928. *The Dipole Moments of Some Acetylamino-compounds and the Preferred Conformation of the Acetylamino-Group.*

By J. W. Smith.

The dipole moments of acetanilide and various nuclear-substituted acetanilides have been determined for benzene solutions at 25°. The results are interpreted as indicating that the preferred conformation is that in which the angle between the C_{ar}–N–C_{carb} and N–C_{carb}–O planes is about 30°, the oxygen atom being on the same side of the former plane as is the lone pair of electrons on the nitrogen atom.

The dipole moments of the acetyl derivatives of arylamines are of interest in view of the possibility that even in the free molecule the carbonyl group may assume a preferred conformation relative to the C_{ar}–N–$C_{carb.}$ plane. Measurements have therefore been made of the moments of a number of these compounds in benzene solution at 25°, and the results are shown in Table 1, which also includes the corresponding values for the parent amines. The moment of acetanilide now reported is rather lower than the value

(4·01 D) deduced by Le Fèvre and Le Fèvre[1] from measurements on more concentrated solutions in benzene.

TABLE 1.

Dipole moments in benzene solution.

	μ (D)		μ (D)		μ (D)
Acetanilide	3·65	Acetylaminodurene	$3{\cdot}8_4$	*p*-Toluidine	1·32[c]
p-Chloroacetanilide	4·32	Acetyl-α-naphthylamine	3·67	*m*-Toluidine	1·45[d]
p-Bromoacetanilide	4·36	Acetyl-β-naphthylamine	3·68	*o*-Toluidine	1·59[d]
Acetyl-*p*-toluidine	3·74	Aniline	1·53[a]	Aminodurene	1·45[e]
Acetyl-*m*-toluidine	3·69	*p*-Chloroaniline	3·01[b]	α-Naphthylamine	1·50[f]
Acetyl-*o*-toluidine	3·71	*p*-Bromoaniline	3·01[c]	β-Naphthylamine	1·77[g]

[a] Few and Smith, *J.*, 1949, 753. [b] *Idem*, *J.*, 1949, 2781. [c] Smith and Walshaw, *J.*, 1957, 3217. [d] Tiganik, *Z. phys. Chem.*, 1931, **14**, *B*, 135 (recalculated). [e] Smith, *J.*, 1953, 109. [f] Smith, *J.*, 1961, 81. [g] Vasiliev and Syrkin, *Acta Physicochem. U.R.S.S.*, 1941, **14**, 414.

In some hydrogen-bonded structures the amide group is probably planar, but it seems unlikely that this is the case for the free acetanilide molecule, which shows some basic properties although it is a weaker base than water. In benzene solution the dipole moment of aniline is 1·53 D. Its dipole is effectively directed along an axis at about 48·5° to the $N-C_{ar}$ bond and in a plane including this bond and bisecting the angle between the two N–H bonds. This moment can be resolved into components μ_a $(=1{\cdot}42$ D) along the axis of the $N-C_{ar}$ bond and μ_b $(=1{\cdot}22$ D) along the axis of the lone-pair orbital.[2] The dipole moment of acetone (μ_c) is 2·78 D[3] and is directed along the $C_{carb}-O$ bond. As a first approximation, therefore, it may be assumed that the dipole moment of acetanilide comprises the vector sum of μ_a, μ_b, and μ_c, together with an additional component μ_d acting along the $C_{carb}-N$ bond. The latter arises through the replacement of the C–C, three C–H, and the H–N bond by the $C_{carb}-N$ bond. If it is further assumed that the $C_{ar}-N-C_{carb}$ angle is tetrahedral and the $N-C_{carb}-O$ angle is 120°, the general expression for the resultant moment is

$$\mu^2 = \mu_a^2 + \mu_b^2 + \mu_c^2 + \mu_d^2 - \tfrac{1}{3}(2\mu_a\mu_b + \mu_a\mu_c + \mu_b\mu_c - 2\mu_b\mu_d + 3\mu_c\mu_d) + (1{\cdot}633\mu_a\mu_c - 0{\cdot}8165\mu_b\mu_c)\cos\phi + 1{\cdot}4142\mu_b\mu_c\sin\phi, \quad (1)$$

where ϕ is the angle between the $C_{ar}-N-C_{carb}$ and $N-C_{carb}-O$ planes. On substituting the values of μ_a, μ_b, and μ_c given above this reduces to

$$\mu^2 = 7{\cdot}632 + 4{\cdot}796\sin\phi + 3{\cdot}677\cos\phi + \mu_d^2 - 1{\cdot}02\mu_d. \quad (2)$$

Evidently when $\mu_d = 1{\cdot}02$ D the terms involving it cancel out, whilst for any positive value below about 1·4 D its effect on the result is small. Further, it appears very improbable that this component will have a large negative value such as to affect the resultant moment appreciably. Hence, by neglecting the terms in μ_d it is possible to calculate the resultant moment for various conformations of the acetyl group. The maximum and minimum values of μ (3·70 and 1·26 D, respectively) occur when ϕ is 52·5° and 232·5°, respectively, whilst for free rotation about the $C_{carb}-N$ bond the calculated moment is 2·76 D.

