View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

Hydrogen Bonding and Substituent Group Effects in Phénols. Part I. Apparent Dipole Moments and Infrared Spectra of *N*-(4-Hydroxybenzylidene)-4-Substituted-Anilines in Benzene, Carbon Tetrachloride, and Dioxan

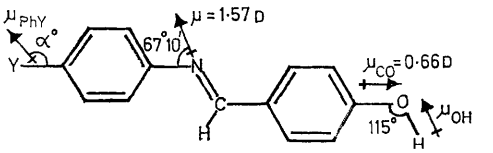
By **D. C. Colinese**, Department of Chemistry, Derby and District College of Technology, Derby DE3 1GB

Apparent dipole moments in benzene and dioxan of benzylideneaniline and its two *para*-methyl derivatives have been determined, and used to obtain the inclination of the resultant moment to the N–C(ring) axis in each solvent. The moments in dioxan of 4-hydroxystilbene and 13 *N*-(4-hydroxybenzylidene)-4-substituted anilines are reported together with hydroxy-group stretching frequencies ν(OH) in carbon tetrachloride and dioxan. To explain the observed moments in dioxan, values of hydroxy-group bond moments μ(O–H) have been calculated. Both ν(OH) and μ(O–H) are found to be linearly related to the Hammett substituent constant, σ. The relative frequency shift in dioxan being adopted as a measure of the enthalpy change on solute–solvent association, these results provide another illustration of the dependence of μ(O–H) on the strength of hydrogen bonding.

CONSIDERABLE insight into the factors controlling the strength and polarity of hydrogen bonds formed by phenols, and the transmission of substituent group effects in phenolic compounds, has arisen from studies of dipole moments, μ, and hydroxy-group bond moments, μ(OH); stretching frequencies, ν(OH), and band intensities A(OH); dissociation constants, K_a; and association constants, K, corresponding frequency shifts $\Delta\nu$(OH), and enthalpy changes for hydroxy-group association with various electron donors. Many linear relationships between the preceding variables (together with substituent group constants, σ) have been established.[1-14]

Until now, little attention has been given [4] to phenolic systems with extended conjugation, from which intramolecular [14] bonding is absent. Extension of the studies of hydroxyazobenzenes [4] to phenolic benzylideneanilines permits investigation of the effect of two different orientations of the azomethine linkage on the hydrogen-bonding ability and polarity of the hydroxy-group, and the transmission of substituent group effects to the latter.

In this paper apparent dipole moment determinations for benzylideneaniline (I, X = Y = H), *N*-(4-methylbenzylidene)aniline (I; X = Me, Y = H), and *N*-(benzylidene)-4-methylaniline (I; X = H, Y = Me) in benzene and dioxan are reported, together with the moments in dioxan of 4-hydroxystilbene and a series of *N*-(4-hydroxybenzylidene)-4-substituted anilines (I; X = OH). Fundamental hydroxy-group stretching frequencies in carbon tetrachloride and dioxan are given for all the phenolic compounds.



Model for the calculation of hydroxy-group bond moments

(I) 4-X·C_6H_4·CH=N·C_6H_4·Y-4

It is found that the resultant moment of benzylideneaniline is inclined at the angle 67° 46′ to the N–C(ring) axis in benzene solution, and 67° 10′ in dioxan. Using the latter result, we found that the calculated O–H bond moment of *N*-(4-hydroxybenzylidene)aniline in dioxan is greater than for phenol; the OH group stretching frequency is significantly less, and the frequency shift $\Delta\nu$(OH) on association appreciably

[1] J. P. B. Sandall, M.Sc. Thesis, University of London, 1963.
[2] D. A. Ibbitson and J. P. B. Sandall, *J. Chem. Soc.*, 1964, 4547.
[3] B. Erić, E. V. Goode, and D. A. Ibbitson, *J. Chem. Soc.*, 1960, 55.
[4] D. C. Colinese, D. A. Ibbitson, and C. W. Stone, *J. Chem. Soc.* (*B*), 1971, 574.
[5] D. A. Ibbitson, T. Jackson, A. McCarthy, and C. W. Stone, *J. Chem. Soc.*, 1960, 5127.
[6] A. V. Few and J. W. Smith, *J. Chem. Soc.*, 1949, 753 and 2781.
[7] J. W. Smith, *J. Chem. Soc.*, 1953, 109.
[8] J. W. Smith and S. M. Walshaw, *J. Chem. Soc.*, 1957, 3217.
[9] P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc.*, 1959, *A*, **250**, 22.
[10] J. D. S. Goulden, *Spectrochim. Acta*, 1954, **6**, 129.
[11] A. G. Catchpole, W. B. Foster, and R. S. Holden, *Spectrochim. Acta*, 1962, **18**, 1353.
[12] T. D. Flynn, R. L. Werner, and B. H. Graham, *Austral. J. Chem.*, 1959, **12**, 575.
[13] L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.
[14] G. M. Badger and A. G. Moritz, *J. Chem. Soc.*, 1958, 3437.

View Article Online

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

greater, than for phenol. These findings parallel the behaviour of 4-hydroxyazobenzene[4] and may also be attributed to the additional conjugation in the benzylideneanilines. As in the case of the phenols and 4-hydroxyazobenzenes,[4] both ν(OH) and μ(OH) give a linear plot against Hammett's substituent parameters, σ, the former decreasing and the latter increasing with increasing electron-attracting character of the substituent. The slope of the ν(OH) regression line is of opposite sign to that reported for *N*-(4-substituted benzylidene)-2-hydroxyanilines, in which intramolecular association occurs.[14]

EXPERIMENTAL

Materials.—Solvents. Benzene and dioxan, dried by prolonged refluxing over sodium, were distilled through a 1-m column packed with Fenske helices. The fractions of b.p. 80·1° at 760 mmHg and 101·4° at 760 mmHg, respectively, were collected and stored under anhydrous conditions. Dioxan was used on the same day for dipole moment measurements. Carbon tetrachloride ('Spectrosol') was dried over molecular sieve (Type 4A).

Phenols. Phenol was distilled and the middle fraction recrystallised from light petroleum (b.p. 60—80°); m.p. 41·5°. *p*-Hydroxystilbene was prepared by a published method;[15] m.p. 189·5—190·0°.

