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Molecular Conformation of Pyridinic Aromatic Esters. II. Electronic Absorption Spectra and Dipole Moments by Semiempirical Methods

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The semiempirical MIM method was applied to calculate the UV spectra of nine pyridine-aromatic-ester derivatives (having the general formula $R_1-COO-R_2$) assuming a planar geometry. Benzene, pyridine and formic acid were adopted as component systems. The dipole moments of the same compounds were evaluated at the MIM and INDO levels and the equilibrium percentage of the conformers was deduced from experimental and theoretical values. Comparable results were generally obtained. On the whole the results are satisfactory but not sufficient to affirm with certainty if the molecular skeleton is or is not planar.

INTRODUCTION

In a previous paper¹ the most probable conformation of nine pyridine aromatic ester derivatives having the general formula $R_1-COO-R_2$ — where R_1 (fragment A) and R_2 (fragment C) are either a phenyl or a pyridil — was discussed on the grounds of a comparison between the experimental and vectorially calculated dipole moments. In the same paper an assignment of the bands of the UV spectra was attempted on the basis of experimental features.

The objective of this paper is to discuss the same problem using a theoretical approach with a semiempirical method. It is known that the »localized orbital model«² or the MIM method with the inclusion of configuration interaction, has been successfully used to calculate the UV spectra and dipole moments of numerous molecules³⁻⁹ just as the PPP approximation¹⁰⁻¹². It is

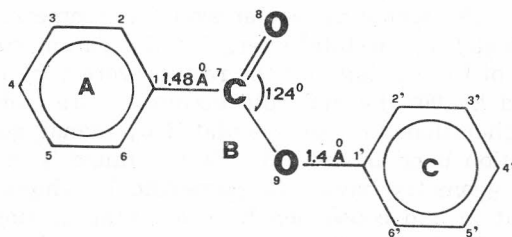


Figure 1. Topology of phenyl-benzoate. The same numbering system is preserved in all the molecules studied.

also known, however, that the latter method generally overestimates the dipole moments. Moreover, its resulting wavefunctions for the electronic states of a molecule, especially when the configuration interaction is included, are often hardly understandable so that a configuration analysis procedure¹³ is necessary for their interpretation in terms of locally excited and charge transfer configurations of the localized orbital model. The experimental electronic spectra and the dipole moments of the title compounds seem to indicate¹ the near planarity of the molecules and a weak conjugation involving the whole π -system, so we think that the MIM method, usually suggested for weak conjugation, is the most appropriate for our purpose. Above all, the dipole moments are important to elucidate the equilibrium between the possible conformers when one or more nitrogen atom(s) is present in the *ortho* or *meta* position in one or both rings. For a better test and discussion they were further evaluated at the INDO level, which takes into account both the σ and π electrons.

THEORY AND CALCULATIONS

When a molecule (R—S) can be considered to be composed of two or more component systems (R and S, where R and S are unsaturated hydrocarbon residues) its UV spectrum is related to the spectrum of the RH and SH fragments. In particular, the spectrum of R—S includes states associated with local electronic excitations inside the R and S systems (Λ_1^j) and states associated with the transfer of an electron from a bonding orbital of a fragment to an antibonding orbital of the other fragment (T_m^k). The MIM method takes into account the interactions between these configurations according to the formulae given in refs. 2 and 14. In our calculations the fragments considered were benzene, pyridine and formic acid. Their π -SCFMOs, excited states and related energies, ionization potentials and electron affinities are reported in Table I. The six-member rings were assumed to be regular hexagons with bond lengths of 1.4 Å. The formic acid was assumed as having bond lengths of 1.24 and 1.31 Å for C=O and C—OH respectively with a bond angle of 124^{0.5}. The O₁—R₂ distance was taken as equal to 1.4 Å. Benzene and pyridine were considered as being either a donor or acceptor while formic acid was considered only as an acceptor system.

The resonance integrals were evaluated by Kon's relationship¹⁸; the two center coulomb integrals were estimated by the Pariser-Parr semiempirical formula:

$$\gamma (pp/qq) = a + b r + c r^2$$

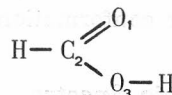
using the parameter values reported in Table II.

