CROATICA CHEMICA ACTA CCACAA **47** (4) 569—575 (1975)

YU ISSN 0011-1643
547.582
Original Scientific Paper
CCA-901

Molecular Conformation of Aza-substituted Benzanilides by Electronic Absorption Spectra and Dipole Moments

S. Fasone, G. Buemi, D. Grasso, and C. Gandolfo

Institute of Physical Chemistry, University of Catania, Viale A. Doria 8, 95125 Catania, Italy

Received February 18, 1975

The electronic absorption spectra of thirteen pyridine aromatic amides of general formula $R_1—CO—NH—R_2$ (R_1, R_2 = pyridil or phenyl) were obtained in methanol and dioxane solution.

The band assignment is briefly discussed.

The dipole moments were measured in dioxane at 25 ± 0.1 °C and compared with values calculated by both the S. H. M. O. method and vectorial model. The comparison suggests the most probable conformation of derivatives which have the nitrogen either in the *ortho* or *meta* position in one or both rings of the molecule.

INTRODUCTION

In a recent paper[1] the molecular conformation of pyridinic aromatic esters was investigated by using both electronic absorption spectra and dipole moment data. As an extension of this work, the present paper reports a similar study on several pyridinic aromatic amides. The aims of this study are to contribute to the elucidation of: (a) the molecular conformation, *i. e.* the twist angle around the amide bond; (b) the equilibrium between the possible conformers when one or more nitrogen atom(s) is present in the *ortho,* or *meta* position; (c) the main features of the electronic transitions of the molecules. Due to its biological interest, the stereochemistry of the amidic group is a very often discussed problem. Many papers dealing with this problem are reported in the literature and different approaches have beeen used to gain information on this problem.

Some of these papers are quoted in ref.[2]

For our compounds the relevant literature data concern only the electronic absorption spectrum and the dipole moment of benzanilide[3] and the electronic absorption spectra of three pyridil-benzamide isomers[4].

EXPERIMENTAL

Materials

The compounds *1—9* and *13,* reported in Table I, were prepared according to the Kushuer and Dalalian method[5].

The unknown *10—12* compounds were prepared following the same procedure. Their analitical and physical data are reported in Table II.

UV Absorption Spectra

Absorption spectra were measured by an Hitachi-Perkin-Elmer 124 UV-VIS spectrophotometer. The methanolic solutions were analyzed in the 210—350 nm

TABLE I

Electronic Absorption Data of Aza-Substituted Benzanilides

Compound	No.	Methanol			Dioxane		
		λ_{max}/nm[a]	log ε_{max}	*f*	λ_{max}/nm	log ε_{max}	*f*
N-2-pyridil benzamide	*1*	279.5 250 (230)	4.150 4.088 4.023	0.23 0.22	281 251.7	4.157 4.107	0.21 0.24
N-3-pyridil benzamide	*2*	258.5 (228)	4.186 4.048	0.41	260	4.149	0.41
N-4-pyridil benzamide	*3*	261 (230)	4.340 3.993	0.51	257.5	4.251	0.50
Picolin anilide	*4*	275 221	4.077 4.174	0.39 0.45	283	4.040	0.36
Nicotin anilide	*5*	269 (220)	4.052 4.079	0.37	270	4.098	0.38
Isonicotin anilide	*6*	271 (220)	3.999 4.060	0.25	270	4.048	0.35
N-2-pyridil picolinamide	*7*	285 (255) 221.5	4.218 3.956 4.125	0.29 0.25	286 (255)	4.194 3.901	0.29
N-2-pyridil nicotinamide	*8*	280 (250) 216	4.148 3.973 4.063	0.25 0.24	281 (255)	4.158 4.020	0.22
N-3-pyridil nicotinamide	*9*	270 (220)	4.150 4.037	0.39	271	4.125	0.37
N-4-pyridil nicotinamide	*10*	263.5 (220)	4.274 4.043	0.44	263	4.207	0.42
N-2-pyridil isonicotinamide	*11*	279 (245) (212)	4.149 3.845 4.150	0.28	281 (250)	4.149 3.924	0.25
N-3-pyridil isonicotinamide	*12*	270 (225)	4.108 3.890	0.36	270.5	4.101	0.41
N-4-pyridil isonicotinamide	*13*	264 220	4.248 4.049	0.48	264	4.167	0.40

[a] Wavelengths in parentheses denote inflections.

TABLE II.