Intermediates. *p*-t-Butylaniline, prepared by Craig's method,[16] had b.p. 240—242° at 774 mmHg. Other amines and aldehydes were of AnalaR or reagent grade, and were redistilled or recrystallised before use.

Benzylideneanilines. These compounds are easily prepared.[17] Since they are readily hydrolysed,[17a,18] the reaction was conducted in non-aqueous media. In the general method, the aldehyde (0·1 mol. equiv.) was heated with the amine (0·1 mol. equiv.) in either toluene, or toluene–n-pentyl alcohol containing sufficient alcohol to render the reactants soluble. The mean volume of water (removed by azeotropic distillation) from 30 syntheses was 1·71 cm³ (theoretical: 1·80 cm³). The solid product obtained after cooling and filtration was recrystallised to constant m.p., by use of light petroleum (b.p. 40—60°) for the non-hydroxy-compounds, and pure dioxan for the phenolic compounds. M.p.s (Kofler hot-stage apparatus; corrected) and physical characteristics are shown in Table 1. All the compounds were characterised by their i.r. spectra,[19a] and potentiometrically by titration as bases in anhydrous acetic acid, with acetous perchloric acid as titrant.[19b] Since many benzylideneanilines are phototropic,[20] they were stored in dark brown bottles in an atmosphere of dry nitrogen.

Dipole Moments.—Dielectric constants (relative permittivities), ε, and refractive indices, n_D, of solutions of graded weight fraction, *w*, of each compound in the appropriate solvent were determined at 298·20 ± 0·02 K (N.P.L. calibrated thermometer).

Dielectric constants, accurate to 0·0001, were measured with an internally thermostatted, heterodyne-beat dipole-

TABLE 1

N-(4-Substituted benzylidene)-4-substituted-anilines $X{\cdot}C_6H_4{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}Y$

No.	X	Y	Appearance [a]	M.p./°C (Corr.)	M.p. (lit.)
(1)	H	H	V.p.y.pl.	51·0—51·5	52 [b]
(2)	H	Me	V.p.y.n.	33·5—34·0	35 [c]
(3)	Me	H	V.p.y.h.pr.	44·5—45·0	
(4)	HO	NMe_2	g.h.pr.	257—258	
(5)	HO	OMe	p.y.h.pr.	212·5—213·0	211·0—211·5 [d] (corr.)
(6)	HO	Bu^t	p.y.h.n.	183·5—184·0	
(7)	HO	Me	p.y.h.pr.	217—218	218 [c,d] (corr.)
(8)	HO	H	p.y.n.	196·0—196·5	194—195 [c]
(9)	HO	F	p.y.h.pr.	182·5—183·0	
(10)	HO	Cl	p.y.h.n.	187·0—187·5	184—185 [d] (corr.) †
(11)	HO	Br	p.y.h.n.	198·0—198·5	193—194 [d] (corr.) †
(12)	HO	I	p.y.h.n.	210·0—210·5	
(13)	HO	CO_2Et	y.h.pl.	176·5—177·0	
(14)	HO	COMe	y.h.n.	214·5—215·0	
(15)	HO	CN	b.y.n.	164—165	
(16)	HO	NO_2	b.y.h.n.	204·5—205·5	
(17)	*p*-Hydroxystilbene		w.pl.	189·5—190·0	189,[c] 184·5 [e]

[a] V = very, p = pale, b = bright, w = white, y = yellow, g = golden, h = hexagonal, n = needles, pl = plates, pr = prisms. [b] *Org. Synth.*, 1946, Coll. Vol. I, 2nd edn., p. 80. [c] I. M. Heilbron and H. M. Bunbury, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1943. [d] A. Senier and R. B. Forster, *J. Chem. Soc.*, 1914, **105**, 2462. [e] Ref. 16.

† Dimorphous (ref. *d*); trituration yields variety with m.p. 193—194° (Cl); 203—204° (Br).

meter, type DM 01, manufactured by Wissenschaftlich-Technische Werkstätten, G.m.b.H.

The thermostatted dielectric cell, type D.F.L.1, of 20 cm³ capacity, had gold-plated internal plates. The linear capacitor was calibrated by means of benzene (ε = 2·2725), carbon tetrachloride (ε = 2·2274), and cyclohexane (ε = 2·0139). Reproducibility was ensured by switching the instrument on 5 h before use and by suspending the flasks containing the solutions in a thermostatted bath 30 min before measurements.

TABLE 2

100*w*	ε	n_D	100*w*	ε	n_D
(1) *N*-(Benzylidene)aniline in benzene			(1) *N*-(Benzylidene)aniline in dioxan		
0·0000	2·2725	1·49714	0·0000	2·2109	1·42014
0·2279	2·2769	1·49745	0·1946	2·2156	1·42044
0·4524	2·2813	1·49783	0·3874	2·2200	—
0·6805	2·2851	1·49808	0·3885	—	1·42100
0·9089	2·2894	1·49838	0·5807	2·2247	—
1·1394	2·2937	1·49870	0·5847	—	1·42149
1·3635	2·2980	1·49905	0·7798	2·2294	1·42187
			0·9739	2·2341	1·42229
			1·1644	2·2385	1·42268
α = 1·873; ν = 0·417; $_0P_{2\infty}$ = 49·47 cm³; μ_B = 1·56 D			α = 2·375; ν = 0·621; $_0P_{2\infty}$ = 50·54 cm³; μ_D = 1·57 D		

[15] J. T. Hewitt, W. Lewcock, and F. G. Pope, *J. Chem. Soc.*, 1912, **101**, 604.
[16] D. Craig, *J. Amer. Chem. Soc.*, 1935, **57**, 195.
[17] (*a*) R. L. Reeves and W. F. Smith, *J. Amer. Chem. Soc.*, 1963, **85**, 724; (*b*) J. Weinstein and E. McIninch, *J. Amer. Chem. Soc.*, 1960, **82**, 6064; (*c*) F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 1949, 2971; (*d*) G. M. Bennett and W. L. C. Pratt, *J. Chem. Soc.*, 1929, 1465.
[18] O. H. Wheeler and P. H. Gore, *J. Org. Chem.*, 1961, **26**, 3298.
[19] (*a*) D. C. Colinese, Ph.D. Thesis, University of London, 1966; (*b*) D. C. Colinese, unpublished results.
[20] V. G. Lindemann, *Z. wiss. Phot.*, 1955, **50**, 347.