The problem of the whole molecular skeleton geometry was faced at the INDO level by calculating the total energy of the parent compound assuming different rotations of the R₂ ring, but the results were very poor. In particular, when R₂ is rotated by 90⁰ the molecule becomes more stable and the dipole moment slightly higher than the one calculated by planar geometry (+0.04 D). The weak conjugation band in the 275—280 nm range is in contrast with this result because the geometry having R₂ perpendicular should lead to an interruption of conjugation and consequently to a destabilization of the molecule. On the other hand it is known that more sophisticated theoretical calculations (e. g. MINDO/3, MNDO) also fail in the barrier determination^{19,20}, above all

TABLE I

SCF-MOs, Excited States, Energies, Ionization Potentials and Electron Affinities Adapted for the Fragments of MIM Method

Benzene ^{a,c}	
$\varphi_1 = 1/\sqrt{12} (2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6)$	$\Lambda_1 = 1/\sqrt{2} (\lambda_2^4 - \lambda_1^3) E^b = 4.71 \text{ eV (band } \alpha)$
$\varphi_2 = 1/2 (\chi_2 + \chi_3 - \chi_5 - \chi_6)$	$\Lambda_2 = 1/\sqrt{2} (\lambda_2^3 + \lambda_1^4) E^b = 5.96 \text{ eV (band } \rho)$
$\varphi_3 = 1/2 (\chi_2 - \chi_3 + \chi_5 - \chi_6)$	$\Lambda_3 = 1/\sqrt{2} (\lambda_2^4 + \lambda_1^3) E^b = 6.76 \text{ eV (band } \beta)$
$\varphi_4 = 1/\sqrt{12} (-2\chi_1 + \chi_2 + \chi_3 - 2\chi_4 + \chi_5 + \chi_6)$	$\Lambda_4 = 1/\sqrt{2} (\lambda_2^3 - \lambda_1^4) E^b = 6.76 \text{ eV (band } \beta')$
$IP = 9.25^f \text{ eV; } EA = -0.54^f \text{ eV.}$	
Pyridine ^{c,d}	
$\psi_1 = 0.1815 (\chi_2 + \chi_6) - 0.3610 (\chi + \chi_5) - 0.6113 \chi_4 + 0.5475 \chi_N$	
$\psi_2 = 0.4970 (\chi_2 - \chi_6) + 0.5030 (\chi_3 - \chi_5)$	
$\psi_3 = 0.3383 (\chi_2 + \chi_6) + 0.2728 (\chi_3 + \chi_5) - 0.5893 \chi_4 - 0.5244 \chi_N$	
$\psi_4 = 0.5030 (\chi_2 - \chi_6) - 0.4970 (\chi_3 - \chi_5)$	
$\Lambda_1 = 0.8202 \lambda_3^4 - 0.5720 \lambda_2^5$	$E^b = 4.90 \text{ eV (band } \alpha)$
$\Lambda_2 = 0.8688 \lambda_3^5 + 0.4950 \lambda_2^4$	$E^b = 6.38 \text{ eV (band } \rho)$
$\Lambda_3 = 0.4950 \lambda_3^5 - 0.8688 \lambda_2^4$	$E^b = 7.07 \text{ eV (band } \beta')$
$\Lambda_4 = 0.5720 \lambda_3^4 + 0.8208 \lambda_2^5$	$E^b = 7.07 \text{ eV (band } \beta)$
$IP (2) = 10.212 \text{ eV; } IP (3) = 9.54 \text{ eV; } EA (4) = -1.06 \text{ eV; } EA (5) = -1.347 \text{ eV.}$	
Formic acid ^e	
$\psi_1 = 0.3903 \chi_1 + 0.6143 \chi_C + 0.6858 \chi_3$	
$\psi_2 = 0.6792 \chi_1 + 0.2399 \chi_C - 0.6936 \chi_3$	
$\psi_3 = 0.5877 \chi_1 - 0.7273 \chi_C + 0.3544 \chi_3$	
$EA = -0.15 \text{ eV.}$	