Elementary Analysis and Physical Data of Aza-Substituted Benzanilides

Compound No.	Carbon		Hydrogen		Nitrogen		M. P/°C	Cryst. Solv.
	calcd.	found	calcd.	found	calcd.	found		
10	66.32	66.56	4.56	4.49	21.10	21.37	185—87	H_2O
11	66.32	66.52	4.56	4.44	21.10	21.32	135—37	ligroin
12	66.32	66.77	4.56	4.54	21.10	21.39	171—73	H_2O

range in silica cells having an optical path of 1 cm. The dioxane solutions were analyzed in the 235—350 nm range in cells of 5 mm optical path. The wavelengths of absorption maxima are given in Table I together with the extinction coefficients. The oscillator strengths calculated according to Mulliken[6] are also reported.

Dipole Moments

Electric dipole moments were evaluated from the dielectric constants and the refractive indices of anhydrous dioxane solutions at 25 ± 0.1 °C by using the Hederstrand method[7].

Dielectric constants ε were measured on a W. T. W. dipolmeter DMO1 with a gold plated DFL1 measuring cell ($\Delta \varepsilon / \varepsilon \approx 10^{-5}$ at 2 MHz).

The refractive indices n (for Na-D-light) were measured with an Abbé refractometer with an accuracy of $\pm 3.10^{-5}$.

Calculation Procedure

The dipole moments were calculated by the vectorial model and the SHMO method. In the calculation the *s-trans*-planar configuration was assumed for the amide group (see below).

For all the compounds bond angles of 120° were assumed.

The following bond lengths were used : 1.395 Å for phenyl and pyridine ring; 1.48 Å for C_{ar}—C; 1.235 Å for C=O; 1.335 Å for C—N and 1.43 Å for N—C_{ar}. The h and k values reported by Streitwieser[8] were used. For the labelling of atoms and coordinates see Fig. 1.

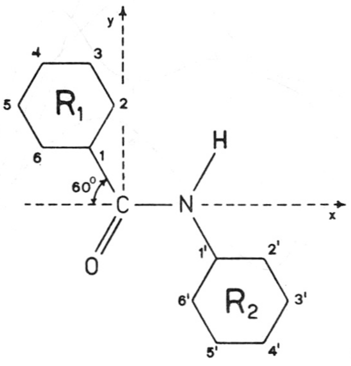

Fig. 1 — Schematic diagram of molecular geometry and the numbering of atoms.

The calculated dipole moment values are evaluated from the moment value of the O=C—NH group, the mesomeric moment of the molecule and the σ moment. For the evaluation of the μ-vector components of the O=C—NH group, a vectorial composition of the moments in benzene solution of the chlorobenzene (1.58 D)[9] benzanilide (3.38 D)[9] and *N*-phenyl-*p*-chlorobenzamide (3.17 D)[9] was made. The direction of the dipole moment found in benzene was then assumed to be maintained in the dioxane solution.

The components of the 0=C—NH μ-vector in dioxane was obtained from the experimental μ value of benzanilide in this solvent.*

In this procedure the following assumptions were made: a) the same molecular conformation was taken for the benzanilide and *p*-chlorobenzanilide; b) π-moment was assumed to be equal in both derivatives.

---

* This procedure has been used since μ values for cholorobenzene, benzanilide and *N*-phenyl-*p*-chlorobenzamide in dioxane solution were not available.

For the σ bond-moments literature values were used (H→C=0.4 D[10], C→N=0.45 D[10], N= 0.58 D[11]).

The percentage of equilibrium conformations of the isomers with only one pyridine ring was calculated by

$$\mu^2_{\text{exp}} = X \mu^2_{1\,(\text{theor})} + (1 - X) \mu^2_{2\,(\text{theor})} \qquad (1)$$

The percentage of equilibrium conformations of the compounds having two pyridine rings were obtained by keeping for the R_1 and R_2 nitrogen the distributions found for the compounds with only one pyridine ring.

RESULTS AND DISCUSSION

Electronic Spectra

The spectra of the compounds studied in methanol and dioxane solution are nearly coincident. They have the same general features as the benzanilide spectrum. In particular, the compounds show two bands in the 220—230 nm and 260—280 nm region, except for the 2-pyridil-derivatives having a third band at about 250 nm. Some typical spectra of the compounds in MeOH solution are shown in Fig. 2.

