[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NAGOYA]

The Dipole Moments and Near Ultraviolet Spectra of Some Compounds Containing the CONH Groups[1]

BY AKIRA KOTERA, SHUZO SHIBATA AND KÔZÔ SONE

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The dipole moments of a series of aromatic amides, $C_6H_5(CH_2)_mNHCO(CH_2)_nC_6H_5$, in dioxane solution are about 3.9 *D*, and the CONH group of these molecules has a *trans* form and requires a considerable contribution from the polar resonance form. The ultraviolet absorption spectra of these molecules gave supplementary information about their resonance state.

Only a few measurements[2] have been made of dipole moments of compounds containing a CONH group, which are of considerable interest because of their relation to proteins. We have measured the moments of a series of aromatic amides, *e.g.*, phenylpropionphenethylamide, which may be considered as the unit of polymeric amides, such as polyphenylalanine $[-CH(CH_2C_6H_5)NHCO-]_n$. The compounds investigated are listed in Table I and nature of the CONH group in these compounds is discussed and their ultraviolet absorption spectra were measured in an attempt to elucidate their resonance behavior.

TABLE I

THE PHYSICAL CONSTANTS OF DIOXANE AND AMIDES

	B.p., °C.	Dielectric constant 25.0°	Dielectric constant 40.0°	Density 25.0°	Density 40.0°
Dioxane	100.6 ± 0.2	2.2138	2.1941	1.0268	1.0099
	101.0 ± 0.3	2.2192	2.1957	1.0277	1.0108
				M.p., °C.	
Benzanilide				162	
Phenylacetanilide				116.5	
Phenylpropionanilide				97	
Benzbenzylamide				104	
Phenylacetbenzylamide				121.5	
Phenylpropionbenzylamide				85	
Phenylacetphenethylamide				95	

I. Dipole Moments

Experimental

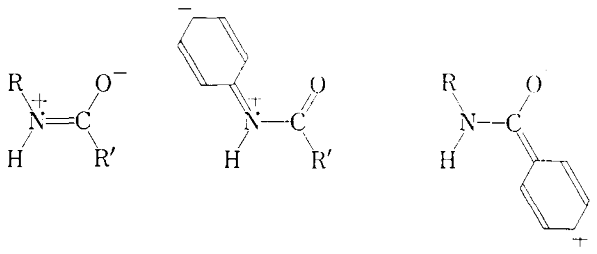
The compounds, which were prepared by the direct combination of aromatic amines and acids,[3] were recrystallized several times from alcohol. Dioxane was used as the solvent for the dipole measurements because these compounds are more soluble in this solvent than in benzene and association of amide molecules is less likely to occur. Commercial dioxane from which the water and acetal had been removed[4] was boiled with metallic sodium and allowed to stand for a long time, and then the product was distilled.

The dielectric constants were measured by the heterodyne beat parallel capacitance method at 25 and 40° and the densities were measured with Ostwald pycnometer. In the calculation of the dipole moments we assume that the sum of the electronic and atomic polarizations of the solute is equal to the molecular refraction calculated by addition of the atomic refractions for the D-line.

Discussion

Our experimental results are summarized in Table II, in which ϵ denotes the dielectric constant, *d* the density, *P* the molecular polarization, *w* the weight fraction, and μ the dipole moment. In general the dipole moments are about 3.9 *D*. In the general formula $C_6H_5(CH_2)_mNHCO(CH_2)_nC_6H_5$, the dipole moment increases with increasing *m* and decreasing *n*, as a rule. The deviations from the mean moment, however, are relatively small. With the exception of benzanilide *P* increases with increasing concentration at 25° even in dioxane solution; this anomaly, however, is too small to be a result of association. The results at 40° show the same trend except for slight change in the slope of molar polarization–solute concentration curve.

The resonance structures of these aromatic amides are shown in Fig. 1. A would usually be present in all of these compounds, but B and C would occur only in compounds in which there is no CH_2 radical between the phenyl and CONH groups. This behavior of the CH_2 radical is known as the "insulator effect."



A B C

Fig. 1.—The resonance structures of aromatic amides. In B and C, other resonance formulas having orthocharged phenyl radicals should be taken into account. R, R′ = C_6H_5, $C_6H_5CH_2$, $C_6H_5CH_2CH_2$.