^a Determined by symmetry (ref 9); ^b Experimental value; ^c The lowest occupied and the highest vacant orbitals are not given since they are not necessary to afford a good interpretation of the symmetry of the benzene and pyridine electronic spectra¹⁵; ^d Ref 3 and 16; ^e Ref 5 and therein; ^f Ref 17; ¹ $1 \text{ eV} \approx 1.60219 \cdot 10^{-19} \text{ J.}$

TABLE II

Parameters for two Centre Electron Repulsion Integrals Calculation

p—q	a	b	c	$r_{\text{lim}}^a / \text{\AA}$
C—C	11.130	-2.912	0.253	4.80
C=O	13.200	-4.205	0.452	3.95
C—N	11.735	-3.255	0.302	4.50
C—O	15.388	-5.393	0.603	4.30

^a For $r > r_{\text{lim}}$ the two center repulsion integrals are evaluated as e^2/r .

when small barrier differences would determine structure prediction (e. g. an error of -1.9 kcal/mol is found for the rotation barrier in ethane, where the experimental barrier value is 2.9 kcal/mol²⁰). A calculation test at the MIM level was performed on phenyl-benzoate and some derivatives assuming R_2 rotated by 20° or 45° . Again the results are not definitive: in fact, apart from a slight increase in the dipole moment (above all in the x-component) they do not show sensible variation in the state composition but only an energetic order inversion between the second and the third electronic states. The π -bond order relative to the R_1 -C bond in the ground state of the planar parent compound results in about 0.11 while that of O_9 - R_2 bond (maintaining R_2 coplanar) is much lower (~ 0.04). This confirms that conjugation between the R_2 ring and the rest of the molecule is also very poor when the molecular geometry is at the optimum for its existence. Therefore one can deduce that the rotation barrier should be near to the value of a single bond rotation and not sensibly influenced by losing the conjugation consequent to the R_2 rotation.

In several simple carboxylic esters a rotation of 20° to 30° of the C—O—R triangle around the C—O bond is justified²¹; when the R-alkyl group is substituted by a phenyl or a pyridil ring one could think that conjugation should be higher (but not much higher owing to the strong resonance of the $-\text{CO}_2$ group) and therefore the cited rotation angle should be lower. On the other hand, in a recent paper relating to dielectric relaxation in esters and out of plane conformation²² Saksena deduces that phenyl-benzoate (and other similar esters) has not a rigid *trans* planar configuration and suggests free rotatory oscillations around the C—O bond in the *trans* conformation of the ester. As things are, and since the dipole moments calculated for the all-planar structure in phenyl-benzoate and phenyl-isonicotinate nicely agree with the experimental values, we have decided to perform our calculations assuming a planar conformation for all the compounds.

RESULTS AND DISCUSSION

Electronic Spectra

The results of the calculations referring to the electronic spectra of the compounds are collected in Table III with the experimental UV absorption data obtained in a cyclohexane solution. When different isomers are possible, the theoretical data are reported only for one of them owing to the close resemblance of the results.

TABLE III
Composition (%) of the Excited Electronic States of the Studied Compounds

State	$\Delta E/\text{eV}$		f		Dominating Configuration %
	theor.	exptl.	theor.	exptl.	
<i>Phenyl-benzoate</i>					
Ψ_1	4.37	4.41	0.01	0.01	65 Λ_1 (A), 32 T_{2A}^{Ac}
Ψ_2	4.52		0.14		51 Λ_1 (C), 17 T_{1A}^{Ac} , 16 T_{2C}^{Ac}
Ψ_3	4.58		0.28		51 T_{1A}^{Ac} , 25 Λ_1 (C)
Ψ_4	4.88	5.39	0.02	0.36	11 T_{1A}^{Ac} , 63 T_{1C}^{Ac}
Ψ_5	5.35		0.02		27 Λ_1 (A), 45 T_{2A}^{Ac} , 13 T_{2C}^{Ac}
Ψ_6	5.36		0.08		14 Λ_1 (C), 11 T_{2A}^{Ac} , 53 T_{2C}^{Ac}