View Article Online

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

TABLE 2 (*Continued*)

$100w$	ε	n_D
(2) *N*-(Benzylidene)-4-methylaniline in benzene		
0·0000	2·2725	1·49678
0·2304	2·2763	1·49708
0·4587	2·2802	1·49738
0·6884	2·2836	1·49769
0·9126	2·2873	1·49802
1·1411	2·2907	1·49830
1·3737	2·2945	1·49861
$\alpha = 1·615$; $\nu = 0·399$; $_0P_{2\infty} = 44·49$ cm^3; $\mu_B = 1·48$ D		
(3) *N*-(4-Methylbenzylidene)-aniline in benzene		
0·0000	2·2725	1·49695
0·2295	2·2768	1·49723
0·4589	2·2820	1·49753
0·6905	2·2868	1·49776
0·9195	2·2918	1·49818
1·1434	2·2965	1·49838
1·3726	2·3018	1·49875
$\alpha = 2·092$; $\nu = 0·381$; $_0P_{2\infty} = 62·65$ cm^3; $\mu_B = 1·75$ D		
(4) *N*-(4-Hydroxybenzylidene)-4-dimethylaminoaniline in dioxan		
0·0000	2·2093	1·41988
0·0495	2·2104	1·42006
0·0974	2·2132	1·42014
0·1955	2·2161	1·42043
0·2439	2·2181	1·42057
0·2926	2·2191	1·42067
$\alpha = 3·459$; $\nu = 0·798$; $_0P_{2\infty} = 102·28$ cm^3; $\mu_D = 2·24$ D		
(6) *N*-(4-Hydroxybenzylidene)-4-t-butylaniline in dioxan		
0·0000	2·2084	1·41984
0·1013	2·2119	1·42007
0·1938	2·2155	1·42025
0·2912	2·2188	1·42046
0·3916	2·2231	1·42071
0·4821	2·2259	1·42087
0·5837	2·2295	1·42113
$\alpha = 3·635$; $\nu = 0·617$; $_0P_{2\infty} = 123·58$ cm^3; $\mu_D = 2·46$ D		
(8) *N*-(4-Hydroxybenzylidene)-aniline in benzene		
0·0000	2·2725	1·49714
0·1146	2·2763	1·49727
0·1733	2·2783	1·49733
0·2307	2·2801	1·49743
0·2876	2·2821	1·49749
0·3470	2·2840	1·49753
0·4038	2·2859	1·49761
$\alpha = 3·321$; $\nu = 0·350$; $_0P_{2\infty} = 110·10$ cm^3; $\mu_B = 2·32$ D		
(9) *N*-(4-Hydroxybenzylidene)-4-fluoroaniline in dioxan		
0·0000	2·2086	1·41997
0·1012	2·2163	1·42007
0·1959	2·2253	1·42035
0·2925	2·2335	1·42054
0·3895	2·2419	1·42074
0·4870	2·2509	1·42092
0·5847	2·2583	1·42111
$\alpha = 8·514$; $\nu = 0·542$; $_0P_{2\infty} = 281·10$ cm^3; $\mu_D = 3·71$ D		

$100w$	ε	n_D
(2) *N*-(Benzylidene)-4-methylaniline in dioxan		
0·0000	2·2095	1·42000
0·1952	2·2140	1·42036
0·3907	2·2175	1·42084
0·5876	2·2215	1·42134
0·7799	2·2253	1·42173
0·9729	2·2292	1·42210
1·1694	2·2334	1·42250
$\alpha = 2·049$; $\nu = 0·616$; $_0P_{2\infty} = 44·18$ cm^3; $\mu_D = 1·47$ D		
(3) *N*-(4-Methylbenzylidene)-aniline in dioxan		
0·0000	2·2110	1·41987
0·1942	2·2162	1·42028
0·3892	2·2212	1·42077
0·5835	2·2268	1·42124
0·7791	2·2319	1·42170
0·9759	2·2368	1·42207
1·1690	2·2421	1·42254
$\alpha = 2·665$; $\nu = 0·652$; $_0P_{2\infty} = 62·67$ cm^3; $\mu_D = 1·75$ D		
(5) *N*-(4-Hydroxybenzylidene)-4-methoxyaniline in dioxan		
0·0000	2·2134	1·41990
0·0983	2·2186	1·42013
0·1941	2·2235	1·42042
0·2899	2·2283	1·42068
0·3872	2·2339	1·42087
0·4864	2·2385	1·42106
0·5873	2·2444	1·42141
$\alpha = 5·227$; $\nu = 0·719$; $_0P_{2\infty} = 165·90$ cm^3; $\mu_D = 2·85$ D		
(7) *N*-(4-Hydroxybenzylidene)-4-methylaniline in dioxan		
0·0000	2·2142	1·41992
0·0980	2·2189	1·42014
0·1948	2·2233	1·42021
0·2903	2·2271	1·42064
0·3894	2·2316	1·42082
0·4868	2·2360	1·42108
0·5819	2·2403	1·42130
$\alpha = 4·507$; $\nu = 0·648$; $_0P_{2\infty} = 131·85$ cm^3; $\mu_D = 2·54$ D		
(8) *N*-(4-Hydroxybenzylidene)-aniline in dioxan		
0·0000	2·2102	1·41998
0·0973	2·2154	1·42025
0·1963	2·2206	1·42045
0·2953	2·2261	1·42072
0·3877	2·2311	1·42096
0·4864	2·2364	1·42121
0·5839	2·2414	1·42148
$\alpha = 5·364$; $\nu = 0·720$; $_0P_{2\infty} = 148·65$ cm^3; $\mu_D = 2·70$ D		
(10) *N*-(4-Hydroxybenzylidene)-4-chloroaniline in dioxan		
0·0000	2·2098	1·41963
0·1015	2·2175	1·41982
0·1966	2·2247	1·42010
0·2936	2·2324	1·42029
0·3894	2·2393	1·42050
0·4885	2·2474	1·42078
0·5897	2·2543	1·42096
$\alpha = 7·615$; $\nu = 0·644$; $_0P_{2\infty} = 263·77$ cm^3; $\mu_D = 3·59$ D		