If the hydrogen atom, the phenyl group, and the lone pair on the nitrogen atom exerted equal repulsive effects towards the approach of the methyl group or the oxygen atom of the acetyl group there would be six equivalent positions of minimum potential energy with $\phi = 30°, 90°, 150°, 210°, 270°$, and 330°, respectively, *i.e.*, I—VI. The fact that these repulsive effects will not be equal, however, must cause the potential energy wells to be of unequal depths and to be displaced slightly from this symmetrical arrangement. Further, the conformations (I) and (IV) should be favoured by the circumstance that

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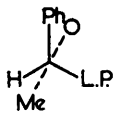
[1] Le Fèvre and Le Fèvre, *J.*, 1936, 1136.

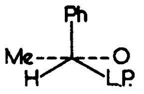
[2] Smith, *J.*, 1961, 81.

[3] Wesson, " Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

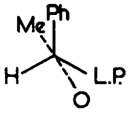
they yield the greatest overlap of the lone-pair orbital with the p_π-orbital of the C_{carb} atom, thus leading to a conjugation of this π-electron system with that of the aromatic ring. Apart from such considerations, however, the repulsion between the lone pair and the oxygen atom might cause conformation (II) to have a slightly higher potential energy than (I), whilst repulsions between the phenyl and the methyl group will raise the potential energy of (IV): form (III), where both these effects come into play may have a still higher potential energy. Conformations (V) and (VI) would seem to be favoured sterically, but do not permit very large overlap of the lone-pair orbital with the p_π-orbital of the C_{carb} atom



(I)

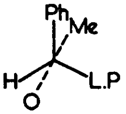


(II)

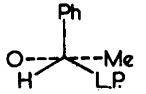


(III)

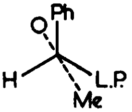
L.P. = lone pair



(IV)



(V)



(VI)

From these considerations it is to be inferred that (I) should be the most favoured conformation. In this connexion it seems pertinent that Brown and Corbridge[4] found that in the crystal ϕ is 37° 54′.

The values of the dipole moment of acetanilide in the various conformations, calculated according to eqn. 2 with $\mu_d = 0$, are shown under *a* in the third column of Table 2. The observed moment (3·65 D) is very near to the calculated moment for form (I) and is much greater than that for any of the other conformations. Hence it may be inferred that a conformation near to (I) predominates for the molecules in solution as well as in the crystal.

TABLE 2.

Calculated dipole moments of acetanilide and its *para*-derivatives in various conformations.

		Calculated dipole moment (D)					
Conformation	ϕ	Acetanilide		*p*-Chloro- and *p*-bromo-acetanilide		Acetyl-*p*-toluidine	
		a	*b*	*a*	*b*	*a*	*b*
cis	0°	3·36	2·84	4·93	4·33	3·06	2·77
I	30°	3·63	3·16	5·02	4·45	3·39	3·11
	38°	3·67	3·22	4·99	4·43	3·45	3·18
II	90°	3·52	3·29	4·18	3·80	3·48	3·34
III	150°	2·62	2·59	2·23	2·21	2·83	2·89
trans	180°	1·99	2·26	1·00	1·27	2·31	2·47
IV	210°	1·43	1·56	0·44	1·07	1·79	2·01
V	270°	1·69	1·52	2·80	2·43	1·60	1·60
VI	330°	2·90	2·39	4·51	3·94	2·59	2·32

[a] Values calculated by using "idealised" valency angles. [b] Values calculated by using valency angles found in the crystal.

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[4] Brown and Corbridge, *Acta Cryst.*, 1954, **7**, 711.

This inference receives general support from a comparison of the measured moments of derivatives of acetanilide with their calculated values, deduced by inserting the appropriate values of μ_a in eqn. 1. For *p*-chloro- and *p*-bromo-acetanilide $\mu_a = 3{\cdot}18$ D, and the calculated moment shows a much greater variation with ϕ than does that of acetanilide itself. The high observed moments for these compounds suggest that conformation (I) or (VI) must predominate and that relatively few molecules can exist in conformations (II—V) (Table 2, column 5). For acetyl-*p*-toluidine $\mu_a = 1{\cdot}05$ D, and the observed moment is higher than the calculated value for any of the conformations. Of the latter, (II) and (I) have the highest calculated moments. This result may therefore be interpreted as confirming the relative absence of the conformations (III—VI).