The following points must be taken into account regarding the CONH group: (1) the magnitude of the group moment and the possible existence of resonance type A, (2) the existence of either the *cis* or *trans* form and (3) the possibility of keto–enol tautomerism.

If A contributes significantly to the normal state of the molecule, *cis–trans* isomerism must occur; and if we accept the presence of the keto form, the existence of which seems probable from recent X-ray[5] and infrared data,[6] we can easily calculate the moment of these compounds in their *trans* and *cis* forms by vector addition. With the assumption of their reasonable geometry ($\angle HNC$, $\angle CNC(R)$, $\angle HNC(R)$, $\angle NCC(R')$, $\angle OCC(R')$ and $\angle NCO = 120°$) the dipole moments of these compounds

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[1] Presented at the 4th annual meeting of the Chemical Society, Japan held on April 8, 1951.

[2] (a) W. D. Kumler and C. W. Porter, THIS JOURNAL, **56**, 2549 (1934); (b) S. Mizushima, T. Shimanouchi, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, *ibid.*, **72**, 3490 (1950); (c) W. W. Bates and M. E. Hobbs, *ibid.*, **73**, 2151 (1951).

[3] C. N. Webb, *Org. Syntheses*, **1**, 75 (1921).

[4] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Univ. Press, New York, N. Y., 1935.

[5] (a) F. Senti and D. Harker, THIS JOURNAL, **62**, 2008 (1940); (b) J. B. Carpenter and J. Donohue, *ibid.*, **72**, 2315 (1950).

[6] R. E. Kichard and H. W. Tompson, *J. Chem. Soc.*, 1248 (1947).

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND MOLECULAR POLARIZATIONS OF DIOXANE SOLUTIONS AND DIPOLE MOMENTS

	25.0°					40.0°			
	w	ϵ	d	P	μ^a	ϵ	d	P	μ^a
Benzanilide	0.00000	2.2138	1.0268	365	3.83	2.1941	1.0099	350	3.83
	.01916	1.4117	1.0295	367.4		2.3725	1.0128	348.8	
	.02767	2.5014	1.0306	362.5		2.4570	1.0140	347.7	
	.04100	2.6529	1.0326	360.7		2.5973	1.0161	346.9	
Phenylacetanilide	.00000	2.2192	1.0277	360	3.77	2.1957	1.0108	357	3.77
	.01906	2.3990	1.0300	365.2		2.3639	1.0130	354.3	
	.03651	2.5810	1.0320	367.1		2.5275	1.0151	351.7	
	.05074	2.7472	1.0337	371.2		2.6842	1.0171	357.6	
Phenylpropionanilide	.00000	2.2246	1.0278	342	3.62	2.2003	1.0110	335	3.66
	.01867	2.3784	1.0298	349.5		2.3469	1.0134	342.5	
	.03644	2.5423	1.0315	355.4		2.4965	1.0150	343.2	
	.05138	2.7008	1.0330	363.0		2.6438	1.0169	350.5	
Benzbenzylamide	.00000	2.2138	1.0268	385	3.93	2.1941	1.0099	365	3.90
	.02041	1.4148	1.0289	380.0		2.3770	1.0121	364.7	
	.03359	2.5578	1.0301	381.8		2.5064	1.0136	364.4	
	.05309	2.7866	1.0326	381.5		2.7116	1.0162	362.1	
Phenylacetbenzylamide	.00000	2.2138	1.0268	385	3.90	2.1941	1.0092	375	3.93
	.01867	2.3900	1.0287	392.7		2.3585	1.0118	376.8	
	.02746	2.4728	1.0291	386.5		2.4322	1.0125	373.5	
	.03543	2.5578	1.0298	390.0		2.5066	1.0130	373.1	
Phenylpropionbenzylamide	.00000	2.2192	1.0277	363	3.73	2.1957	1.0108	360	3.77
	.01921	2.3761	1.0294	370.0		2.5467	1.0124	366.4	
	.03660	2.5462	1.0305	386.2		2.4950	1.0139	368.9	
	.04300	2.6158	1.0310	386.4		2.5617	1.0145	376.9	
Phenylacetphenethylamide	.00000	2.2246	1.0278	405	3.99	2.2003	1.0110	400	4.06
	.01979	2.4148	1.0280	408.5		2.3725	1.0126	406.2	
	.03588	2.5692	1.0304	409.6		2.5144	1.0138	394.0	
	.05168	2.7488	1.0322	413.8		2.6671	1.0157	390.6	

