978. *Molecular Polarisability: The Conformations of Acetanilide and Certain* para-*Substituted Acetanilides as Solutes in Benzene and Dioxan.*

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From considerations of polarity and polarisability it is concluded that the angle ϕ between the C_{ar}–N–C_{CO} and the N–C_{CO}–O plane is about 80° for acetanilide and its *p*-bromo-derivative in benzene, and within the range 65—85° for these substances and for the related *p*-chloro- and *p*-methyl-acetanilide in dioxan.

IN this paper we apply bond and group polarity and polarisability data to calculations of the dipole moments and molar Kerr constants corresponding to various conformations of acetanilide and certain of its *para*-substituted derivatives. We then compare such predictions with results from observations on solutions in benzene or dioxan, and thereby deduce the preferred orientations of the carbonyl groups relative to the C_{ar}–N–C_{CO} planes of the molecules concerned.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were recrystallised immediately before use from aqueous alcohol, giving acetanilide, m. p. 114°, acetyl-*p*-toluidine, m. p. 153°, *p*-chloro-acetanilide, m. p. 179°, and *p*-bromoacetanilide, m. p. 167°. Benzene and dioxan were purified by refluxing them over, and then distilling them from, sodium.

Apparatus, techniques, symbols used, and methods of calculation have been described

TABLE 1.

Incremental Kerr effects, refractive indexes, dielectric constants, and densities, for solutions at 25°.

Acetanilide in benzene

$\Delta B = 0$ for all concentrations up to $w_2 = 0{\cdot}01$.

p-*Bromoacetanilide in benzene*

10^5w_2	225	268	283	307	340
$10^7\Delta B$	0·007	0·008	0·009	0·009	0·012

whence $\sum 10^7\Delta B/\sum w_2 = 3{\cdot}16$.

Acetanilide in dioxan

10^5w_2	968	1227	1463	1658	1761	1845	2100
$10^7\Delta B$	0·051	0·060	0·071	0·077	0·085	0·096	0·118

whence $\sum 10^7\Delta B/\sum w_2 = 5{\cdot}06$.

10^5w_2	466	690	966	1123	1200	1379	1775	1804
ε^{25}	2·2770	2·3127	2·3479	2·3792	2·3913	2·4162	—	2·4734
d_4^{25}	1·02842	—	1·02887	1·02901	—	1·02924	1·02959	1·02962

whence $\sum\Delta\varepsilon/\sum w_2 = 14{\cdot}9$; $\sum\Delta d/\sum w_2 = 0{\cdot}090$.

10^5w_2	737	968	1123	1555	1804	2101
$10^4\Delta n$	12	16	18	24	28	33

whence $\sum\Delta n/\sum w_2 = 0{\cdot}158$.

*Acetyl-*p*-toluidine in dioxan*

10^5w_2	792	880	1307	1564	1730
$10^7\Delta B$	0·010	0·011	0·013	0·017	0·018

whence $\sum 10^7\Delta B/\sum w_2 = 1{\cdot}10$.

10^5w_2	690	1041	1240	1552	1874
ε^{25}	2·3010	2·3486	2·3805	2·4223	2·4684
d_4^{25}	1·02838	1·02852	1·02865	1·02879	1·02896
$10^4\Delta n$	9	14	17	21	25

whence $\sum\Delta\varepsilon/\sum w_2 = 13{\cdot}5$; $\sum\Delta d/\sum w_2 = 0{\cdot}052$;
$\sum\Delta n/\sum w_2 = 0{\cdot}134$.

p-*Chloroacetanilide in dioxan*

10^5w_2	593	801	956	1134	1309	1473	1822
$10^7\Delta B$	0·058	0·073	0·096	0·122	0·130	0·159	0·170

whence $\sum 10^7\Delta B/\sum w_2 = 9{\cdot}99$.

