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Studies on the Electronic Absorption Spectra of Some Selected Furan Derivatives. Molecular Orbital Calculations

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The electronic absorption spectra of three groups of furan derivatives: 2-formyl, 2-acetylfuran, and 2-furoic acid, *N*-(2-furylmethylene)amines and phenylfurans were investigated. The predominant conformation as well as the polarity of the molecule could be predicted from its spectrum. The investigated molecules were proved to be "all planar" configuration which led to substantial interaction between the electronic states of the subsystems. The preferred conformations of *N*-(2-furylemthylene)methylamine and *N*-(2-furylemthylene)aniline were predicted with the aid of molecular orbital calculations.

The electronic absorption spectra of furan derivatives are rarely found in the literature. Horvath and Kiss[1] attributed the long wavelength absorption of extremely low intensity in the spectrum of furan to a singlet-triplet transition and the main absorption band in the UV region to a singlet $\pi\rightarrow\pi^*$ transition. The triplet states of furan, thiophene, and pyrrole were detected by variable-angle electron impact spectroscopy.[2] In furan, the singlet-triplet transition occurs with maximum intensity at 3.99 and 5.22 eV.

The absorption spectra of numerous furfural acetals[3] and 2-arylfuran[4] have been reported. The conformation of 2-furylphenyl ketone has been investigated by means of spectroscopic methods.[5] It was suggested that furyl conjugation with the carbonyl group is superior to phenyl conjugation with the same group.[5] The absorption spectra of some furylcarbonyl derivatives have been measured, and the band maxima were correlated to the reactivity of the carbonyl group of the compounds.[5] Head and Jones[6] investigated the electronic absorption spectra of some *N*-(2-furylmethylene)arylamines in ethanol. The dipole moments of some furfural derivatives in benzene, dioxane, and CCl_4 were determined from dielectric data.[7,8]

In this work the electronic absorption spectra of three groups of furan derivatives: acylfurans and 2-furoic acid, *N*-(2-furylmethylene)amines, and phenylfurans, have been investigated. The results give much information on the nature of the spectra of furan derivatives as well as on the conformation of the composite furan derivatives. Molecular orbital calculations were performed on representative examples of the compounds studied. The SCF-Cl and the MIM methods were used and proved to be useful for conformational analysis.

Experimental

Methanol, ethanol, and cyclohexane were BDH reagent grade chemicals and were purified by the conventional methods reported.[9]

2-Acetylfuran and furfural (Koch light reagent grade) were used after purification by vacuum distillation. 2-Furoic acid (BDH reagent grade) was purified by crystalization. 2-Phenylfuran was prepared by suspending stabilized benzene diazonium salt (0.1 mol) in furan (150 ml) and vigorously stirring throughout the preparation while adding sodium hydroxide and sodium acetate.[4] After 24 h of stirring, the product was steam distilled. The product was extracted with ether and then vacuum distilled (bp 94 °C/10 mmHg, 1 mmHg≈133.322 Pa). In a similar way 2-(*p*-chlorophenyl)furan was prepared. 2,4-Diphenylfuran was prepared by oxidizing 1,3-diphenyl-2-buten-1-one (0.1 mol) with selenium dioxide (0.05 mol) in dioxane. The product was distilled in a vacuum (200 °C/3 mmHg) and solidified in the side arm. The compound was purified by recrystallization from ethanol (mp 109—110 °C).[11] 2,5-diphenylfuran was prepared by heating 1,4-diphenyl-1,4-butanedione, which was prepared from phenacyl bromide,[12] with concentrated HCl (one part of 1,4-diphenyl-1,4-butanedione to two parts of HCl) at 130—150 °C. The product was precipitated from ice cold water and purified by crystallization from ethanol (mp 91 °C).[13]

N-(2-Furylmethylene) amines were prepared by mixing the stoichiometric amounts of furfural and an appropriate amine in benzene.[6] The temperature of the mixture was kept near 5 °C for 1 h. The benzene solution was dried over magnesium sulfate and evaporated to give the imines that were purified by vacuum distillation or recrystallization. The compounds thus prepared were *N*-(2-furylmethylene)-methylamine, *N*-(2-furylmethylene)aniline, *N*-(2-furylmethylene)-*o*-toluidine, *N*-(2-furylmethylene)-*p*-toluidine, *N*-(2-furylmethylene)-*o*-chloroaniline, *N*-(2-furylmethylene)-*o*-methoxyaniline, *N*-(2-furylmethylene)-*p*-methoxyaniline, *N*-(2-furylmethylene)-*p*-nitroaniline, and *N*-(2-furylmethylene)-2-pyridinamine. Melting points and boiling points agreed with the values reported in the literature.[14—16]

The absorption spectra were measured with a Beckman DK-1 spectrophotometer using 1.0 cm fused silica cells.