TABLE 2 (*Continued*)

$100w$	ε	n_D
(11) *N*-(4-Hydroxybenzylidene)-4-bromoaniline in dioxan		
0·0000	2·2079	1·41983
0·1018	2·2145	1·42005
0·2013	2·2218	1·42024
0·2948	2·2278	1·42048
0·3941	2·2340	1·42068
0·4893	2·2397	1·42088
0·5884	2·2467	1·42109
$\alpha = 6·624$; $\nu = 0·609$; $_0P_{2\infty} = 271·31$ cm^3; $\mu_D = 3·64$ D		
(13) *N*-(4-Hydroxybenzylidene)-4-ethoxycarbonylaniline in dioxan		
0·0000	2·2113	1·41992
0·0989	2·2192	1·42012
0·1975	2·2266	1·42035
0·2963	2·2342	1·42059
0·3893	2·2414	1·42084
0·4861	2·2487	1·42104
0·5843	2·2562	1·42123
$\alpha = 7·723$; $\nu = 0·644$; $_0P_{2\infty} = 311·19$ cm^3; $\mu_D = 3·90$ D		
(15) *N*-(4-Hydroxybenzylidene)-4-cyanoaniline in dioxan		
0·0000	2·2101	1·41981
0·1003	2·2318	1·42006
0·1988	2·2529	1·42031
0·2962	2·2736	1·42062
0·3910	2·2933	1·42075
0·4868	2·3134	1·42104
0·5924	2·3363	1·42132
$\alpha = 21·336$; $\nu = 0·721$; $_0P_{2\infty} = 752·52$ cm^3; $\mu_D = 6·07$ D		
(17) 4-Hydroxystilbene in dioxan		
0·0000	2·2106	1·41997
0·1010	2·2136	1·42008
0·1927	2·2165	1·42024
0·2925	2·2198	1·42056
0·3893	2·2226	1·42092
0·4836	2·2255	1·42113
0·5845	2·2286	1·42142
$\alpha = 3·083$; $\nu = 0·797$; $_0P_{2\infty} = 71·37$ cm^3; $\mu_D = 1·87$ D		

$100w$	ε	n_D
(12) (4-Hydroxybenzylidene)-4-iodoaniline in dioxan		
0·0000	2·2095	1·42001
0·0978	2·2144	1·42021
0·1958	2·2198	1·42037
0·2929	2·2252	1·42060
0·3937	2·2303	1·42087
0·4895	2·2358	1·42092
0·5825	2·2399	1·42120
$\alpha = 5·282$; $\nu = 0·569$; $_0P_{2\infty} = 248·08$ cm^3; $\mu_D = 3·49$ D		
(14) *N*-(4-Hydroxybenzylidene)-4-acetylaniline in dioxan		
0·0000	2·2085	1·41986
0·1005	2·2216	1·42012
0·1974	2·2353	1·42032
0·2932	2·2465	1·42059
0·3895	2·2605	1·42086
0·4856	2·2710	1·42111
0·5871	2·2859	1·42149
$\alpha = 13·135$; $\nu = 0·738$; $_0P_{2\infty} = 486·39$ cm^3; $\mu_D = 4·88$ D		
(16) *N*-(4-Hydroxybenzylidene)-4-nitroaniline in dioxan		
0·0000	2·2114	1·42002
0·0994	2·2340	1·42032
0·1956	2·2562	1·42057
0·2924	2·2773	1·42085
0·3894	2·2996	1·42113
0·4868	2·3219	1·42152
0·5838	2·3445	1·42168
$\alpha = 22·717$; $\nu = 0·825$; $_0P_{2\infty} = 870·37$ cm^3; $\mu_D = 6·53$ D		

Refractive indices, accurate to 0·00003, were measured with a precision Abbé refractometer.

Specific volumes of benzene (mean $v = 1·14540$ cm^3 g^{-1}) and dioxan (mean $v = 0·97383$ cm^3 g^{-1}) were obtained by a standard technique.

The results are given in Table 2, the symbols having their usual significance.

The molar orientation polarisation at infinite dilution, $_0P_{2\infty}$, of each solute was calculated from equation (1) in

$$_0P_{2\infty} = 3M_2v_1[\alpha/(\varepsilon_1 + 2)^2 - \nu/(n_1^2 + 2)^2] \qquad (1)$$

which M_2 = molecular weight of the solute; v_1, ε_1, and n_1 are the specific volume, dielectric constant, and refractive index respectively of the solvent at 298·2 K; $\alpha = (\partial\varepsilon/\partial w)_{w=0}$, $\nu = (\partial n^2/\partial w)_{w=0}$ were calculated from the experimental data by the method of least squares.

Dipole moments, μ, (in Debye units) calculated from

View Article Online

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

equation (2) are summarised in Table 3 (S.I. unit: 1 D = $3{\cdot}335640 \times 10^{-30}$ C m).

$$\mu = 0{\cdot}012812({}_{0}P_{2\infty} \times T)^{\frac{1}{2}} \quad (2)$$

TABLE 3

Apparent dipole moments and hydroxy-group stretching frequencies of benzylideneanilines $X{\cdot}C_6H_4{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}Y$ at 298·20 ± 0·02 K

No.	X	Y	$_{C}\nu$(OH) †/ cm^{-1}	$_{D}\nu$(OH) †/ cm^{-1}	μ_B †/ D	μ_D †/ D	μ_B (lit.)
(1)	H	H	—	—	1·56	1·57	1·57,[e] 1·58,[f] 1·56[g]
(2)	H	Me	—	—	1·48	1·47	1·53[e]
(3)	Me	H	—	—	1·75	1·75	1·80[e]
—	Me	Me	—	—	—	—	1·58[e]
—	Cl	Cl	—	—	—	—	1·57[f]
(4)	HO	NMe_2	3603	3304	—	2·24	
(5)	HO	OMe	3603	3297·5	—	2·85	
(6)	HO	Bu^t	3602	3296	—	2·46	
(7)	HO	Me	3602	3295	—	2·54	
(8)	HO	H	3602	3292·5	2·32	2·70	
(9)	HO	F	3602	3291·5	—	3·71	
(10)	HO	Cl	3601	3290	—	3·59	
(11)	HO	Br	3601	3289	—	3·64	
(12)	HO	I	3601	3289	—	3·49	
(13)	HO	CO_2Et	3601	3286	—	3·90	
(14)	HO	COMe	3600·5	3283	—	4·88	
(15)	HO	CN	3599	3281·5	—	6·07	
(16)	HO	NO_2	3598	3278	—	6·53	
(17)	*p*-Hydroxystilbene		3607·5	3318	—	1·87	
—	Phenol		3610·5[a]	3333[b]	1·54[c]	1·86[d]	

† B = Benzene; C = carbon tetrachloride; D = dioxan.