10^5w_2	550	670	950	956	1261	1562	1626	1822
ε^{25}	2·2977	2·3197	2·3603	—	2·4139	2·4627	2·4729	—
d_4^{25}	1·02907	—	1·02979	1·02989	1·03088	1·03095	1·03126	1·03132
$10^4\Delta n$	—	11	15	—	20	24	25	—

whence $\sum\Delta\varepsilon/\sum w_2 = 16{\cdot}2$; $\sum\Delta d/\sum w_2 = 0{\cdot}197$; $\sum\Delta n/\sum w_2 = 0{\cdot}157$.

p-*Bromoacetanilide in dioxan*

10^5w_2	766	1049	1360	1378	1412	1614
$10^7\Delta B$	0·061	0·083	0·108	0·109	0·115	0·134

whence $\sum 10^7\Delta B/\sum w_2 = 8{\cdot}05$.

10^5w_2	666	766	878	1046	1293	1378	1412	1527	1598	2091	2193
ε^{25}	2·2963	—	2·3216	—	2·3718	—	—	—	2·4154	2·4809	2·4954
d_4^{25}	1·03034	1·03067	—	1·03158	1·03252	1·03266	—	1·03348	—	—	—
$10^4\Delta n$	—	—	—	—	—	18	19	20	20	26	28

whence $\sum\Delta\varepsilon/\sum w_2 = 12{\cdot}9$; $\sum\Delta d/\sum w_2 = 0{\cdot}348$; $\sum\Delta n/\sum w_2 = 0{\cdot}128$.

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions at 25°).

Solute	Solvent	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	μ (D) †	$10^{12}\,{}_\infty({}_mK_2)$
Ph·NHAc	Benzene	10·9 ‡	0·231 ‡	0·051 ‡	0	312 ‡	40·4 ‡	3·65 ‡	3·63 ‡	−45
p-Br·C_6H_4·NHAc	,,	9·83 ‡	0·418 ‡	0·393 ‡	7·71	438 ‡	48·4 ‡	4·36 ‡	4·35 ‡	+53
Ph·NHAc	Dioxan	14·9	0·088	0·111	74·4	366	41·3	3·98	3·97	+107
p-Br·C_6H_4·NHAc	,,	12·9	0·339	0·090	118	495	48·9	4·67	4·66	+280
p-Cl·C_6H_4·NHAc	,,	16·2	0·192	0·111	147	491	47·4	4·66	4·64	+276
p-Me·C_6H_4·NHAc	,,	13·5	0·051	0·094	16·2	371	45·1	3·99	3·97	+18

* Calc. by assuming ${}_DP = R_D$. † Calc. by assuming ${}_DP = 1·05R_D$. ‡ From ref. 4.

before.[1-3] Observations are recorded in Table 1 and results summarised in Table 2. The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indexes, and Kerr constants, respectively, of the solvents and of solutions containing weight fractions w_2 of solute. The following values apply at 25° to the two solvents:

	ε_1	d_1	$(n_1)_D$	10^7B_1	$10^{12}{}_sK_1$
Benzene	2·2725	0·87378	1·4973	0·410	0·0756
Dioxan	2·2090	1·0280	1·4202	0·068	0·0116

Previous Measurements.—The following dipole moments (D) have been recorded (numerals in parentheses being references): acetanilide, 4·01 (in C_6H_6, 5); 3·62 (in C_6H_6, 6); 3·65 (in C_6H_6, 4); 4·02 (in dioxan, 7); 3·97 (in dioxan, 6); 3·5 (in CCl_4, 8); acetyl-*p*-toluidine, 3·74 (in C_6H_6, 4); *p*-chloroacetanilide, 4·32 (in C_6H_6, 4); *p*-bromoacetanilide, 4·36 (in C_6H_6, 4).