Results and Discussion

A. Electronic Absorption Spectra. *(I) Carbonyl and Carboxy Derivatives of Furan*: Figure 1a shows the electronic absorption spectra of furan, furfural, 2-acetylfuran, and 2-furoic acid in a nonpolar solvent. The spectrum of furan has been investigated.[1,2] Substitution, in the furan nucleus, by a formyl, acetyl or carboxyl group reduced the symmetry from C_{2v} to C_s and perturbed significantly the electronic spectrum of furan (Fig. 1a). At least two $\pi\rightarrow\pi^*$ transitions (280—210 nm) appear in the spectra of substituted compounds in addition to an $n\rightarrow\pi^*$ (≈330 nm) transition. The spectra of the formyl and acetyl derivatives show much similarities but differ basically from that of 2-furoic acid. Such differences are mainly due to the dimerization of the acid, specially in nonpolar solvent. A large increas in intensity of the

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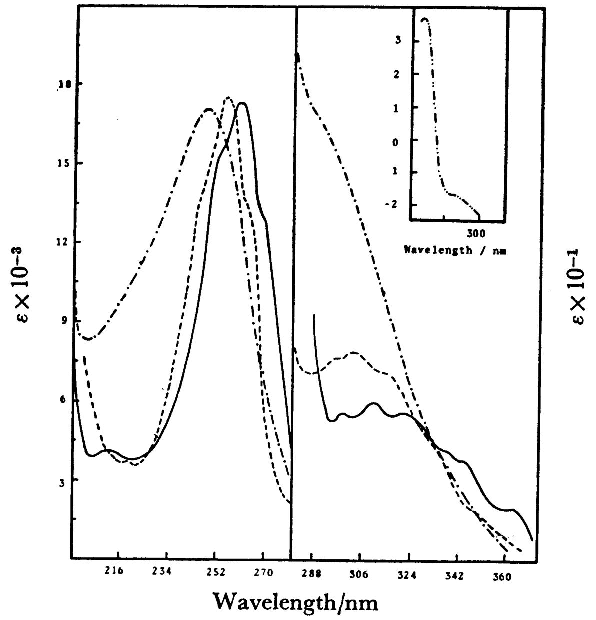


Fig. 1a. Electronic absorption spectra of: —··—··— furan in hexane, —— furfural in cyclohexane, ---- 2-acetylfuran in cyclohexane, —·—·— 2-furoic acid in cyclohexane.

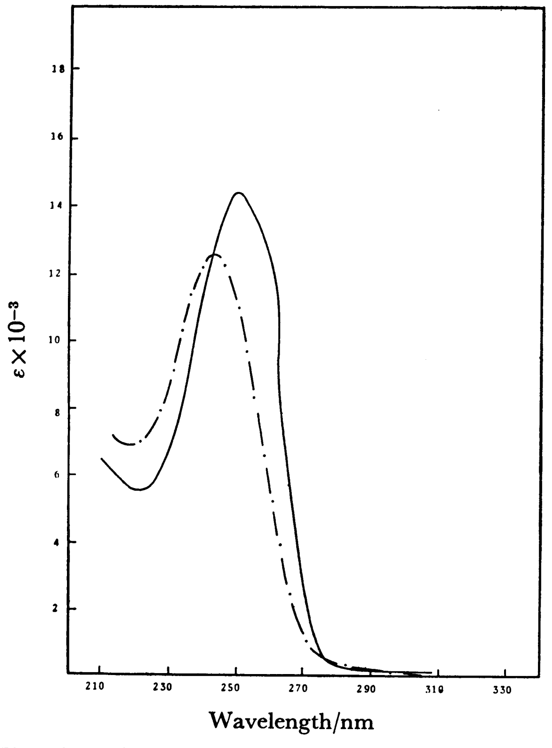
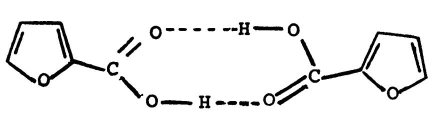


Fig. 1b. Electronic absorption spectra of 2-furoic acid (dil soln).
—— In cyclohexane, —·—·— in methanol.