[a] 3610·1 cm^{-1}, ref. 13; 3611 cm^{-1}, L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220; 3612 cm^{-1}, L. J. Bellamy, G. Eglington, and J. F. Morman, *J. Chem. Soc.*, 1961, 4762. [b] 3315 cm^{-1}, L. J. Bellamy and H. E. Hallam, ref. *a*; 3340 cm^{-1}, J. P. B. Sandall, personal communication. [c] E. V. Goode and D. A. Ibbitson, *J. Chem. Soc.*, 1960, 4265. [d] Ref. 3. [e] F. Feichtmayr and F. Würstlin, Festchrift Carl Wurster zum 60 Geburstag, 1960, 177. [f] V. de Gaouck and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1938, 741. [g] E. Hertel and M. Schinzel, *Z. phys. Chem.*, 1941, *B*, **48**, 289.

I.r. Spectra.—Measurements were made at 298·20 ± 0·02 K on a Unicam SP 700C double-beam recording spectrophotometer, fitted with (*a*) an SP 790 absorbance unit; (*b*) an SP 770 constant-temperature cell housing connected to a thermostatted water bath; and (*c*) masks and germanium filters in the cell-housing entrance windows to remove unwanted radiation. The range 4000—3000 cm^{-1} was investigated with radiation from a tungsten filament lamp, which was dispersed by a Merton–N.P.L. replica grating (blazed at 3333 cm^{-1}, 1st order) and detected by a Mullard lead sulphide cell. The chopper motor, a source of unwanted radiation when hot,[21] was turned off between experiments.

Solutions in carbon tetrachloride (5×10^{-4} mol l^{-1}) and in dioxan (5×10^{-2} mol l^{-1}) were examined quantitatively in matched pairs of Infrasil cells of path-length 40 mm and 0·5 mm respectively. Frequencies at the absorbance maxima, reproducible to 0·5 cm^{-1}, were located at the intersection of the bisector of a series of horizontal chords of the band with the band contour, and measured with a vernier scale. In carbon tetrachloride, the bisector was vertical, indicating band symmetry; in dioxan, slight asymmetry appeared. At the end of each interrupted series of measurements, frequency calibration was carried out, using the atmospheric water vapour bands [22] at 3700—3500 cm^{-1}, and the indene peak [22] at 3297 ± 1·5 cm^{-1}. The control settings shown in Table 4 were used. Fundamental hydroxy-group stretching frequencies $_{C}\nu$(OH) and $_{D}\nu$(OH) are recorded in Table 3 (intensities will be reported in a later paper).

TABLE 4

	In CCl_4	In $C_4H_8O_2$	H_2O vap.
Chart speed/cm h^{-1}	200	300	200
Absorbance range	−0·3 to +0·8	−0·3 to +0·8	Energy
Damping	3	3	3
Scan speed/cm^{-1} min^{-1}	26	78	26
Resolution	3	3	5
Markers/cm^{-1}	20	20	20
Slit width/mm	Auto	Auto	0·11

DISCUSSION

Dipole Moments.—The moments in dioxan of benzylideneaniline and two *para*-methyl derivatives [compounds (1)—(3) in Table 3] are the same as the corresponding moments in benzene within experimental error, indicating that solvent effects on the charge distributions in these compounds are quantitatively similar. However, the dipole moment of *N*-(4-hydroxybenzylidene)-aniline [compound (8) of Table 3] is greater in dioxan than in benzene. This effect is attributed to hydrogen bonding of the hydroxy-group to an oxygen atom of a dioxan molecule; the same explanation was offered recently [4] for the enhanced moments of phenols and 4′-substituted 4-hydroxyazobenzenes in dioxan. A direct comparison of the moments of these two classes with those of hydroxybenzylideneanilines is not significant, because of the influence of the azomethine unit in the latter. The apparent moments [compounds (4)—(16), Table 3] are resultant moments, and may be regarded as compounded vectorially from the component moments of the C(ring)–O, O–H, and Y–C(ring) bonds, and that of the azomethine unit [containing contributions from the C(ring)–C, C–H, C=N and N–C(ring) bonds], allowing for interaction between these moments. The hydroxy-group bond moment, μ(O–H), in phenols and hydroxyazobenzenes is a useful quantitative index of the strength of hydrogen-bonding to dioxan and the influence of substituent groups.[4] To see if this is so for the series of compounds in Table 3, and to assess the effect of the azomethine unit, the following vectorial analysis was made.

Orientation of the Benzylideneaniline Moment.—In these and subsequent calculations, the following structural information was taken into account.

Attempts to isolate *cis*-benzylideneanilines have failed.[23] Smith has pointed out [24] that the dipole moments of the dimethyl- and dichloro-compounds (Table 3) are virtually the same as that of the parent,

[21] C. G. Cannon, personal communication.
[22] I.U.P.A.C., 'Tables of Wavenumbers for the Calibration of Infrared Spectrometers,' Butterworths, London, 1961.
[23] van Alpen, *Rec. Trav. chim.*, 1942, **61**, 875; F. Krohnke, *Ber.*, 1938, **71**, 2593.
[24] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955.