DISCUSSION

From steric considerations Smith[4] concluded that in acetanilide there would be six positions of minimum potential energy defined by $\phi = 30°, 90°, 150°, 210°, 270°$, and $330°$; ϕ, the angle between the C_{Ar}–N–C_{CO} and N–C_{CO}–O planes, is zero for an *s-cis*-arrangement of the group Ph–N–C=O (for diagrams and a detailed description of these structures see ref. 4, pp. 4701—4702). Smith calculated, by vector addition of bond and group moments, the theoretical values for acetanilide and for its *p*-methyl-, *p*-chloro-, and *p*-bromo-derivatives in various conformations listed in Table 2 of ref. 4. Comparison of Smith's calculated and observed dipole moments shows clearly that structures with $\phi > 90°$ need not seriously be considered. Within the limits $0 < \phi < 90°$, the magnitude of μ_{calc} is relatively insensitive to changes in ϕ, so that, in view of the assumptions underlying these calculations, a more definite specification of ϕ in this range is not possible from dipole moments alone. The purpose of the present work is to examine the computed molar Kerr constants as functions of ϕ and to compare the theoretical molar Kerr constants with those from experiment in order to establish, with greater certainty, the conformations of these compounds as solutes at high dilution in non-polar media. Following Smith, we assume that the moment of acetanilide arises from the addition of an aniline-like component (1·53 D, acting at 48·5° to the N–C_{Ar} bond) and a carbonyl link moment (taken as $\mu_{acetone} = 2·78$ D), that the amino-group is so disposed as to give the maximum overlap of the nitrogen lone-pair orbital with the benzene-ring π-electrons, and that the nitrogen valency angles are tetrahedral and those of C_{CO} are 120° (the bond angles given

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[1] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

[2] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

[3] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*b*) Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 3rd edn., Vol. I, p. 2459.

[4] Smith, *J.*, 1961, 4700.

[5] Le Fèvre and Le Fèvre, *J.*, 1936, 1136.

[6] Estok and Sood, *J. Phys. Chem.*, 1962, **66**, 1372.

[7] Nagakura and Kuboyama, *Rept. Inst. Sci. Technol., Univ. Tokyo*, 1951, **5**, 27.

[8] Suzuki, Tsuboi, Shimanouchi, and Mizushima, *Spectrochim. Acta*, 1960, **16**, 471.

by Brown and Corbridge[9] for the acetanilide crystal lead to calculated moments considerably lower than that observed). Bond and group polarisabilities used in the following calculations are: $b_{L}^{Ph} = b_{T}^{Ph} = 1{\cdot}056$, $b_{V}^{Ph} = 0{\cdot}672$, $b_{L}^{C=O} = 0{\cdot}230$, $b_{T}^{C=O} = 0{\cdot}140$, $b_{V}^{C=O} = 0{\cdot}046$, $b_{L}^{N-C} = 0{\cdot}057$, $b_{T}^{N-C} = b_{V}^{N-C} = 0{\cdot}069$, $b_{L}^{N-H} = 0{\cdot}050$, $b_{T}^{N-H} = b_{V}^{N-H} = 0{\cdot}083$, $b_{L}^{C-C} = 0{\cdot}099$, $b_{T}^{C-C} = b_{V}^{C-C} = 0{\cdot}027$, $b_{L}^{C-H} = b_{T}^{C-H} = b_{V}^{C-H} = 0{\cdot}064$ ($\times 10^{-23}$ c.c., throughout).

Acetanilide and p-*Bromoacetanilide as Solutes in Benzene.*—The computational procedures are outlined in ref. 3(*b*), pp. 2483—2486. Table 3 lists the polarisability semi-axes calculated for conformations of acetanilide; their locations with reference to the orthogonal axes *X*, *Y*, *Z* (see Fig. 1 (a) and (b); and the calculated dipole moments and molar Kerr constants. Exaltations of polarisability are assumed to be analogous to those found for aniline:[10] $\Delta b_{XX} = +0{\cdot}22$, $\Delta b_{YY} = -0{\cdot}10$, $\Delta b_{ZZ} = -0{\cdot}06$. The dipole moment components in the *X*, *Y*, and *Z* directions for any conformation of acetanilide are: $\mu_X = 1{\cdot}53 \cos 48{\cdot}5 + \mu^{C=O} l_X^{C=O}$; $\mu_Y = \mu^{C=O} l_Y^{C=O}$; $\mu_Z = 1{\cdot}53 \sin 48{\cdot}5 + \mu^{C=O} l_Z^{C=O}$, where $l_X^{C=O}$, $l_Y^{C=O}$, and $l_Z^{C=O}$ are the direction cosines locating the carbonyl link moment within the co-ordinate system $0XYZ$.