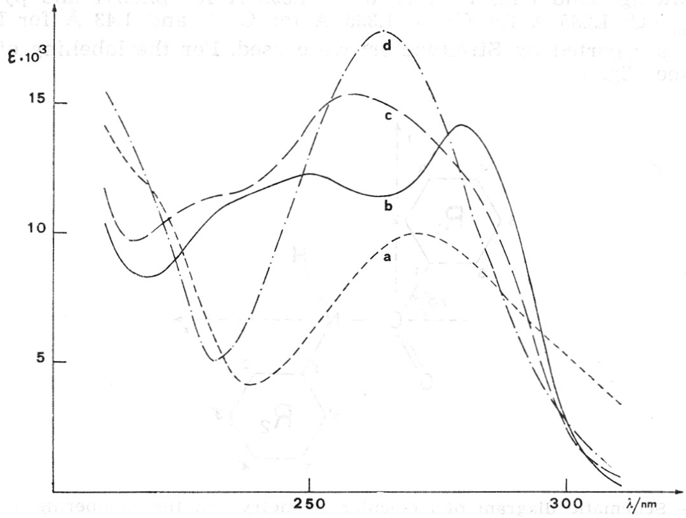

Fig. 2 — UV spectra in MeOH of: a: isonicotin-anilide; b: *N*-2-pyridil-benzamide; c: *N*-3-pyridil--benzamide; d: *N*-4-pyril-isonicotin-amide.

All the above bands should be due to π*—π transitions.

This is supported by their intensity, energy and characteristic solvent effect. The band at longer wavelength seems to be indicative of the molecular conformation.

The aza-substitution in R_1 and R_2 causes some displacement of this band with respect to benzanilide. In particular, substitution in R_2 shows a greater effect than in R_1.

In the R_2 case, the shift is bathochromic when the nitrogen atom is in the *ortho* and hypsochromic when N is in the *meta* or *para* position. Similar effects, except for compounds *9* and *12*, are also found if R_1 and R_2 are both

TABLE III.

Dipole Moments of Aza-Substituted Benzanilides

Com ound	Conformation	$\mu_{calc.}/D^{a}$	Weight % of the conformations[a]	$\mu_{calc.}/D^{b}$	Weight % of the conformations[b]	μ_{exp}/D
1	N in 6′	5.72	10.0	5.53	6.0	2.17
	N in 2′	1.32	90.0	1.64	94.0	
2	N in 5′	6.33	19.0	6.05	27.0	3.84
	N in 3′	3.00	81.0	2.96	73.0	
3	N in 4′	5.39	—	5.06	—	5.12
4	N in 6	6.29	13.0	6.05	14.0	3.42
	N in 2	2.77	87.0	2.96	86.0	
5	N in 5	5.72	29.0	5.53	34.0	3.30
	N in 3	1.43	71.0	1.64	66.0	
6	N in 4	3.84	—	3.67	—	3.88
7	N in 6 and 6′	8.06	1.3	7.60	1.0	1.90
	N in 2 and 6′	3.70	8.7	3.83	6.0	
	N in 2 and 2′	1.66	78.3	1.42	80.0	
	N in 6 and 2′	3.77	11.7	3.83	13.0	
		(2.42)*		(2.13)*		
8	N in 5 and 6′	7.93	2.9	7.51	2.4	2.64
	N in 3 and 6′	3.71	7.1	3.66	2.7	
	N in 3 and 2′	1.32	64.0	0.88	62.3	
	N in 5 and 2′	3.59	26.0	3.66	32.6	
		(2.70)*		(2.58)*		
9	N in 5 and 5′	8.01	5.5	7.60	7.8	3.27
	N in 3 and 5′	3.85	13.5	3.85	15.2	
	N in 3 and 3′	1.56	57.5	1.42	50.8	
	N in 5 and 3′	3.80	23.5	3.85	26.2	
		(3.33)*		(3.39)*		
10	N in 5	6.32	25.0	6.05	33.0	4.13
	N in 3	3.12	75.0	2.96	67.0	
11	N in 6′	6.25	2.0	5.84	8.0	2.96
	N in 2′	2.86	98.0	2.51	92.0	
12	N in 5′	5.73	22.8	5.53	20.0	3.06
	N in 3′	1.40	77.2	1.64	80.0	
13	N in 4 and 4′	3.71	—	3.83	—	3.45

alculated by HMO method.

alculated by vectorial composition of benzanilide and pyridine experimental dipole moments.

esulting theoretical μ moment from the μ total of each conformer and corresponding per- entage (columns 3—4 and 5—6, respectively).

pyridine rings. The strong hypsochromic effect of this band when going from the studied compounds (or benzanilide), to acetanilide and benzamide to 240 nm[12] and 226 nm[13] respectively, suggests that the corresponding transition involves the whole molecular π-system.

On the other hand, the absorption spectra of the aza-substituted benzanilides are entirely different from the sum of the two separate chromophores R_1—NH_2 and R_2—CO. This indicates that the twist angle of the O=C—NH group is small, if at all different from zero. In other words, the studied molecules in their most probable conformation should be more likely planar than non-planar.