<i>Phenyl-isonicotinate (N in 4)</i>					
Ψ_1	4.51	4.68	0.06	0.12	68 Λ_1 (A), 30 T_{2A}^{Ac}
Ψ_2	4.54		0.01		74 Λ_1 (C), 19 T_{2C}^{Ac}
Ψ_3	4.82	5.82	0.25	0.32	72 T_{1C}^{Ac}
Ψ_4	5.28		0.18		68 T_{1A}^{Ac}
Ψ_5	5.39		0.04		63 T_{2C}^{Ac} , 16 Λ_1 (C)
Ψ_6	5.72		0.01		31 Λ_1 (A), 60 T_{2A}^{Ac}
<i>Phenyl-nicotinate (N in 3)</i>					
Ψ_1	4.54	4.79	0.02	0.11	74 Λ_1 (C), 19 T_{2C}^{Ac}
Ψ_2	4.66		0.29		45 Λ_1 (A), 36 T_{2A}^{Ac}
Ψ_3	4.81	5.63	0.13	0.31	35 Λ_1 (A), 11 T_{1A}^{Ac} , 37 T_{1C}^{Ac}
Ψ_4	5.01		0.01		11 T_{1A}^{Ac} , 28 T_{2A}^{Ac} , 30 T_{1C}^{Ac}
Ψ_5	5.41		0.04		16 Λ_1 (C), 69 T_{2C}^{Ac}
Ψ_6	5.96		0.19		11 Λ_1 (A), 58 T_{1A}^{Ac} , 10 T_{2C}^{Ac}
<i>2-Pyridil-benzoate (N in 2')</i>					
Ψ_1	4.37	4.40	0.01	0.01	56 Λ_1 (A), 32 T_{2A}^{Ac}
Ψ_2	4.60	4.79	0.38	0.11	10 Λ_2 (A), 76 T_{1A}^{Ac}
Ψ_3	4.79		0.02		85 Λ_1 (C)
Ψ_4	5.36	5.37	0.05	0.35	33 Λ_1 (A), 57 T_{2A}^{Ac}
Ψ_5	5.39		0.11		10 Λ_2 (C), 66 T_{2C}^{Ac}
<i>3-Pyridil-benzoate (N in 3')</i>					
Ψ_1	4.37	4.39	0.01	0.01	66 Λ_1 (A), 32 T_{2A}^{Ac}
Ψ_2	4.59	4.77	0.40	0.11	10 Λ_2 (A), 73 T_{1A}^{Ac}
Ψ_3	4.81		0.03		32 Λ_1 (C), 12 T_{2C}^{Ac}
Ψ_4	5.11	5.34	0.02	0.36	13 Λ_1 (C), 61 T_{2C}^{Ac}
Ψ_5	5.37		0.06		33 Λ_1 (A), 58 T_{2A}^{Ac}
<i>2-Pyridil-isonicotinate (N in 4 and 2')</i>					
Ψ_1	4.51	4.47	0.06	0.05	69 Λ_1 (A), 30 T_{2A}^{Ac}
Ψ_2	4.78	4.69	0.09	0.15	86 Λ_1 (C), 10 T_{2C}^{Ac}
Ψ_3	5.21		0.36		62 T_{1A}^{Ac} , 13 T_{2C}^{Ac}
Ψ_4	5.45	5.82	0.04	0.26	10 Λ_2 (C), 15 T_{1A}^{Ac} , 56 T_{2C}^{Ac}
Ψ_5	5.73		0.01		31 Λ_1 (A), 61 T_{2A}^{Ac}
<i>3-Pyridil-isonicotinate (N in 4 and 3')</i>					
Ψ_1	4.52	4.74	0.06	0.16	69 Λ_1 (A), 30 T_{2A}^{Ac}
Ψ_2	4.30		0.13		78 Λ_1 (C), 19 T_{2C}^{Ac}
Ψ_3	5.05	5.79	0.21	0.29	17 Λ_1 (C), 16 T_{2A}^{Ac} , 47 T_{2C}^{Ac}
Ψ_4	5.32		0.11		61 T_{1A}^{Ac} , 15 T_{2C}^{Ac}
Ψ_5	5.74		0.01		30 Λ_1 (A), 62 T_{2A}^{Ac}
<i>2-Pyridil-nicotinate (N in 3 and 2')</i>					
Ψ_1	4.68	4.79	0.23	0.12	57 Λ_1 (A), 33 T_{2A}^{Ac}
Ψ_2	4.79		0.06		79 Λ_1 (C), 10 T_{2C}^{Ac}
Ψ_3	4.92	5.60	0.13	0.28	24 Λ_1 (A), 20 T_{1A}^{Ac} , 36 T_{2A}^{Ac}
Ψ_4	5.44		0.08		12 Λ_1 (C), 68 T_{2C}^{Ac}
Ψ_5	5.97		0.18		11 Λ_1 (A), 58 T_{1A}^{Ac} , 10 T_{2A}^{Ac}
<i>3-Pyridil-nicotinate (N in 3 and 3')</i>					
Ψ_1	4.67	4.77	0.26	0.14	54 Λ_1 (A), 34 T_{2A}^{Ac}
Ψ_2	4.80		0.10		12 Λ_1 (A), 66 Λ_1 (C), 16 T_{2C}^{Ac}
Ψ_3	4.90	5.58	0.10	0.31	22 Λ_1 (A), 19 Λ_1 (C), 17 T_{1A}^{Ac} , 27 T_{2A}^{Ac}
Ψ_4	5.17		0.01		10 T_{2A}^{Ac} , 57 T_{2C}^{Ac}
Ψ_5	5.98		0.18		10 Λ_1 (A), 58 T_{1C}^{Ac} , 11 T_{2A}^{Ac}