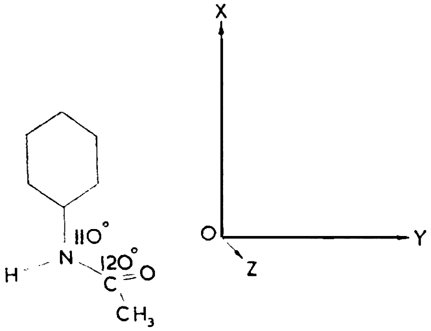

FIG. 1(a)

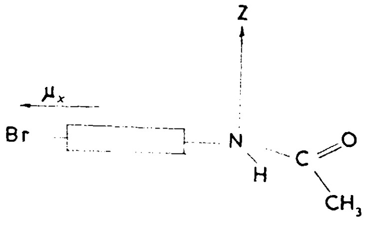

FIG. 1(b)

TABLE 3.

Polarisabilities, dipole moments, and molar Kerr constants calculated for conformations of acetanilide in benzene.

ϕ	b_i (calc.)	Direction cosines with *X*	*Y*	*Z*	$\mu_{calc.}$ (D)	$10^{12}{}_mK$ (calc.)
0°	$b_1 = 1{\cdot}948$	+0·998	+0·057	−0·033	3·36	+592
	$b_2 = 1{\cdot}536$	−0·062	+0·983	−0·171		
	$b_3 = 1{\cdot}112$	+0·023	+0·172	+0·985		
30°	$b_1 = 1{\cdot}910$	+0·988	+0·135	+0·072	3·63	+443
	$b_2 = 1{\cdot}559$	−0·129	+0·988	−0·084		
	$b_3 = 1{\cdot}126$	−0·083	+0·074	+0·994		
60°	$b_1 = 1{\cdot}817$	+0·988	+0·085	+0·130	3·68	+119
	$b_2 = 1{\cdot}581$	−0·093	+0·994	+0·049		
	$b_3 = 1{\cdot}197$	−0·125	−0·061	+0·990		
70°	$b_1 = 1{\cdot}789$	+0·993	+0·005	+0·114	3·65	0
	$b_2 = 1{\cdot}583$	−0·016	+0·995	+0·101		
	$b_3 = 1{\cdot}224$	−0·113	−0·102	+0·988		
80°	$b_1 = 1{\cdot}771$	+0·992	−0·109	+0·070	3·60	−102
	$b_2 = 1{\cdot}575$	+0·098	+0·986	+0·137		
	$b_3 = 1{\cdot}249$	−0·084	−0·129	+0·988		
90°	$b_1 = 1{\cdot}770$	+0·978	−0·208	+0·008	3·52	−174
	$b_2 = 1{\cdot}558$	+0·205	+0·969	+0·136		
	$b_3 = 1{\cdot}268$	−0·036	−0·132	+0·991		

With the *para*-substituted derivatives examined, only *p*-bromoacetanilide was sufficiently soluble in benzene to produce differences ΔB_{12} large enough to be measured with

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[9] Brown and Corbridge, *Acta Cryst.*, 1954, **7**, 711.
[10] Aroney and Le Fèvre, *J.*, 1960, 2161.