View Article Online

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

indicating that the C–Me (or C–Cl) dipoles are antiparallel, and showing that each compound is the *trans*-isomer. In chloro-derivatives of salicylideneaniline, which are stabilised *trans* by intramolecular hydrogen-bonding, ∠C(ring)NC = ∠NCC(ring) = 122°, and the rings are parallel to within 1° of their respective normals.[25] The suggestion [25] that repulsive interactions between non-bonded atoms are relieved by twisting of the rings out of the C–C=N–C plane is supported by the recent *X*-ray data of Bürgi and Dunitz [26] for *trans*-benzylideneaniline and two *para*-derivatives; the aniline rings are twisted by 40—55°, the benzylidene rings being twisted in the opposite sense by 8—14°. The bond angles are ∠C(ring)NC = 119·9° and 120·6°; ∠NCC(ring) = 122·7° and 120·2°, for benzylideneaniline, and *N*-(4-methylbenzylidene)-4-nitroaniline, respectively. Since the crystal reflectance spectra are similar to the solution spectra, these authors [26] consider that the stable conformations of the free molecules are not too different from those found in the crystalline state. Accordingly, these results are relevant in the present vectorial analysis, in which the planarity of C–C=N–C, and the equality ∠C(ring)NC = ∠NCC(ring), are assumed.

In evaluating the angle of inclination (α) of the C=N dipole axis to the N–C(ring) axis in benzylideneaniline, it was assumed, in accord with Marsden and Sutton,[27] that the moment of the latter was unperturbed by the introduction of a *para*-methyl substituent. The angle (α = 70° 46′) has been calculated from the moments in benzene of benzylideneaniline (A; μ_B = 1·56 D), *N*-(benzylidene)-4-methylaniline (MeA; μ_B = 1·48 D), and toluene (PhMe; μ_B = 0·37 D), from equation (3).

$$\mu^2_{MeA} = \mu^2_A + \mu^2_{PhMe} + 2\mu_A\mu_{PhMe}\cos(180° - \alpha) \quad (3)$$

Similarly, the angle of inclination (β = 64° 46′) of the C=N dipole axis to the C(ring)–C axis has been deduced from μ_A, μ_{PhMe}, and the moment in benzene of *N*-(4-methylbenzylidene)aniline (Me′A; μ_B = 1·75 D), by use of equation (4). If it is assumed that the N–C(ring) and

$$\mu^2_{Me'A} = \mu^2_A + \mu^2_{PhMe} + 2\mu_A\mu_{PhMe}\cos\beta \quad (4)$$

C(ring)–C axes are parallel, the best value for the angle of inclination in benzene is the mean (5). Analogous

$$\theta = [(\alpha + \beta)/2] = 67° 46' \quad (5)$$

calculations with the corresponding moments in dioxan [compounds (1)—(3) in Table 3] yield α = 67° 42′, β = 66° 38′. The mean [equation (6)] in dioxan is close

$$\theta = [(\alpha + \beta)/2] = 67° 10' \quad (6)$$

to that in benzene, indicating that there is no significant difference between the orientations of the azomethine group moment in these two solvents. To test the validity of θ in equation (5), the moment of *N*-(benzylidene)-4-chloroaniline (I; X = H, Y = Cl) in benzene has been predicted from the moments of chlorobenzene (1·58 D) and *N*-(benzylidene)aniline (1·56 D; θ = 67° 46′) in benzene, from equation (7), which yields μ_{pred} = 2·61 D,

$$\mu^2_{pred} = (1·56)^2 + (1·58)^2 + 2(1·56)(1·58)\cos 67° 46' \quad (7)$$

in satisfactory agreement with the observed value,[28] μ_{obs} = 2·58 D, and the general finding that interaction moments in chloro-compounds are small, and do not increase markedly with increasing length of the attached conjugated system.[24,29]

Hydroxy-group Bond Moments.—In extending the preceding results to predict the moments of phenolic benzylideneanilines, allowances must be made for rotation of the OH group about the C(ring)–O axis.[30] For two dipole vectors μ_1, μ_2 making fixed angles θ_1, θ_2 respectively with an axis about which mutual free rotation occurs, the predicted root-mean-square moment (assuming all mutual orientations around the axis to be equally probable) is [24] given by equation (8). From

$$\mu_{pred} = (\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2\cos\theta_1\cos\theta_2)^{\frac{1}{2}} \quad (8)$$

equation (8), the moment in benzene (μ_{pred} = 2·21 D) of *N*-(4-hydroxybenzylidene)aniline has been predicted from the moment of *N*-(benzylidene)aniline (μ_1 = 1·56 D, θ_1 = 67° 46′), and that of phenol (μ_2 = 1·54 D, θ_2 = 180° − 87° 47′) in benzene, the angle (87° 47′) between the directions of the C–OH group moment and the O–C(ring) bond reported previously being adopted.[29] The agreement between μ_{pred} = 2·21 D and μ_{obs} = 2·32 D is only fair; the effective value of at least one of the dipole vectors must differ from that in the parent benzylideneaniline or phenol molecule. In a parallel situation, the enhanced moment of 4-hydroxyazobenzene (μ_B = 1·66 D) over that of phenol (μ_B = 1·54 D) can be interpreted [4] in terms of an increased mesomeric release from the oxygen atom to the more extended conjugated system in the azo-compound. A useful index of this change, and additional changes upon hydrogen-bonding, is the hydroxy-group bond moment, μ(O–H), necessary to explain the observed moment.[4]

Calculation of μ(O–H). The influence of substitution upon the hydrogen-bonding tendency of the OH group in *N*-(4-hydroxybenzylidene)-4-substituted anilines has been assessed by evaluating μ(O–H) values necessary to explain the observed moments in dioxan.

A C–O–H valency angle of 115° in phenol, a dipole moment of phenol in dioxan of 1·86 D, and an angle of 83° 44′ between the directions of the C–OH group moment and the O–C(ring) bond being assumed, the moments associated with the O–H and C–O bonds have been derived previously [4] as 2·04 D and 0·66 D respectively.

[25] J. Bregman, L. Leiserowitz, and K. Osaki, *J. Chem. Soc.*, 1964, 2086; J. Bregman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2068.
[26] H. B. Bürgi and J. D. Dunitz, *Chem. Comm.*, 1969, 472.
[27] R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 599.
[28] A. L. McClellan, ' Tables of Experimental Dipole Moments,' W. H. Freeman and Co., London, 1963.
[29] E. V. Goode and D. A. Ibbitson, *J. Chem. Soc.*, 1960, 4265.
[30] Ref. 9; L. Pauling, ' Nature of the Chemical Bond,' Cornell Univ. Press, New York, 2nd edn., 1948, p. 323.