* 1 eV \approx 1.60219 \cdot 10⁻¹⁹ J.

Λ_1 are the locally excited states of ring fragments (A or C).

T_1^{Ac} are the charge transfer configurations from ring (A or C) to acceptor (Ac).

At first comparison between the experimental and theoretical data, it seems that there are many theoretical transitions with respect to the experimental evidence, but a careful analysis of the UV spectra shows several inflections or small maxima. The experimental UV spectrum of the parent compound (phenyl-benzoate) and that of 2-pyridil-benzoate are reported, as for example, in Figure 2. The comparison of the oscillator strengths is not very significant because their experimental evaluation for each single transition is difficult.

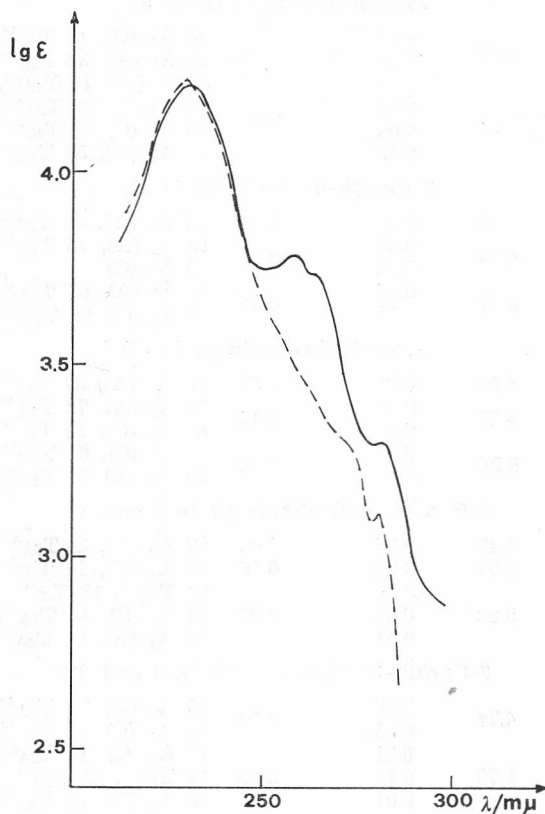


Figure 2. UV absorption spectra of phenyl-benzoate (---) and 2-pyridil-benzoate (—) in cyclohexane solution.