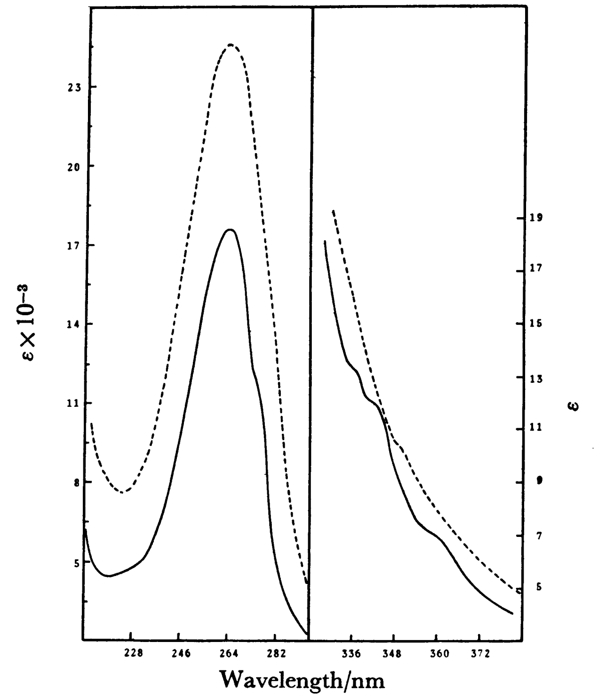


Fig. 2a. Electronic absorption spectra of *N*-(2-furylmethylene)methylamine.
—— In cyclohexane, ---- in ethanol.

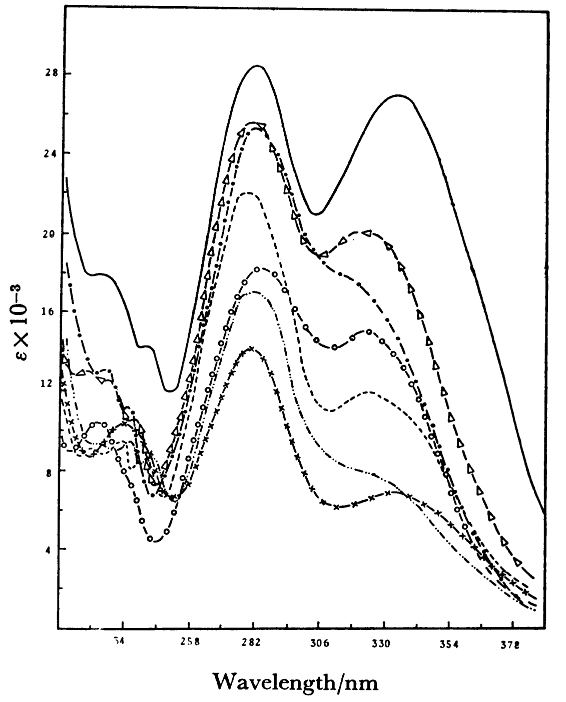
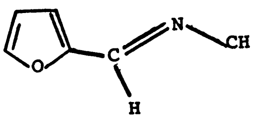


Fig. 2b. Electronic absorption spectra (in cyclohexane) of:
—·—·— *N*-(2-furylmethylene)aniline, ---- *N*-(2-furylmethylene)-*o*-toluidine, —··—··— *N*-(2-furylmethylene)-*o*-chloroaniline, —×—×— *N*-(2-furylmethylene)-*o*-methoxyaniline, ---- *N*-(2-furylmethylene)-*p*-toluidine, —O—O— *N*-(2-furylmethylene)-*p*-chloroaniline, —— *N*-(2-furylmethylene)-*p*-methoxyaniline.

longest wavelength transition of the acid, in nonpolar solvent, suggests that such a transition is not n→π* but π→π* of the dimer. The n→π* band is probably somewhere in the 280 nm region. The spectrum of

2-furoic acid in methanol is that of a mixture of the monomer and dimer, and the 310 nm band partially comprises an n→π* transition. On dilution, the longest wavelength band disappears and the spectrum obtained is only that of the monomer (Fig. 1b). Table 1 shows the values of band maxima and band intensities of furfural, 2-acetylfuran, and 2-furoic acid.

(II) Furylmethylenes: In a previous study[17] the electronic absorption spectra of *N*-(2-thenylidene) amines were investigated. In this work the spectra of a variety of *N*-(2-furylmethylene) amines were studied (Figs. 2a and 2b). Although *N*-(2-furylmethylene)-methylamine (**a**) and 2-acetylfuran (**b**) are π-isoelectronic and of the same symmetry and their π→π* transitions are of nearly the same energy, the n_N→π* transition being of much lower energy and having lower intensity than the n_O→π* transition (Tables 1 and 2). The spectrum of *N*-(2-furylmethylene)aniline differs basically from that of the methylamine derivative. Figure 2b suggests that the interaction between the subsystems of *N*-(2-furylmethylene)methylamine and benzene is pronounced as will be discussed below. The spectreum of *N*-(2-furylmethylene)aniline provides some important information about the conformation of the molecule. If the molecule is a "free rotator"