reasonable confidence. The calculated values for conformations of this molecule are summarised in Table 4. The polarisability semi-axes for the C_{Ar}–Br bond ($b_L = 0{\cdot}627$, $b_T = 0{\cdot}245$, $b_V = 0{\cdot}220$) were obtained by subtraction of the phenyl group semi-axes from the polarisability specifications for bromobenzene.[11] In *p*-bromoacetanilide the μ_X component of the calculated dipole moment for any conformation is augmented above that for acetanilide by ($\mu^{C-Br} + \mu_I$) where μ_I is the " interaction moment."[12] From Smith and Walshaw's value[12] of 3·01 D for the dipole moment of *p*-bromoaniline in benzene, ($\mu^{C-Br} + \mu_I$) = 1·77 D, and this acts in the $+X$ direction.

TABLE 4.

Polarisabilities, dipole moments, and molar Kerr constants calculated for conformations of *p*-bromoacetanilide in benzene.

ϕ	b_i (calc.)	Direction cosines with			μ (calc. (D)	$10^{12}{}_{\mathrm{m}}K$ (calc.)
		X	Y	Z		
0°	b_1 = 2·510	+0·999	+0·029	−0·021	4·93	+2384
	b_2 = 1·717	−0·032	+0·986	−0·163		
	b_3 = 1·269	+0·016	+0·163	+0·986		
30°	b_1 = 2·468	+0·997	+0·066	+0·050	5·02	+1988
	b_2 = 1·743	−0·062	+0·996	−0·071		
	b_3 = 1·284	−0·054	+0·067	+0·996		
60°	b_1 = 2·375	+0·996	+0·031	+0·078	4·76	+960
	b_2 = 1·764	−0·035	+0·998	+0·057		
	b_3 = 1·357	−0·076	−0·060	+0·995		
70°	b_1 = 2·349	+0·998	−0·001	+0·066	4·60	+598
	b_2 = 1·764	−0·005	+0·995	+0·096		
	b_3 = 1·383	−0·066	−0·096	+0·993		
80°	b_1 = 2·331	+0·998	−0·040	+0·042	4·40	+248
	b_2 = 1·757	+0·034	+0·992	+0·120		
	b_3 = 1·407	−0·047	−0·119	+0·991		
90°	b_1 = 2·327	+0·997	−0·075	+0·010	4·18	−39
	b_2 = 1·744	+0·074	+0·990	+0·121		
	b_3 = 1·424	−0·019	−0·120	+0·993		

The observed quantities being ${}_{\infty}({}_{\mathrm{m}}K_2) = -45 \times 10^{-12}$, $\mu = 3{\cdot}65$ D (for acetanilide), and ${}_{\infty}({}_{\mathrm{m}}K_2) = +53 \times 10^{-12}$, $\mu = 4{\cdot}36$ D (for *p*-bromoacetanilide), it may be inferred that for these substances in benzene solution ϕ is about 80° (*i.e.*, the mean of 74° and 87°). Small changes in the assumed bond angles do not seriously affect the conclusions. If, for example, the nitrogen valency angles are taken as 113°, the calculated values for conformations of acetanilide having ϕ equal to 69° and to 74° are:

ϕ	b_i (calc.)	Direction cosines with			μ (calc.) (D)	$10^{12}{}_{\mathrm{m}}K$ (calc.)
		X	Y	Z		
69°	b_1 = 1·793	+0·993	+0·035	−0·116	3·70	−45
	b_2 = 1·575	−0·020	+0·992	+0·128		
	b_3 = 1·227	+0·119	−0·125	+0·985		
74°	b_1 = 1·783	+0·992	+0·085	−0·097	3·68	−99
	b_2 = 1·570	−0·070	+0·987	+0·147		
	b_3 = 1·241	+0·108	−0·139	+0·984		