Generally the first two calculated transitions show a composition which prevails locally, excited and corresponding principally to the α band of benzene and/or pyridine, except in 2-pyridil-benzoate and 3-pyridil-benzoate where the transition due to Λ_1 of R_2 ring is shifted to an energy value slightly higher than the charge transfer one. The O_9-R_2 bond orders relative to these excited states give a higher result than those of the ground and other excited states and confirm the little character of the conjugation band experimentally evidenced. The third electronic transition, which is very close in energy to the second, is prevailing due to a charge transfer from the R_1 ring to the $-\text{CO}_2$ group and, in our opinion, is to be assigned, together with the subsequent three charge-transfer transitions, to the absorption band experimentally observed in

the range 213—230 nm. This assignment would be in agreement with the similar one done for the UV spectrum of benzoic acid²³ to which the general spectral trend resembles.

An investigation of electronic states theoretical energies shows that the presence of a nitrogen atom in the R₂ ring, in the *ortho* or *meta* position (2-pyridil-benzoate and 3-pyridil-benzoate) maintains the energies of the two lowest and highest transitions with respect to the parent phenyl-benzoate, while it increases the energies of the third transition. This situation is experimentally evidenced by the appearance of an intermediate absorption band at 4.79—4.77 eV. The presence of a nitrogen atom in R₁ ring in the *meta* or *para* position (phenyl-nicotinate and phenyl-isonicotinate) produces a displacement of the first, third and fourth transitions to a higher energy with respect to the parent compound; it can be experimentally observed an iperchromic and ipsochromic effect of the lowest energy band passing from the phenyl-benzoate to the pyridil-compounds.

The molecules with two pyridine rings have UV absorption spectra with the same general trend and excited states composition as previous ones; the theoretical results seem to confirm this displacement of the experimental absorption bands toward higher energy with respect to the phenyl-benzoate spectrum. A final evaluation of the theoretical results shows that, when one has N atoms in the *ortho* or *meta* positions, results nearly like in energy and state composition are obtained for the different possible conformations (N in 2' and 6' or 3' and 5' and so on).

Dipole Moments

More interesting, for the aim of the present paper, are the results concerning the dipole moment values. Their theoretical figures at the MIM level were obtained vectorially adding the calculated π value to the σ ones obtained by vectorial composition of bond moments, using the values reported by Smith²⁴. Also if it is not certainly constant in all the isomers, an empirical medium value of -0.58 D for the lone pair of the nitrogen atom (obtained from the pyridine experimental dipole moment) was also considered⁵. It is to be noted that the vectorial method used in ref 1 completely neglects the conjugation and the dipole moments are obtained from the experimental values of phenyl-benzoate and pyridine. In the MIM method the calculated π -moment includes the conjugation term. The nearly equal results for all the molecules cannot be casual also if it is possible that several errors can be mutually compensated.

The resulting dipole moments and relative direction for the different conformations are reported in Table IV together with those obtained by the INDO method and the experimental ones; in the same table the values of ref 1 are also reported for easier comparison. In the last columns of the same table are reported the weights (%) of the different conformers obtained by the three methods and calculated as described in ref 25. A comparison among the data shows that the agreement between the theoretical and experimental dipole moments for phenyl-benzoate and phenyl-isonicotinate — which are the only directly comparable data — is satisfactory, but the INDO method slightly underestimates the moment of the latter compound. The difference, however, is close to the order of the experimental error which can be made in the