(**a**)

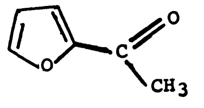

(**b**)

Table 1. Numerical values of band maxima and band intensities of furfural, 2-acetylfuran and 2-furoic acid in cyclohexane and methanol[a)]

Compound	λ_{max}/nm	ε/M^{-1} cm^{-1}	*f*
Furfural	317(314)	60(80)	0.002(0.002)
	266(270)	17400 (9400)	0.350(0.210)
	218(218)	4240 (3100)	0.100(0.130)
2-Acetylfuran	309(307)	79(95)	0.003(0.001)
	261(267)	17500(18700)	0.350(0.400)
	(219)	(4600)	(0.260)
2-Furoic acid	294	170	0.005
	255(240)	17200(12500)	0.440(0.330)
	228	11000	0.470

a) Values in parentheses are those when methanol was used as a solvent.

Table 2. Numerical values of band maxima and band intensities of *N*-(2-furylmethylene) amines[a)]

Compound	λ_{max}/nm	ε/m^{-1} cm^{-1}	*f*
N-(2-Furylmethylene)methylamine	360(354)[b)]	7.5(10.5)	—
	264(264)[b)]	17600(24, 740)	0.420(0.667)
N-(2-Furylmethylene)aniline	318(315)	17500(27, 200)	0.512(0.763)
	282(285)	25150(27, 600)	0.644(0.755)
	228(228)	13200(13, 900)	0.352(0.461)
	324(312)	11840(12, 200)	0.346(0.420)
N-(2-Furylmethylene)-*o*-toluidine	279(285)	22000(22, 400)	0.615(0.594)
	234(231)	9400 (8, 200)	0.259(0.299)
N-(2-Furylmethylene)-*p*-toluidine	323(321)	20000(23, 700)	0.584(0.640)
	280(282)	25600(22, 070)	0.650(0.565)
	222(222)	12800(11, 800)	0.422(0.454)
N-(2-Furylmethylene)-*o*-chloroaniline	324(318)	7860(11, 000)	0.230(0.303)
	280(282)	17000(18, 700)	0.430(0.457)
	236(234)	9300 (8, 900)	0.276(0.272)
N-(2-Furylmethylene)-*p*-chloroaniline	324(318)	14890(23, 500)	0.395(0.692)
	285(288)	18400(21, 940)	0.525(0.638)
	225(222)	10400(12, 850)	0.343(0.508)
N-(2-Furylmethylene)-*o*-methoxyaniline	333(330)	6910 (8, 910)	0.209(0.298)
	282(280)	14140(15, 300)	0.345(0.439)
	234(228)	10340(11, 250)	0.314(0.608)
N-(2-Furylmethylene)-*p*-methoxyaniline	335(333)	26900(27, 100)	0.730(0.749)
	282(282)	28500(23, 100)	0.896(0.811)
	225(220)	17900(16, 100)	0.533(0.544)
N-(2-Furylmethylene)-*p*-nitroaniline	323(341)	14900(22, 370)	0.587(0.782)
	218(218)	9900(14, 270)	0.466(0.672)
N-(2-Furylmethylene)-2-pyridineamine	315(324)	16350 (6, 500)	0.458(0.147)
	282(294)	12000 (9, 340)	0.293(0.302)
	222(231)	12540(16, 400)	0.434(0.385)

a) Values in parentheses are those when methanol was used as a solvent. b) In ethanol.

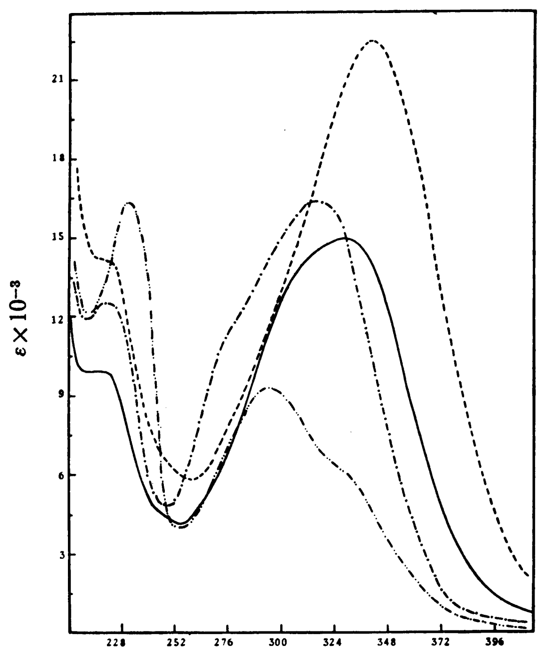
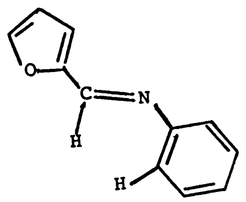