This conclusion is in agreement with recent structural determinations of several amidic derivatives[14]. In addition, due to the steric hindrance effect of the phenyl rings, we can conclude that these compounds should exist in *s-trans* form.

Dipole Moments

Experimental dipole moments are reported in Table III together with the calculated values. The calculated values, (column 3 and 5 of Table III) indipendently evaluated by the HMO method and vectorial model, respectively, are in good agreement. This supports the conclusions which can be drawn from these data. In spite of the approximations involved in the calculation procedure, a good agreement is found between experimental and calculated data whenever a comparison can be made (compounds *3, 6, 7, 8, 9, 13*).

This supports the assumed *s-trans* planar conformation.

The percentages of the equilibrium conformations reported in columns 4 and 6 of Table III, show that the most probable form is that having the nitrogen atom on the opposite side of the C = O group. This result is similar to that previously found for the pyridinic aromatic esters[1].

Acknowledgement. This work was supported by a grant from the Italian CNR.

REFERENCES

1. S. Fasone, D. Grasso, and C. Gandolfo, *J. Mol. Struct.* **20** (1974) 449.
2. M. A. Robb and I. G. Csizmadia, *Theor. Chim. Acta* **10** (1968) 269; C. C. Costain and J. M. Dowling, *J. Chem. Phys.* **32** (1960) 158; S. T. King, *J. Phys. Chem.* **75** (1971) 405; S. T. King, *Spectrochim. Acta, Part A* **28** (1972) 165; T. Darkenberg and S. Forsen, *J. Phys. Chem.* **74** (1970) 1; P. N. Skancke and I. Danesland, *Acta Chem. Scand.* **26** (1972) 2614; M. Kimura and M. Aoki, *Bull. Chem. Soc. Japan* **26** (1953) 429; C. J. Brown and D. C. E. Corbridge, *Acta Cryst.* **7** (1954) 711; A. L. Love, T. D. Alger, and R. K. Olsen, *J. Phys. Chem.* **76** (1972) 853; W. W. Bates and M. E. Hobbs, *J. Amer. Chem. Soc.* **73** (1951) 2151; A. Kotera, S. Shibata, and K. Sone, *J. Amer. Chem. Soc.* **77** (1955) 6183; G. K. Estok and S. P. Sood, *J. Phys. Chem.* **66** (1962) 1372; J. E. Worsham and M. E. Hobbs, *J. Amer. Chem. Soc* **76** (1954) 206.
3. P. Grammaticakis, *Bull. Soc. Chim. Fr.* (1948) 979.
4. P. Grammaticakis, *Bull. Soc. Chim. Fr.* (1958) 480.
5. S. Kushuer and H. Dalalian, *J. Org. Chem.* **13** (1948) 834.
6. R. S. Mulliken, *J. Chem. Phys.* **7** (1934) 14.
7. G. Hederstrand, *Z. Phys. Chem. (Frankfurt am Main)* 2 (1929) 428.
8. A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists,* Wiley, New York 1962.
9. A. L. McClellan, *Tables of Experimental Dipole Moments,* Freeman, San Francisco 1963.

10. J. W. Smith, *Electric Dipole Moments*, Butterworths, London 1955.
11. D. G. Leis and B. C. Curran, *J. Am. Chem. Soc.* **67** (1945) 79.
12. J. Tanaka, *Bull. Chem. Soc. Japan* **36** (1963) 841.
13. G. Palazzo, G. Strani and M. Tavella, *Gazz. Chim. Ital.* **91** (1961) 1091.
14. G. Avitabile, E. Benedetti and M. R. Ciaiolo, *IX Congresso Associazione Ital. di Chimica Fisica„* Napoli 1 Novembre 1974.

SAŽETAK

Određivanje konformacije aza-supstituiranih benzanilida pomoću elektronskih apsorpcijskih spektara i dipolnih momenata

S. Fasone, G. Bueni, D. Grasso i C. Gandolfo

Snimljeni su apsorpcijski spektri 13 aromatskih amida opće formule R_1—CO—NH—R_2 (R_1, R_2 = piridil ili fenil) u metanolu i dioksanu. Ukratko je razmatrana asignacija vrpci.

Izmjereni su dipolni momenti u dioksanu na (25 ± 0.1) °C i uspoređeni s vrijednostima dobivenim metodom S. H. M. O. kao i s pomoću vektorskog modela. Iz ove usporedbe slijedi da je najvjerojatnija konformacija derivata ona, u kojoj je dušik u *orto-* ili *meta*-položaju u jednomu ili u oba prstena molekule.

INSTITUTE OF PHYSICAL CHEMISTRY
UNIVERSITY OF CATANIA
95125 CATANIA, ITALIA

Prispjelo 18. veljače 1975.