Acetanilide, p-*Bromoacetanilide,* p-*Chloroacetanilide, and Acetyl*-p-*toluidine in Dioxan.*—The increased solubility of these substances in dioxan and the smallness of B_{dioxan} result in conveniently measurable values of ΔB_{12} from which δ and thence ${}_{\infty}({}_{\mathrm{m}}K_2)$ may, in each case, be readily estimated. Smith and his co-workers[12-14] have shown that the higher moments observed for aniline, *N*-methylaniline, and nuclear-substituted anilines arise through hydrogen bonding between an amino-hydrogen atom and an oxygen atom of the dioxan

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[11] Le Fèvre and Rao, *J.*, 1958, 1465.
[12] Smith and Walshaw, *J.*, 1957, 3217.
[13] Few and Smith, *J.*, 1949, 753, 2781.
[14] Smith, *J.*, 1953, 109.

molecule, and that " an appreciable increase in molecular polarisation, and consequently in apparent dipole moment, accompanies the hydrogen bonding only when an increase in the mesomeric effect can occur, *i.e.*, when it results in an increased donation of electron density from the amino-nitrogen atom to the ring." Thus the differences between the apparent moments in dioxan and in benzene can be attributed to a moment component μ_d acting along the 1,4-axis in the positive X direction (in Fig. 1a), so that, by analogy, the dipole moment components μ_X for all conformations of *p*-X·C_6H_4·NHAc (where X = Br, Cl, or Me) are $\mu_x = 1{\cdot}53 \cos 48{\cdot}5 + \mu^{C-X} + \mu_I + \mu_d + \mu^{C=O} l_X^{C=O}$. The aggregate values of $(\mu^{C-X} + \mu_I + \mu_d)$ follow from the data in ref. 12 as: +2·14 (X = Br); +2·18 (X = Cl); and $-0{\cdot}04_5$ (X = Me); for X = H, $\mu_d = +0{\cdot}33$ (all in Debye units). For the following calculations the polarisability semi-axes for the C_{Ar}–Cl bond ($b_L = 0{\cdot}422$, $b_T = 0{\cdot}199$, $b_V = 0{\cdot}149$) and for the group C_{Ar}–CH_3 ($b_L = 0{\cdot}219$, $b_T = 0{\cdot}345$, $b_V = 0{\cdot}207$) were obtained by subtraction of the phenyl group semi-axes from the polarisability specifications[11] for chlorobenzene and toluene, respectively. No allowance has been made for any contributions of the associated dioxan molecules to the calculated anisotropic polarisabilities of the structure examined, but this should not be significant—see ref. 15 in which $b_1^{\text{dioxan}} = 0{\cdot}76$—$0{\cdot}79$, $b_2^{\text{dioxan}} = 0{\cdot}89$—$0{\cdot}98$, $b_3^{\text{dioxan}} = 0{\cdot}83$—$0{\cdot}87$. The calculated dipole moments for the various conformations of acetanilide and of *p*-bromoacetanilide (in dioxan) if taken in conjunction with the polarisability semi-axes of Tables 3 and 4, respectively, lead to the theoretical molar Kerr constants listed in Table 5. The

TABLE 5.

Dipole moments and molar Kerr constants calculated for conformations of acetanilide and *p*-bromoacetanilide in dioxan.

	Acetanilide		p-*Bromoacetanilide*	
ϕ	μ (calc.) (D)	$10^{12}{}_mK$ (calc.)	μ (calc.) (D)	$10^{12}{}_mK$ (calc.)
0°	3·63	+722	5·29	+2788
30	3·86	+597	5·34	+2359
60	3·85	+196	5·03	+1227
70	3·78	+56	4·86	+815
80	3·70	−69	4·64	+430
90	3·59	−165	4·39	+105

TABLE 6.

Polarisabilities, dipole moments, and molar Kerr constants calculated for conformations of *p*-chloroacetanilide in dioxan.