Fig. 3. Electronic absorption spectra of: *N*-(2-furylmethylene)-2-pyridineamine; —·—·— in cyclohexane, —··—··— in methanol, *N*-(2-furylmethylene)-*p*-nitroaniline; —— in cyclohexane, ---- in methanol.

around the single bond (C–C) or (N–C), its spectrum may become superposition of the spectra of its subsystems. On the other and, if the steric factor owing to the H–H repulsion is pronounced, the molecular structure would be distorted and the spectrum of the composite molecule would resemble either of the sepectra of its constituents. From the spectrum of the molecule (Fig. 2b), one can predict that the molecule is not a "free rotator" and the molecular structure is not apparently distorted. This will be theoretically confirmed below. The position of the band maxima did not vary on scanning the spectrum in polar solvent. Therefore, it can be said that the molecule has no strong dipole. The feature of the overlap of the transitions is very significant in the spectra of *N*-(2-furylmethylene) amines as in the spectra of the related compounds, *N*-benzylidene-anilines and azobenzenes.



To confirm the relation between the spectra of *N*-(2-furylmethylene) amines and the conformations of these compounds, the spectra of a series of *N*-(2-furylmethylene)anilin derivatives have been investigated (Fig. 2b). An important result is that the feature of the spectra of all derivatives (except the nitro derivatives) is very much similar to that of the parent compound *N*-(2-furylmethylene)aniline. The spectra show three $\pi \rightarrow \pi^*$ electronic transitions with a degree of overlap and intensity depended on the substituents, whose band maxima are not so different from each other. This indicates that planarity of the molecule is pronounced. It is true that, generally, transitions in *N*-(-*o*)-substituted(2-furylmethylene)anilines have lower intensity than those in *p*-substituted furyl isomers.

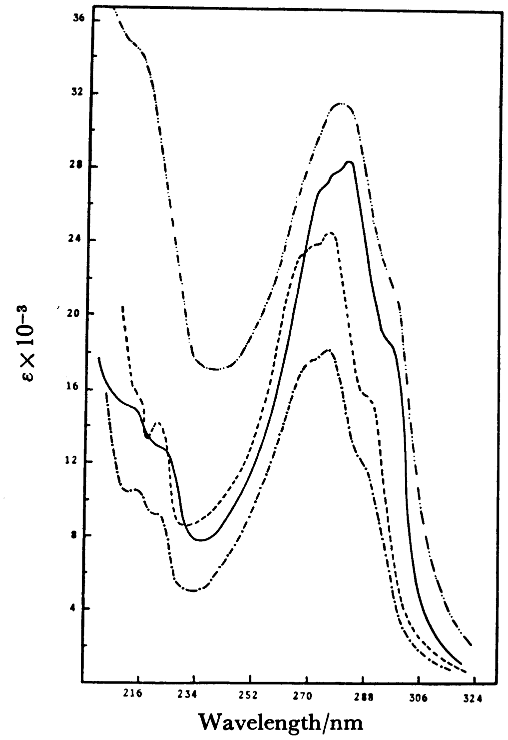


Fig. 4. Electronic absorption spectra of: 2-phenylfuran; ---- in cyclohexane, —·—·— in methanol, 2-(*p*-chlorophenyl)furan; —— in cyclohexane, —··—··— in methanol.

The spectra of the nitro derivatives (Fig. 3), differ significantly from those of *N*-(2-furylmethylene) amines as a result of the perturbation of a nitro group. From the spectra one can tell that the nitro derivatives have nearly the "all-planar" configuration. If planarity of the molecule is apparently distorted, the spectrum of the composite molecule should be similar to those of the subsystems as stated above. Such behavior is not encountered in the spectra of the compounds studied.

The absorption spectra of *N*-(2-furylmethylene)-2-pyridinamine in cyclohexane and methanol are shown in Fig. 3. The internal rotation of either the furan or the pyridine nucleus seems to be restricted, since the spectrum observed differs significantly from those of the subsystems. The molecule will aquire a quasi-rigid configuration, and the electronic interaction between the two subsystems (pyridine and 2-furylmethylene) is significant. All transitions observed are $\pi \rightarrow \pi^*$, which shift to red in polar media. This suggests that the excited state has a polar structure. Table 2 gives the values of band maxima and intensities of *N*-(2-furylmethylene) amines.