[a] Error of μ value is estimated to be ±0.02 D in all cases.

are 2.6 D for the *cis* form and 3.3 D for the *trans* form by using bond moments of 0.45, 2.5, 0.3 and 1.3 D for the C–N, C=O, H–C and H–N bonds, respectively, and the direction of the latter moment must make an angle of 60° with the C–N axis. The assumption of the geometrical configuration is not exactly right, but if X-ray[5] and electron diffraction[7] data are used for the bond angles, the value of the dipole moment is not affected seriously. If the moments are calculated for various rotational isomers, values of 3.2, 3.0 and 2.7 D are obtained for the twisted angles 45, 90 and 135°, respectively. From a comparison of the calculated value with the observed data, it is fairly clear that the CONH group must be present in the *trans* form. This conclusion is in accord with the above diffraction data. Furthermore, the *cis* form seems to be excluded because of the steric repulsion of R and R′ groups (especially if R and R′ = C_6H_5) and the twisted form is also excluded on the basis of the ultraviolet absorption spectra which are described later. The observed moments are about 0.6 D greater than the calculated ones; this difference may be attributable to the contribution of A, which was not given sufficient weight in the above calculation. As such a polar resonance structure increases the stability in dioxane, A might make a greater contribution to the total dipole moment. If we use the bond moments obtained for thiouracil and its derivatives,[8] *i.e.*, 1.9, 4.0, 0.4 and 1.3 D for C–N, C=O, H–C and H–N bonds (which contain, of course, the contributions from polar resonance structures), we obtain 3.9 D for the *trans* form which agrees with the observed values.

As mentioned above, resonance structures B and C cannot occur in compounds in which a phenyl radical and CONH group are separated by a CH_2 radical (or radicals). Therefore, the difference between the dipole moments of the anilides and benzylamides having the same acid component seems to be attributable to the resonance moment contributed by B in the anilides and the moment induced in the phenyl radical by the greater moment of the CONH group in these compounds. The smaller moment of the anilides is probably due partly to the hindrance of A by B and the direction[9] of the moment produced by B in relation to the molecular moment,[9] and also partly to the inductive moment which is opposite in direction to the total moment in the case of anilides. In the case of benzoic acid amides and phenylacetic acid amides having the same amine component the situation is similar. However, the direction of the moment produced by C is nearly the same as the resultant moment of the CONH group, so that benzoic acid amides have greater moments than phenylacetic acid amides in

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(7) M. Kimura and M. Aoki, *Bull. Chem. Soc. Japan*, **26**, 429 (1953).

(8) W. C. Schneider and I. F. Halverstadt, THIS JOURNAL, **70**, 2626 (1948).

(9) A greater ∠CNC(R) may be expected from the steric repulsion between the phenyl group and the oxygen atom.

spite of the decrease in the moment due to A and that due to the induction effect. Nevertheless, the difference between the moments of benzylamide and phenethylamide compounds with the same acid component seems to be equal only to the difference of the inductive moment. For compounds with the same amine component, the situation may be similar. The inductive moment may give information about the configuration of these molecules. Since the dipole moment is greater the higher the amine component (m) and the lower the acid component (n) are in the series, it seems probable that the amine radical stretches out in the direction of the dipole moment of the CONH group, while the acid radical stretches out at right to it, although the C–C bond of substituent radicals will behave almost as free rotators.

Next we shall discuss whether resonance type A of the CONH group exists and if so, to what extent it contributes to the normal state of the molecule. Since the difference between the observed and the calculated dipole moments of amides is small (0.6 *D*), the highly polar resonance form A may not contribute significantly to the structure of the CONH group, according to Bates and Hobbs.[2c] However, this conclusion seems to be incorrect because the contribution of π electrons to the bond moments used in the calculation is overestimated for some bonds, especially C=O (2.5 *D*). A is regarded as opposing the conjugation of C=O itself (C^+–O^-) which contributes with A to the normal state of the CONH group. To clarify this situation we estimated the resonance moment of the CONH group by the simple LCAO molecular orbital method,[10] using the electron diffraction data of N-methylacetamide[7] (1.21 and 1.36 A. for C=O and C–N bond distances, respectively); the charge distribution and the resultant moment of the CONH group (3.9 *D*) which makes an angle of 40° with the C–N axis are given in Fig. 2. This value is not comparable with the experimental results, because of the uncertainty of the parameters used in the calculation. However, the extent of the contribution of HN^+=CO^- resonance A and C^+–O^- resonance are comparable regardless of the parameters used. If the difference between the observed moment (3.9 *D*) and the calculated σ electron moment (1.6 *D*)[11] is regarded as being equal to the π electron resonance moment (2.4 *D*), the C–O resonance moment is 1.0 *D* and the CONH type A resonance moment is 1.5 *D*. Thus, type A resonance contributes to the normal state to a considerable degree, approximately 14%. Furthermore, the moment of the CONH group itself can be obtained by vector addition of the π resonance moment and the σ bond moments of C–O, C–N and H–N, being estimated to be 4.1 *D*.