		Direction cosines with				
ϕ	b_i (calc.)	X	Y	Z	μ (calc. (D)	$.10^{12}{}_mK$ (calc.)
0°	$b_1 = 2{\cdot}305$	+0·999	+0·037	−0·024	5·31	+2411
	$b_2 = 1{\cdot}670$	−0·040	+0·987	−0·154		
	$b_3 = 1{\cdot}199$	+0·018	+0·155	+0·988		
30°	$b_1 = 2{\cdot}264$	+0·995	+0·084	+0·055	5·34	+2064
	$b_2 = 1{\cdot}696$	−0·080	+0·994	−0·069		
	$b_3 = 1{\cdot}213$	−0·061	+0·064	+0·996		
60°	$b_1 = 2{\cdot}171$	+0·995	+0·042	+0·090	5·03	+1074
	$b_2 = 1{\cdot}717$	−0·047	+0·998	+0·052		
	$b_3 = 1{\cdot}285$	−0·087	−0·056	+0·995		
70°	$b_1 = 2{\cdot}144$	+0·997	−0·001	+0·077	4·88	+726
	$b_2 = 1{\cdot}717$	−0·006	+0·996	+0·090		
	$b_3 = 1{\cdot}312$	−0·077	−0·090	+0·993		
80°	$b_1 = 2{\cdot}127$	+0·997	−0·054	+0·049	4·66	+382
	$b_2 = 1{\cdot}710$	+0·048	+0·992	+0·114		
	$b_3 = 1{\cdot}336$	−0·055	−0·111	+0·992		
90°	$b_1 = 2{\cdot}123$	+0·995	−0·103	+0·011	4·39	+74
	$b_2 = 1{\cdot}696$	+0·101	+0·988	+0·113		
	$b_3 = 1{\cdot}354$	−0·022	−0·111	+0·994		

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[15] Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.

TABLE 7.

Polarisabilities, dipole moments, and molar Kerr constants calculated for conformations of acetyl-*p*-toluidine in dioxan.

		Direction cosines with				
ϕ	b_i (calc.)	X	Y	Z	μ (calc.) (D)	$10^{12}{}_{\mathrm{m}}K$ (calc.)
0°	b_1 = 2·103	+0·996	+0·082	−0·035	3·32	+578
	b_2 = 1·813	−0·085	+0·988	−0·128		
	b_3 = 1·258	+0·024	+0·131	+0·991		
30°	b_1 = 2·069	+0·976	+0·206	+0·067	3·60	+484
	b_2 = 1·836	−0·202	+0·977	−0·071		
	b_3 = 1·270	−0·080	+0·056	+0·995		
60°	b_1 = 1·974	+0·975	+0·179	+0·130	3·66	+161
	b_2 = 1·860	−0·183	+0·983	+0·022		
	b_3 = 1·340	−0·124	−0·045	+0·991		
70°	b_1 = 1·943	+0·994	+0·011	+0·112	3·64	+33
	b_2 = 1·863	−0·019	+0·997	+0·072		
	b_3 = 1·368	−0·111	−0·074	+0·991		
80°	b_1 = 1·930	+0·959	−0·280	+0·052	3·59	−72
	b_2 = 1·851	+0·273	+0·956	+0·110		
	b_3 = 1·394	−0·081	−0·091	+0·993		
90°	b_1 = 1·937	+0·902	−0·432	−0·010	3·51	−152
	b_2 = 1·825	+0·431	+0·897	+0·095		
	b_3 = 1·412	−0·032	−0·090	+0·995		

computed values for *p*-chloroacetanilide are summarised in Table 6 and for acetyl-*p*-toluidine in Table 7.

The observed $10^{12}{}_{\infty}({}_{\mathrm{m}}K_2)$'s are: +107 (acetanilide), +280 (*p*-bromoacetanilide), +276 (*p*-chloroacetanilide), and +18 (acetyl-*p*-toluidine), corresponding to $\phi = 66°$, 85°, 83°, and 71°, respectively. We thus conclude that as solutes in dioxan these molecules exhibit ϕ's in the range 75° ± 10°.

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