(III) 2-Phenylfurans: An objective of this work is to investigate the extent of mixing of the electronic states of furan with those of other subsystems when

the two chromophores are joined through a single bond. The above section has shown that such interaction is significant when furan nucleus is attached to either a carbonyl group or a benzylimino group. A theoretical treatment of the extent of "state mixing" in phenylfurans and bifurans has been reported.[18]) The spectrum of 2-phenylfuran (Fig. 4) consistis of two intense structured band systems (I and II), which are blurred with no shift in band maxima as the solvent is changed from cyclohexane to methanol. The numberical values of band maxima indicate that the bands do not correspond to localized transitions in either the "benzene" or "furan" nucleus. Substitution of a chlorine atom into furan such as 2-(*p*-chlorophenyl) furan did not affect the spectrum significantly. The vibrational components of an electronic transition in a sterically hindered molecule are blurred. This is not to be the case in a non-hindered molecule (compare the spectra of *cis*- and *trans*-stilbenes). Figure 4 indicates clearly the well resolved vibrational components of bands I and II, suggesting that the conformation of 2-phenylfuran is planar or nearly planar. Molecular orbital calculations show that as the angle of twist increases the lowest transition energy increases (reaching to a maximum value when the subsystems are perpendicular).[18]) This result is also confirmed when one considers the spectrum of biphenyl.[19])

A comparison of the electronic spectra of 2-phenylfuran with biphenyl is worthwhile. The lowest $\pi\rightarrow\pi^*$ transition (276 nm) for 2-phenylfuran is at longer wavelength than that of biphenyl (247 nm) although one expected the reverse. It was expected that the higher symmetry and larger delocalization energy of biphenyl might give rise to a lower transition energy for biphenyl than that for 2-phenylfuran. However, the release of steric hindrance in 2-phenyl furan results in the transition energy lower than that of biphenyl.

Figure 5a shows the absorption spectra of 2,4-diphenylfuran. The results indicate that planarity of the 2,4-diphenyl derivative is more distorted than that of the monophenyl derivative. The shoulder shown in the spectrum of 2,4-diphenylfuran ($\lambda\approx300$ nm, $\varepsilon\approx400$) was not observed in the spectra of the furan derivatives studied. This suggests that the band designated as I corresponds to two overlapping transitions. A confirmation of this suggesstion was obtained from molecular orbital calculation.[18]) 2-Phenylfuran had two electronic transitions at 4.33 and 4.92 eV whereas the 3-phenyl derivative had transition energies at 4.58 and 4.98 eV.

The spectra of 2,5-diphenylfuran in cyclohexane and methanol are given in Fig. 5b. The pronounced red shift and intensification of the band corresponding to the lowest energy transition, compared to that of 2,4-diphenylfuran, are evidence of a nearly "all planar" conformation for the 2,5-diphenyl derivative. This result indicates the dependence of the electronic absorption spectrum on the conformation of the molecule. Table 3 shows the values of band maxima and intensities of the studied phenylfurans.

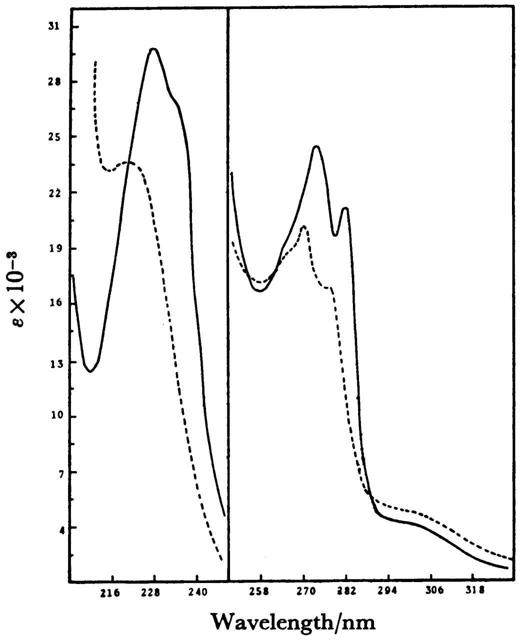


Fig. 5a. Electronic absorption spectra of 2,4-diphenylfuran.
—— In cyclohexane, ---- in methanol.