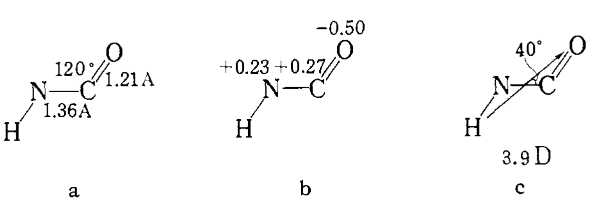

Fig. 2.—M. O. treatment of CONH system. The system consists of 3 nuclei and 4 electrons, *i.e.*, one electron each on C and O and two electrons on N (sp_2 hybridization): (a) geometry of CONH group (the value of ∠NCO was assumed); (b) charge distribution; (c) magnitude and direction of CONH resonance moment.

II. Ultraviolet Spectra

Experimental

The ultraviolet absorption spectra of the compounds in Fig. 3 and Table III were measured in alcoholic solution with a Spekker spectrophotometer and a quartz spectrograph.

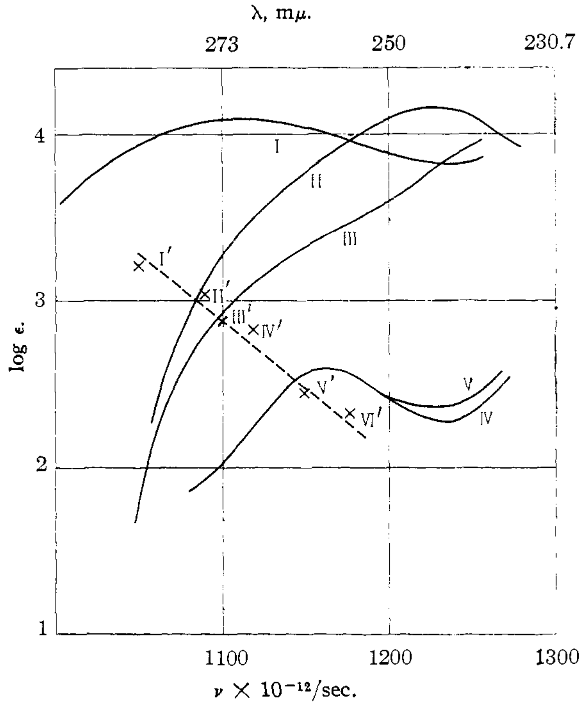

Fig. 3.—The absorption spectra of aromatic amides: I, benzanilide[12a]; II, phenylacetanilide; III, benzbenzylamide; IV, phenylacetbenzylamide; V, phenylacetphenethylamide. The dotted line was obtained by connecting the maxima of the absorption bands of the following benzene derivatives: I′, aniline[a]; II′, acetophenone[b]; III′, acetanilide[12a]; IV′, benzamide[12b]; V, toluene[c]; VI′, benzene[c]; (these absorptions were measured in alcohol solution).

[a] K. L. Wolf and W. Herold, *Z. physik. Chem.*, **B13**, 206 (1931). [b] H. Ley und H. Wingchen, *Ber.*, **67**, 501 (1934). [c] W. R. Orndorff, *et al.*, THIS JOURNAL, **50**, 835 (1928).

TABLE III

WAVE LENGTH, λ AND MOLECULAR EXTINCTION COEFFICIENT, ε, FOR ABSORPTION BANDS OF AROMATIC AMIDES

	Compound	λmax. (mμ)	log εmax.
I	$C_6H_5NHCOC_6H_5$	270	4.1
II	$C_6H_5NHCOCH_2C_6H_5$	(276)	(3.1)
III	$C_6H_5CH_2NHCOC_6H_5$	(273)	(2.9)
IV	$C_6H_5CH_2NHCOCH_2C_6H_5$	260	2.57
V	$C_6H_5CH_2CH_2NHCOCH_2C_6H_5$	260	2.57

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(10) C. Sandorfy, *Bull. soc. chim. France*, 615 (1949).