View Article Online

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

Since the moment of 4-hydroxystilbene in dioxan (μ_D = 1·87 D) is the same as that of phenol, within experimental error, μ(O–H) and μ(C–O) in the former can be assumed to equal the values in phenol. Further, both in 4-hydroxystilbene and the hydroxybenzylideneanilines (I), a carbon atom of the inter-ring bridge is directly attached to the *para*-position in phenol; consequently, it is a reasonable approximation to assume that μ(C–O) = 0·66 D in each class. In the vector calculations, the following assumptions were made: (1) a C–O–H valency angle of 115°; (2) a C–O bond moment of 0·66 D; (3) the aromatic rings are planar, and disposed *trans*, with bond axes of bonds directly attached to the rings mutually parallel; (4) a C=N group moment of 1·57 D, inclined at 67° 10′ [equation (6)] to the N–C(ring) axis direction; (5) values of the moments of the monosubstituted benzene derivatives, μ(PhX), in benzene, remaining unaltered in dioxan, of dimethylaniline,[28] 1·57; anisole,[31] 1·30; t-butylbenzene,[29] 0·53; toluene,[24] 0·37; fluorobenzene,[24] 1·48; chlorobenzene,[24] 1·58; bromobenzene,[24] 1·56; iodobenzene,[24] 1·40; ethyl benzoate,[32] 1·93; acetophenone,[33] 2·96; benzaldehyde,[24] 2·92; cyanobenzene,[24] 4·03; and nitrobenzene,[24] 4·01.

For the angular substituents (Y = NMe_2, OMe, CO_2Et, COMe, and CHO) the angles, α, which the substituent group moments make with a direction parallel to the Y–C(ring) axis were calculated, in accord with Marsden and Sutton,[27] from the moments of PhY; the mono-methyl-, -fluoro- or -chloro-benzene, PhZ; and the *para*-disubstituted compound, Z·C_6H_4·Y; the results are in Table 5.

TABLE 5

Angles of inclination (α) of group moments to the substituent ⟶ C(ring) axis

Y	μ(PhY)	Z	μ(PhZ)	μ(Z·C_6H_4·Y)	α
OMe	1·30 [a]	F	1·48 [b]	2·09 [b]	82° 41′
COMe	2·96 [c]	Me	0·37 [b]	3·23 [c]	134° 22′
CO_2Et	1·93 [d]	Cl	1·58 [b]	2·24 [d]	101° 23′
NMe_2	1·57 [e]	Me	0·37 [b]	1·30 [f]	38° 18′
CHO	2·92 [b]	Me	0·37 [b]	3·30 [g]	180° 00′

[a] Ref. 31. [b] Ref. 24. [c] Ref. 33. [d] Ref. 32. [e] Ref. 28. [f] Ref. 27. [g] J. N. Pearce and L. F. Berhenke, *J. Phys. Chem.*, 1935, **39**, 1005.

Values of μ(O–H) were calculated vectorially on the basis of the model shown in the Figure, free rotation of the dipole vectors being assumed about the appropriate substituent–C(ring), N–C(ring), and O–C(ring) axes, from equations (9)—(11), in which μ_H is a resultant

$$\mu_H^2 = [\mu_{OH} \cos 65° - \mu_{CO} + 1{\cdot}57 \cos 67° 10' - \mu_{PhY} \cos \alpha]^2 \quad (9)$$

$$\overline{\mu_V^2} = (\mu_{OH} \sin 65°)^2 + (1{\cdot}57 \sin 67° 10')^2 + (\mu_{PhY} \sin \alpha)^2 \quad (10)$$

$$\mu_{obs}^2 = \mu_H^2 + \overline{\mu_V^2} \quad (11)$$

moment of the molecule, parallel to the O–C(ring) axis; $\overline{\mu_V^2}$ a mean-square moment perpendicular to this axis; μ_{PhY} the moment of the monosubstituted benzene derivative; (1·57 D, 67° 10′) the moment and inclination for the azomethine group in dioxan; μ_{CO} = 0·66 D; μ_{obs} is the observed moment in dioxan, and μ_{OH} the required bond moment. For the inclined substituent group moments, angle α is taken from Table 5; α is 0° for the Me and Bu^t groups, and 180° for the remaining groups with moments directed parallel to the Y–C(ring) axis.

When values of μ(O–H) are plotted against Hammett's substituent constants, σ, an essentially linear trend is apparent. The regression equation of μ(O–H) on σ, derived by assuming no error in σ, is μ(O–H) = 2·25 + 0·892σ, with a mean deviation 0·17 D. The corresponding results for *para*-substituted phenols in dioxan were [4] μ(O–H) = 2·12 + 0·671σ, mean deviation 0·05 D. Relevant numerical data are in Table 6.

It must be stressed that since the hydroxy-group bond-moments rest on a number of assumptions, their absolute values are of dubious significance, and interest resides in the relative values of μ(O–H).

Although the mean deviation for the hydroxybenzylideneanilines is rather high, corresponding to considerable scatter of experimental points about the regression line,

TABLE 6

Hydroxy-group bond moments of phenols and *N*-(4-hydroxybenzylidene)-4-substituted anilines in dioxan

			N-(4-Hydroxybenzylidene)-anilines μ(O–H)/D		Phenols [a] μ(O–H)/D	
No.	4-Substnt.	σ_{para}	Obs.	Calc.†	Obs.	Calc.†
(4)	NMe_2	−0·600	1·33	1·71		
(5)	OMe	−0·268	2·26	2·01		
(6)	Bu^t	−0·197	2·16	2·07		
(7)	Me	−0·170	2·23	2·10	2·01	2·01
(8)	H	0·000	2·30	2·25	2·04	2·12
(9)	F	0·062	2·56	2·31	2·22	2·16
(10)	Cl	0·227	2·33	2·45	2·31	2·27
(11)	Br	0·232	2·41	2·46	2·25	2·28
(12)	I	0·276	2·36	2·50		
(13)	CO_2Et	0·678	2·93	2·86		
(14)	COMe	0·874	2·76	3·03	2·65	2·71
(15)	CN	1·000	2·98	3·14	2·85	2·79
—	CHO	1·126			2·80	2·88
(16)	NO_2	1·270	3·59	3·38	3·01	2·97

