13	−0.03
OMe	CH_3	7.39	2.38	3.01	6.13	−0.03	−0.11	−0.10	−0.02
OEt	H	2.37	2.12	3.01		−0.45	−0.11	−0.12	
NMe_2	H	2.58	2.21	3.31	6.86	−0.39	−0.11	−0.17	

the solvent shift is roughly the same, 0.5 p.p.m., as for the derivatives with a single meta or para substituent, whilst if an ortho substituent is present, it appears to govern the solvent effect. A notable exception is 2,6-dichlorobenzalmalononitrile where the solvent shift is more like that of a 3,4-disubstituted compound.

The small solvent effects on aromatic protons in both benzalmalononitriles and benzaldehydes are probably due to a vague solvation of a dipolar nature, but the large changes in τ value of the ethylenic proton are only explicable on the basis of a specific solvent interaction of the acetone carbonyl oxygen with the ethylenic proton. This is quite different from the behavior of the formyl proton in benzaldehydes, but since this ethylenic proton is more acidic, an interaction of the hydrogen bond type with acetone is not unreasonable, and a substantial downfield shift of the field position of the proton results in compounds without ortho substituents. As might be expected, compounds with electron-withdrawing groups in the para position show an enhanced shift, those with electron-donating groups a reduced one compared to the value for the parent compound. With ortho-substituted benzalmalononitriles the situation is complicated by the long-range shielding effects of the substituent and by the possibility of intramolecular hydrogen bonding of it with the olefinic proton. In those compounds where such bonding is unlikely, the "normal" acetone solvent shift of the corresponding para compound would be observed. This is the case with 2-methylbenzalmalononitrile where the solvent shift is nearly as large as that of the 4-methyl analogue and in 2,6-dichlorobenzalmalononitrile where, for steric reasons, intramolecular interaction is not possible. However, those substituents which may show intramolecular association are also most likely to have large magnetic anisotropic effects, and it is impossible at present to separate these factors. The effects can be discussed generally by considering the equilibrium

$$\text{A} + \text{acetone} \rightleftharpoons \text{solvent complex (B)},$$

where A is the ortho-substituted benzalmalononitrile, perhaps internally complexed. The solvent shift $\Delta\tau$ is then given by

$$\Delta\tau = \alpha(\tau_B - \tau_A),$$

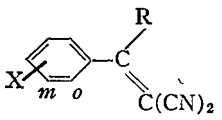
where α is the mole fraction of solvent complex and the τ values are those of the extreme forms (A and B). Association with the solvent disrupts the influence of the magnetic anisotropy of the substituent and of any intramolecular hydrogen bond, both of which contribute to the net effect which is measured by $\tau_B - \tau_A$. In 2-nitrobenzalmalononitrile where formation of a six-membered ring would lend some stability to the intramolecular hydrogen bond which is also aided by a favorable electron distribution, one may expect a smaller α than in the 2-alkoxy compounds. The solvent shift for 2-nitrobenzalmalononitrile is, however, much bigger than that for the 2-methoxy analogue. Hence it appears that $(\tau_B - \tau_A)_{NO_2} > (\tau_B - \tau_A)_{OMe}$, i.e. on solvation with acetone the net change in shielding of the ethylenic proton is less in the methoxy than in the nitro compound.

Benzene Solutions

The solvent shifts are shown in Table V as well as their differences from the solvent shifts of the corresponding protons in benzaldehydes observed by Klinck and Stothers (2).

TABLE V

Solvent shifts (p.p.m.) in d_6-benzene solution (relative to chloroform values) in the system



and differences from corresponding values for benzaldehydes and acetophenones

						Solvent shift differences* at:			
X	R	$\Delta\tau_R$	$\Delta\tau_o$	$\Delta\tau_m$	$\Delta\tau_X$	R	*o*	*m*	X
4-NO_2	H	1.74	1.27	0.96		0.94	0.34	0.24	
4-F	H	1.33	0.88	0.78		0.85	0.28	0.18	
4-Cl	H	1.44	0.95	0.79		0.92	0.34	0.23	
4-CH_3	H	1.11	0.59	0.65	0.57	0.88	0.33	0.18	0.10
4-OCH_3	H	1.01	0.57	0.62	0.76	0.83	0.30	0.22	0.08
4-$N(CH_3)_2$	H	0.75	0.46	0.66	0.97	0.86	0.42	0.26	0.27
H	H	1.15				0.81			
3-NO_2	H	1.66				0.81			
4-Cl	CH_3	0.94	†	†					
4-CH_3	CH_3	0.83	0.53	0.49	0.45	0.43	0.40	0.14	0.08
4-OCH_3	CH_3	0.78	0.52	0.44	0.63	0.40	0.39	0.17	0.04

*These differences are $\Delta\tau$(benzalmalononitrile) minus $\Delta\tau$(benzaldehyde) or $\Delta\tau$(1,1-dicyano-2-phenyl-1-propene) minus $\Delta\tau$(acetophenone).

†Solvent shifts of 0.81 and 0.60 p.p.m. were found for the aromatic protons but they could not be assigned.

The results for a few 1,1-dicyano-2-phenyl-1-propenes are also shown and compared differentially with the values for the acetophenones with the same substituent (2). These comparisons yield the striking result that the differences between the solvent shifts of the corresponding protons in benzalmalononitriles and benzaldehydes are quite large but relatively insensitive to substituent, the average values being 0.88 p.p.m. for the olefinic proton, 0.34 p.p.m. for the ortho proton, and 0.22 p.p.m. for the meta proton. To a good approximation therefore the benzene solvent shifts in benzalmalononitriles can be explained in terms of a complex in which two molecules of benzene participate, one whose substituent-dependent position is similar to that in the Klinck and Stothers model for benzaldehydes, and the other whose location over the side chain is independent of the substituent (Fig. 1). The association with the side chain is reminiscent of the complexing of toluene with acetonitrile (23). Ring current effect calculations (17) show that the above differential solvent shifts result for the ethylenic and ortho protons when the second benzene molecule is centered at about 2.5 ring radii over the carbon atom adjacent to the ring, its plane parallel

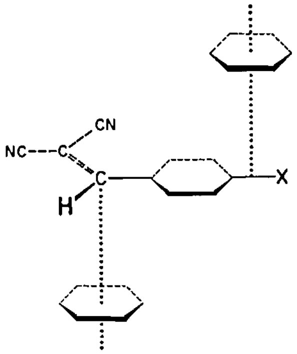


FIG. 1. Association of benzene with a para-substituted benzalmalononitrile. The substituent-dependent position of the benzene molecule at upper right is shown for an electron-donating substituent.

to that of the solute ring. The value calculated for the meta proton is, however, too small by 0.2 p.p.m. A similar model with the second benzene molecule having a position at about 2.5 ring radii over the middle of the bond between the aromatic and olefinic carbons accounts approximately for the observed solvent shifts in the 1,1-dicyano-2-phenyl-1-propenes.

CONCLUSIONS

The strongly electron-attracting cyano groups in benzalmalononitriles cause solvation of the olefinic proton or sites in its vicinity by the donor solvents acetone and benzene, in addition to the solvation normally encountered with these solvents and aromatic molecules. The solvent shifts observed in the n.m.r. spectra are relatively large, but are modified in ortho-substituted compounds.

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