The moments of the same compounds have also been calculated for each conformation on the assumption that the valency angles in the molecules in solution are the same as were found by Brown and Corbridge in the acetanilide crystal, *viz.*, C_{ar}–N–C_{carb} = 129° 18′ and N–C_{carb}–O = 121° 42′. Except for *p*-chloro- and *p*-bromo-acetanilide the highest moments calculated on this basis are those for conformation (II) (cf. Table 2, values under *b*), but they are appreciably less than the measured moments. The calculated moments for (IV) are higher than those based on idealised angles, but nevertheless the values are so low that this conformation cannot make a major contribution to the structure. It is of interest, however, that with these distorted angles the moment of acetyl-*p*-toluidine in certain conformations can exceed that of acetanilide, in accordance with observation.

In the free molecules the valency angles are most probably greater than the idealised values but smaller than those observed in the crystal. The calculations are not very sensitive to the assumptions made regarding the axis of the lone-pair orbital. However, in the limiting case, probably never attained in these compounds, where the bonds around the nitrogen atom become coplanar, conformations (I) and (VI) are mirror images of one another, as are (II) and (V), and (III) and (IV). Assuming the other angles to be the same as in the crystal gives the calculated moments for acetanilide in such conformations as 3·01, 2·45, and 1·62 D, respectively. The evidence suggests, therefore, that in solution the preferred conformation is one in which ϕ is near to 30° and probably very near to the angle of 38° found in the crystal. The proportion of molecules in other conformations must be relatively small, but the nature of the assumptions made in the calculations would render any calculation of the proportions present unjustified.

The dipole moments of the other acetyl derivatives of amines studied indicate that the same general behaviour is followed as for acetanilide. Thus no essential change in the stable conformation is brought about by the presence of the second ring in acetyl-α-naphthylamine or by the *o*-methyl groups in acetyl-*o*-toluidine or acetylaminodurene.

Experimental.—The acetylamino-compounds were prepared by acetylation of the respective amines and recrystallised repeatedly from aqueous alcohol. Thiophen-free benzene was purified by repeated crystallisation, followed by drying over sodium.

The dielectric constants, refractive indices, and specific volumes of the solutions were measured at 25°. The results are shown in Table 3, where the symbols have their usual significance. For some of the compounds, and especially for acetanilide, the apparent molecular polarisation increases rapidly with increasing concentration. Molecular association is presumably responsible for this behaviour, but the number of solutions studied permits fairly accurate extrapolation of the data to zero concentration, where association effects should be absent. Hence the moments derived can be regarded as applying to the monomeric forms.

Owing to the very low solubilities of some of the compounds studied the refractive indices of the solutions differed very little from that of the solvent. Nevertheless, the $[R_D]$ values derived from these results are in good agreement with those calculated from the molecular refraction of acetanilide itself and the appropriate bond refractions of the substituents.[5] Some of the solutions of the *p*-halogenoacetanilides and of acetylaminodurene were actually supersaturated at 25°.

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[5] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

TABLE 3.

Polarisation data.

Acetanilide

10^6w	ε	v	n_D
0	2·2741	1·14460	1·4980
895	2·2841	1·14436	1·4980
1635	2·2925	1·14417	1·4981
1864	2·2958	1·14411	1·4981
2117	2·2984	1·14404	1·4982
2292	2·3007	1·14399	1·4982
2931	2·3084	1·14382	1·4982
3498	2·3160	1·14368	1·4983
4454	2·3291	1·14344	1·4984
5325	2·3407	1·14319	1·4984
5618	2·3448	1·14311	1·4984
6263	2·3544	1·14293	1·4985
10,342	2·4233	1·14185	1·4988

$\varepsilon = 2{\cdot}2741 + 10{\cdot}9w + 303w^2$

$v = 1{\cdot}14460 - 0{\cdot}265w$

$n_D^2 = 2{\cdot}2440 + 0{\cdot}216w$

$P = 312{\cdot}4$ c.c., $[R_D] = 40{\cdot}4$ c.c.

$\mu = 3{\cdot}65$ D.

*Acetyl-*o*-toluidine*

10^6w	ε	v	n_D
1380	2·2888	1·14428	—
2281	2·2983	1·14405	—
4136	2·3194	1·14365	—
4868	2·3306	1·14345	—

$\varepsilon = 2{\cdot}2741 + 10{\cdot}20w + 250w^2$

$v = 1{\cdot}14460 - 0{\cdot}234w$

$P = 326{\cdot}2$ c.c.