† Calculated from the regression equations.
[a] Ref. 4.

the trend suggests a dependence of the hydroxy-group bond moment upon the electrical character of the substituent, μ(O–H) increasing with increasing electron-attracting power of the substituent, as reported for phenols and 4-hydroxyazobenzenes.[4]

Hydroxy-group Stretching Frequencies.—In carbon tetrachloride solution, the OH stretching frequency $\sigma\nu$(OH) of the parent *N*-(4-hydroxybenzylidene)aniline [Table 3, compound (8)] is appreciably less than that of phenol (3610·1 cm^{-1});[13] the extended conjugation arising from introduction of the Ph·N=CH– substituent into

[31] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1950, 1829.

[32] E. Bergmann and A. Weizmann, *J. Amer. Chem. Soc.*, 1935, **57**, 1755.

[33] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

View Article Online

Published on 01 January 1971. Downloaded by Gazi Universitesi on 18/10/2017 06:54:59.

phenol has an effect corresponding to the presence of an electron-attracting substituent of the ethoxycarbonyl type, and resembles the influence of the Ph·N=N– substituent in 4-hydroxyazobenzenes.[4] In contrast, extended conjugation in *trans-p*-hydroxystilbene, which is approximately planar, results in $_{C}\nu$(OH) = 3607·5 cm^{-1}, only slightly less than $_{C}\nu$(OH) of phenol. The greater frequency reduction in the azo- and azomethine compounds may be determined by the higher electronegativity of the nitrogen atoms which replace the carbon atoms of the stilbene bridge, and not solely by the length of the conjugated system.

$_{C}\nu$(OH) values for the derivatives of *N*-(4-hydroxybenzylidene)aniline differ little from that of the parent compound, the maximum change (4 cm^{-1}) arising for the nitro-group, which induces a shift of 15·6 cm^{-1} from $_{C}\nu$(OH) of phenol. Thus, the electronic influence of the substituent is transmitted to the hydroxy-group, but it is attenuated in comparison with the *para*-substituted phenols. This effect could be partially attributed to the pronounced twist of the aniline ring [26] out of the C–N=C–C plane by 40—55°, so diminishing conjugation between Y·C$_6$H$_4$·N= and the phenolic ring. However, the distance of the substituent from the OH group is also important, since similar attenuation occurs in the hydroxyazobenzenes,[4] which are planar [26] and should suffer no restriction of conjugation.

In dioxan solution, $_{D}\nu$(OH) $\ll$ $_{C}\nu$(OH) for the parent compound, the large shift being characteristic of solute–solvent hydrogen bonding. For *N*-(4-hydroxybenzylidene)aniline, $\Delta\nu$(OH) = 309·5 cm^{-1}, which is appreciably greater than for phenol (277·5 cm^{-1}), implying enhanced mesomeric release by the oxygen atom in the hydrogen-bonded complex of the former compound, but slightly less than in the complex [4] of 4-hydroxyazobenzene [$\Delta\nu$(OH) = 316 cm^{-1}]. The additional frequency shifts in the *N*-(4-hydroxybenzylidene)anilines on substitution are larger than the corresponding shifts in carbon tetrachloride solution, but smaller than corresponding shifts in phenols: *e.g.*, the nitro-group produces shifts in dioxan of 14·5 cm^{-1} and 86 cm^{-1} respectively. These effects are apparent on comparing the slopes of the regression lines of ν(OH) upon σ shown in Table 7.

If it is assumed that the relative frequency shift between carbon tetrachloride and dioxan is a measure of the enthalpy change on association, the dependence of the O–H bond moment on the strength of hydrogen-bonding, already demonstrated for phenols and hydroxyazobenzenes,[4] is again illustrated by plots of μ(O–H) against $\Delta\nu$(OH)/$_{C}\nu$(OH). The regression equations are (12) and (13) for the *N*-(4-hydroxybenzylidene)anilines and phenols respectively, with mean deviations 0·16 D and 0·05 D. It has been pointed out that relatively large changes in hydrogen-bond strength occur on *para*-substitution in phenol, with correspondingly significant bond moment changes, whereas a range of 4′-substituents in 4-hydroxyazobenzenes alter μ(O–H) considerably but have little effect on the hydrogen-bond strength.[4] The present results for *N*-(4-hydroxybenzylidene)anilines show that these compounds conform to the same pattern as the hydroxyazobenzenes. Further attention will be given to this point in Part II, concerned with a series of *N*-(4-substituted benzylidene)-4-hydroxyanilines (I; Y = OH).

TABLE 7

Regression equations of ν(OH) upon σ

Series	Equation	Mean deviation/cm^{-1}
4-Y·C$_6$H$_4$·N=CH·C$_6$H$_4$·OH	$_{C}\nu$(OH) = 3601·8 − 2·46σ	0·27
	$_{D}\nu$(OH) = 3293·5 − 12·7σ	0·89
4-Y·C$_6$H$_4$·OH	$_{C}\nu$(OH) = 3610·7 − 12·5σ	0·73
	$_{D}\nu$(OH) = 3336 − 70·4σ	5·4

$$\mu(\text{O–H}) = 0{\cdot}306[10^3\Delta\nu(\text{OH})/_{C}\nu(\text{OH})] - 23{\cdot}92 \quad (12)$$

$$\mu(\text{O–H}) = 0{\cdot}0414[10^3\Delta\nu(\text{OH})/_{C}\nu(\text{OH})] - 1{\cdot}05 \quad (13)$$

For this and the following paper, I thank the S.R.C. for a grant for the purchase of a Unicam SP 700 spectrophotometer, the Derby and Derbyshire Joint Education Committee for facilities, Dr. D. A. Ibbitson for discussions, and Mr. M. S. J. Twiselton for encouragement.

[0/1147 *Received, July 6th*, 1970]