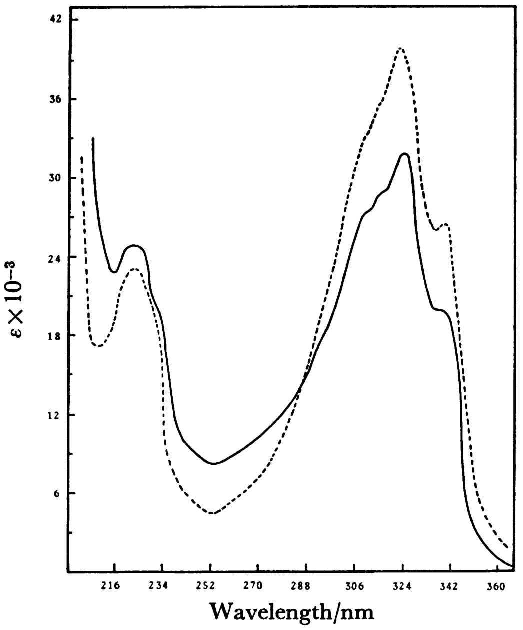


Fig. 5b. Electronic absorption spectra of 2,5-diphenylfuran.
—— In cyclohexane, ---- in ethanol.

B. Molecular Orbital Calculations. The method of molecule-in-molecule[20]) has been very nicely adopted to MO calculations on composite systems such as phenylthiophenes,[21]) bithienyls,[22]) and phenylfurans.[18]) The results encouraged us to adopt this method for calculations on *N*-(2-furylmethylene)aniline.

The two subsystems of the composite molecule, *N*-(2-furylmethylene)aniline, are 2-furylmethyleneamine (A) and benzene (B). The core of the molecule-in-molecule method is to calculate the interaction between the electronic states of subsystems (A) and (B). The PPP[23]) version of the SCF method was applied to the two conformers, Ia and Ib, and the SCF MO's were computed. The CI state functions and the corresponding energies were then calculated. The results

TABLE 3. NUMERICAL VALUES OF BAND MAXIMA AND BAND INTENSITIES OF PHENYLFURANS[a)]

Compound	λ_{max}/nm	ε/M^{-1} cm^{-1}	f
2-Phenylfuran	276(276)	24500(18260)	0.435(0.337)
	216(216)	15680(10500)	0.362(0.249)
2-(*p*-Chlorophenyl)furan	282(282)	28260(31350)	0.662(0.936)
	216(216)	14880(34000)	0.353(1.215)
2,4-Diphenylfuran	300(300)	418(480)	0.006(0.013)
	228(216)	29900(23600)	0.637(0.575)
2,5-Diphenylfuran	324(322)[b)]	32850(40970)	0.163(0.935)
	222(225)[b)]	26050(24000)	0.868(0.799)

a) Values in parentheses are when methanol was used as a solvent. b) In ethanol.

TABLE 4. CONFIGURATION INTERACTION STATE FUNCTIONS AND THE CORRESPONDING ENERGIES(eV) OF *N*-(2-FURYLMETHYLENE)METHYLAMINE

Cis isomer	
$\psi_{\mathrm{EX.\,I}}=0.9424y_4y_5^{*}-0.0861y_4y_6-0.323y_3y_5$ $-0.0076y_3y_6$	4.94
$\psi_{\mathrm{EX.\,II}}=0.3236y_4y_4+0.4675y_4y_6+0.8173y_3y_5$ $+0.0932y_3y_6$	6.21
$\psi_{\mathrm{EX.\,III}}=0.8703y_4y_6-0.0829y_4y_5-0.4760y_3y_5$ $+0.0956y_3y_6$	7.63
$\psi_{\mathrm{EX.\,IV}}=0.9910y_3y_6-0.0335y_3y_5-0.1286y_4y_6$ $-0.0152y_4y_5$	8.74
Trans isomer[b)]	
$\psi_{\mathrm{EX.\,I}}=0.9886y_4y_5-0.0313y_4y_6-0.1464y_3y_5$ $+0.0176y_3y_6$	3.37
$\psi_{\mathrm{EX.\,II}}=0.1431y_4y_5+0.4403y_4y_6+0.8823y_3y_5$ $+0.0853y_3y_6$	6.10
$\psi_{\mathrm{EX.\,III}}=0.8934y_4y_6-0.0385y_4y_5-0.4446y_3y_5$ $+0.0520y_3y_6$	7.64
$\psi_{\mathrm{EX.\,IV}}=0.9948y_3y_6-0.0498y_3y_5-0.0839y_4y_6$ $-0.0279y_4y_5$	8.77

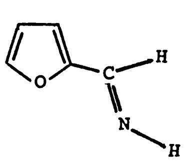
* y_4y_5 = Electronic configuration in which an electron transfers from the fourth MO(y_4) to the fifthe MO(y_5). a) The conformer Ia. b) The conformer Ib.