If $[R_D] = 45{\cdot}2$ c.c., $\mu = 3{\cdot}71$ D.

Acetyl-α-naphthylamine

10^6w	ε	v	n_D
1443	2·2865	1·14414	1·4981
2720	2·2969	1·14373	1·4982
3752	2·3061	1·14338	1·4983$_5$
4318	2·3111	1·14323	1·4984

$\varepsilon = 2{\cdot}2741 + 8{\cdot}17w + 93w^2$

$v = 1{\cdot}14460 - 0{\cdot}320w$

$n_D^2 = 2{\cdot}2440 + 0{\cdot}28w$

$P = 330{\cdot}0$ c.c., $[R_D] = 54{\cdot}6$ c.c.

$\mu = 3{\cdot}67$ D.

*Acetyl-*p*-toluidine*

10^6w	ε	v	n_D
1021	2·2847	1·14434	—
1061	2·2856	1·14433	1·4981
2521	2·3003	1·14396	1·4982
2566	2·3012	1·14395	1·4982
3200	2·3084	1·14378	1·4982
4054	2·3176	1·14357	1·4983
4158	2·3190	1·14355	1·4983

$\varepsilon = 2{\cdot}2741 + 10{\cdot}40w + 100w^2$

$v = 1{\cdot}14460 - 0{\cdot}253w$

$n_D^2 = 2{\cdot}2440 + 0{\cdot}22w$

$P = 331{\cdot}3$ c.c., $[R_D] = 45{\cdot}2$ c.c.

$\mu = 3{\cdot}74$ D.

*Acetyl-*m*-toluidine*

10^6w	ε	v	n_D
1570	2·2901	1·14426	—
2110	2·2957	1·14414	1·4981
2453	2·2991	1·14408	1·4981
3324	2·3089	1·14389	1·4982
6270	2·3409	1·14328	1·4983
6920	2·3478	1·14316	1·4983
9828	2·3812	1·14257	1·4985

$\varepsilon = 2{\cdot}2741 + 10{\cdot}06w + 86w^2$

$v = 1{\cdot}14460 - 0{\cdot}210w$

$n_D^2 = 2{\cdot}2440 + 0{\cdot}153w$

$P = 323{\cdot}7$ c.c., $[R_D] = 45{\cdot}2$ c.c.

$\mu = 3{\cdot}69$ D.

Acetyl-β-naphthylamine

10^6w	ε	v	n_D
1353	2·2855	1·14416	—
2585	2·2962	1·14377	—
4003	2·3091	1·14333	—
5480	2·3232	1·14285	—

$\varepsilon = 2{\cdot}2741 + 8{\cdot}20w + 135w^2$

$v = 1{\cdot}14460 - 0{\cdot}319w$

$P = 331{\cdot}1$ c.c.

If $[R_D] = 54{\cdot}4$ c.c., $\mu = 3{\cdot}68$ D

p-*Chloroacetanilide*

10^6w	ε	v	n_D
649	2·2824	1·14435	1·4980$_5$
773	2·2836	1·14430	1·4981
1196	2·2886	1·14414	1·4981$_5$
1653	2·2940	1·14396	1·4982

$\varepsilon = 2{\cdot}2741 + 12{\cdot}2w$

$v = 1{\cdot}14460 - 0{\cdot}387w$

$n_D^2 = 2{\cdot}2440 + 0{\cdot}35w$

$P = 427{\cdot}3$; $[R_D] = 45{\cdot}2$ c.c.

$\mu = 4{\cdot}32$ D.

Acetylaminodurene

10^6w	ε	v	n_D
427	2·2777	1·14455	—
775	2·2807	1·14450	—
822	2·2811	1·14449	—
842	2·2813	1·14449	—

$\varepsilon = 2{\cdot}2741 + 8{\cdot}5w$

$v = 1{\cdot}14460 - 0{\cdot}13w$

$P = 363{\cdot}4$ c.c.

If $[R_D] = 59{\cdot}0$ c.c., $\mu = 3{\cdot}86$ D.

p-*Bromoacetanilide*

10^6w	ε	v	n_D
1076	2·2848	1·14411	1·4980$_5$
2047	2·2943	1·14362	1·4981
3391	2·3075	1·14297	1·4982
4519	2·3186	1·14243	1·4983

$\varepsilon = 2{\cdot}2741 + 9{\cdot}83w$

$v = 1{\cdot}14460 - 0{\cdot}479w$

$n_D^2 = 2{\cdot}2440 + 0{\cdot}16w$

$P = 438{\cdot}3$ c.c.; $[R_D] = 48{\cdot}4$ c.c.

$\mu = 4{\cdot}36$ D.

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