(11) For this calculation the σ electron moment is assumed to be 0.8 *D*; L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951). The other bond moments are the same as before.

Discussion

These aromatic amide molecules[12] consist of three chromophores, *i.e.*, two phenyl radicals and one CONH group. According to the commonly accepted view that two chromophores separated by one or more "insulator" CH_2 groups will show their characteristic absorption independently, the absorption of these compounds with the exception of benzanilide (I) will be the sum of the absorptions of the two phenyl chromophores since of these chromophores the CONH group does not show any remarkable absorption in the near ultraviolet region. On the other hand, benzene shows a characteristic strong absorption band at 2550 Å., and substitution in the benzene ring cause a shift of this band toward longer wave length (red shift) and also an increase in intensity; the magnitude of these variations is approximately proportional to the resonance effect between the substituent group and the benzene nucleus.[13] For comparison absorption maxima of the spectra of some benzene derivatives are given in Fig. 3.

On the basis of these considerations our results can be explained as follows. Since the three chromophores of benzanilide (I) can interact freely, its absorption is caused by one resonance system arising from the whole molecule, *i.e.*, by a polyene-like chromophoric system consisting of all three chromophores. The strong bathochromic effect of the absorption band of I, together with its remarkable high intensity and extreme broadness in contrast to the absorption of separated chromophores, is consistent with this expectation. If the CONH group were twisted through a rectangle, the absorption of I would be the sum of the two chromophores, C_6H_5NH (aniline) and C_6H_5CO (acetophenone), which do not interact freely; the observed absorption spectrum indicates that the CONH group is not present in this form. Therefore, since its presence as the *cis* form is improbable because of steric repulsion, we can include that the CONH group exists in the *trans* form.

The absorption of phenylacetanilide (II) will be the sum of the spectra of C_6H_5NHCO and $C_6H_5CH_2$. As Fig. 3 indicates, the absorption of the former is much more intense than that of the latter, so that the spectrum of II will be due almost entirely to the C_6H_5NHCO radical and should resemble that of acetanilide (III′)[12a]; this was confirmed experimentally. Although the observed absorption curve of II (Fig. 3) has no explicit absorption maxima at wave lengths longer than 2550 Å., an absorption band probably exists at about 2760 Å., near the intersection of the observation absorption curve with the dotted line connecting the band maxima of the benzene derivatives shown in Fig. 3. Its position between the absorption bands of benzene (VI′) and aniline (I′) can be attributed to the hypsochromic effect of the CO group substituted in the aniline molecule, that is, to the hindrance of B by A which weakens the interaction between the benzene nucleus and substituted nitrogen. From the same considerations, the spectrum of benzbenzylamide (III) should resemble that of benzamide[12b] (IV′), as is actually the case. The hypsochromic absorption of III in comparison to that of acetophenone (II′) indicates the hindrance of type C resonance by CONH resonance type A.

The absorption of phenylacetbenzylamide (IV), in which the CONH group is separated from the two phenyl radicals by two CH_2 groups, is due to three independent chromophores. The absorption of an independent CONH group is very weak in comparison to that of phenyl radicals. Therefore, the absorption of IV will be essentially the same as that of benzene (VI′), as verified experimentally. The small red shift from the benzene absorption can be explained by hyperconjugation. The observed maximum extinction coefficient which is about twice as great as that of benzene is attributable to the two phenyl radicals in the molecule.

As anticipated, the absorption of phenylacetphenethylamide (V) is nearly the same as that of IV.

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DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
NAGOYA UNIVERSITY
NAGOYA, JAPAN

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(12) The absorption spectra of only a few compounds containing a CONH group have been investigated; (a) P. Grammaticakis, *Bull. soc. chim. France*, 979 (1948); (b) P. Ramart-Lucas, *ibid.*, 25 (1943).

(13) For a quantum mechanical treatment of these effects, see: (a) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939); (b) K. F. Herzfeld, *Chem. Revs.*, **4**, 233 (1947); (c) see ref. 9.