TABLE IV

Dipole Moments and Conformations Equilibrium of Pyridinic Aromatic Esters

Compo	Conformation N	A ^a		B ^b		C ^c		μ_{exp}	Conformations ^d /0/0		
		μ_{tot}	α°	μ_{tot}	α°	μ_{tot}	α°		A	B	C
		D		D		D					
1	—	—	—	1.93	69	1.88	46	1.80	—	—	—
2	4	2.14	131	2.23	126	1.67	126	2.03	—	—	—
3	3	3.53	95	3.77	90	3.21	86	2.17	37	33	45
	5	0.43	224	0.17	246	0.47	297		63	67	55
4	2'	3.53	95	3.76	95	3.35	88	2.23	39	34	42
	6'	0.43	224	0.42	208	0.72	315		61	66	58
5	3'	4.03	62	4.19	64	4.01	53	3.22	55	49	45
	5'	1.91	351	1.84	355	2.39	348		45	51	55
6	4 and 2'	4.32	125	4.65	127	3.99	123	3.41	43	28	66
	4 and 6'	2.53	187	2.79	184	1.84	196		57	72	34
7	4 and 3'	3.53	95	3.81	99	3.22	88	2.15	36	30	43
	4 and 5'	0.43	224	0.59	196	0.51	276		64	70	57
8	3 and 2'	5.60	105	5.91	105	5.31	101	3.02	14.4	11.2	18.9
	3 and 6'	2.14	131	2.34	131	1.46	113		22.6	21.8	26.1
	5 and 2'	2.14	131	2.35	130	1.84	122		24.6	22.8	23.1
	5 and 6'	2.61	237	2.65	235	2.37	256		38.4	44.2	31.9
9		(3.05) ^f		(3.08) ^f		(2.91) ^f		2.99			
	3 and 3'	5.48	82	5.77	83	5.24	75		20.3	16.2	20.2
	3 and 5'	1.79	64	1.93	70	1.83	47		16.7	16.8	24.8
	5 and 3'	1.79	64	1.93	70	1.94	47		34.7	32.8	24.8
	5 and 5'	2.34	290	2.22	288	2.61	311		28.3	34.2	30.2
		(3.05) ^f		(2.99) ^f		(3.06) ^f					

^a Calculated by the vectorial method; ^b Calculated by the MIM method; ^c Calculated by the INDO method;

^d The percentage of the isomers with only a pyridine ring was calculated by the formula $\mu_{\text{exp}}^2 = X \cdot \mu_1^2(\text{theor}) + (1 - X) \mu_2^2(\text{theor})$ (see ref 25). The percentage of the isomers having two pyridines rings was obtained by keeping for the R_1 and R_2 nitrogen the distribution found for the compounds with only one pyridine ring.

^e Angle between the dipole moment vector and the positive x-axis (long axis); the rotation is the usual counterclockwise.

^f Resulting theoretical μ moment from the μ total of each conformer and corresponding percentage.²⁵

μ determination. On the whole, the dipole moments calculated at the INDO level are lower than those of the MIM and vectorial methods and their directions are approximately equal with the exception of phenyl-nicotinate (N in 5), 2-pyridil-benzoate (N in 6') and 3-pyridil-isonicotinate (N in 4 and 5'). In this latter compound, however, the INDO calculated x-component of the dipole moment is very small (0.05 D) and of poor significance since a small error in its evaluation causes a strong variation in the dipole direction.

Also the percentage of the possible isomers are roughly similar except in 2-pyridil-isonicotinate where the percentage of the more probable conformer results reversed. Generally, the most probable form is that having the nitrogen atom on the opposite side of the C=O group or, however far enough from it. Similar results were obtained for aza-substituted benzanilides.²⁵

The reasonable agreement between experimental and theoretical data seems to suggest that the choice of planar structure might also be acceptable, if the obtained results are not sufficient to affirm with certainty if the molecular skeleton is or is not planar.

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SAŽETAK

Molekularne konformacije piridinskih aromatskih estera. II. Elektronski apsorpcijski spektri i dipolni momenti metodom MIM

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Semiempirijska metoda »molekule u molekulu« (MIM) primjenjena je za računanje apsorpcijskih uv spektara devet piridinskih aromatskih estera opće formule R_1COOR_2 uz pretpostavku planarne geometrije. Benzen, piridin i mravlja kiselina upotrebjeni su kao komponentni sustavi. Dipolni momenti istih spojeva izračunati su MIM i INDO metodom, te usporedbom eksperimentalnih i teoretskih vrijednosti ocijenjen ravnotežni postotak konformera. Općenito su dobijeni slični rezultati, pa se može kazati da su zadovoljavajući, ali nedovoljni da sa sigurnošću potvrde planarnost molekularnog skeleta.

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