TABLE 5. STATE FUNCTIONS AND THE CORRESPONDING ENERGIES OF *N*-(2-FURYLMETHYLENE)ANILINE[a)]

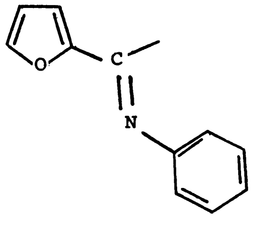
Cis isomer[b)]	Corresponding energy/eV
$\psi_0=0.9986\Gamma+0.0924CR_1+0.0850CR_3$ $+0.0520CR_2$	−0.13
$\psi_{\mathrm{EX.\,I}}=0.6699Y_1+0.70720\theta_\beta-0.1772CR_2$ $+0.1067CR_3$	4.77
$\psi_{\mathrm{EX.\,II}}=-0.7072Y_1+0.69220\theta_\beta$ $-0.0569CR_4$	4.96
$\psi_{\mathrm{EX.\,III}}=0.1151Y_1-0.50060\theta_\beta-0.2193Y_2$ $-0.15420\theta_\alpha-0.5383CR_3$ $-0.6077CR_4$	5.87
Trans isomer[c)]	
$\psi_0=0.9886\Gamma+0.1009CR_2+0.1039CR_4$	−0.17
$\psi_{\mathrm{EX.\,I}}=0.9710Y_1-0.04120\theta_\beta-0.1659CR_1$ $-0.0840CR_2-0.1301CR_4$	3.19
$\psi_{\mathrm{EX.\,II}}=-0.96720\theta_\beta+0.1625CR_2$ $-0.1752CR_4$	4.77
$\psi_{\mathrm{EX.\,III}}=0.1739Y_1-0.5138Y_2-0.59520\theta_\beta$ $-0.20070\theta_{\mathrm{p}}+0.12060\theta_\alpha-0.3914CR_1$ $-0.2364CR_2-0.2915CR_3$	5.80

a) Γ = Ground configuration, Y_1-Y_4 excited states on subsystem A, θ's excited states on subsystem B, *CR*'s charge resonance functions. b) The conformer IIa. c) The conformer IIb.

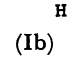
are given in Table 4. The electronic states of the planar conformers, IIa and IIb, of *N*-(2-furylmethylene)aniline were calculated by considering the following interactions between (i) the CI state function of subsystems (A) and (B); (ii) the CI state functions of the subsystems and charge transfer configurations where an electron transfers from (A) to (b) or from (B) to (A); (iii) the ground state and the charge transfer configurations. The results are listed in Table 5.



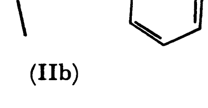
(Ia)



(IIa)



(Ib)



(IIb)

The oscillator strength was calculated from the equation

$$f = 2.085 \times 10^{-5} M^2 \bar{\nu},$$

where M is the electric dipole transition moment and $\bar{\nu}$(cm^{-1}) is the wave number of the electronic transition. The moment, $\vec{M}$, was calculated from the equation

$$\vec{M} = \langle \psi_0 | \hat{M} | \psi_{\mathrm{E}} \rangle,$$

where ψ_0 and ψ_{E} are the ground and excited state wave functions respectively. In the molecule-in-molecule procedure the wave functions have the forms:

$$\psi_0 = a\Gamma + \sum_n b_n T_n,$$

$$\psi_{\mathrm{E}} = \sum_n C_n A_n + \sum_{n'} d_{n'} T_{n'} + e\Gamma,$$

Table 6. Calculated and observed transition energies and oscillator strengths

Compound	Transition energy/eV		Oscillator strength	
	Calcd	Obsd	Calcd	Obsd
cis-*N*-(2-Furylmethylene)-methylamine[a)]	4.94		0.15	
	6.21		0.27	
	7.63			
		4.70		0.33
trans-*N*-(2-Furylmethylene)-methylamine[b)]	3.37		0.01	
	6.10		0.08	
	7.64			
cis-*N*-(2-Furylmethylene)-aniline[c)]	4.90		0.17	
	5.09		0.10	
	6.00			
		3.90		0.51
		4.40		0.64
		5.44		
trans-*N*-(2-Furylmethylene)-aniline[d)]	3.36		0.01	
	4.94		0.08	
	5.97			

a) The conformer Ia. b) The conformer Ib. c) The conformer IIa. d) The conformer IIb.

where Λ_n is the *n*th excited state function of the subsystem and T is the charge transfer state function. In the ZDO approximation

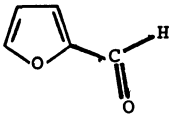
$$\langle\psi_0|\hat{M}|\psi_{\mathrm{E}}\rangle = a\sum_{n}\langle\Gamma|\hat{M}|\Lambda\rangle+\sum_{n}\sum_{n'}b_n d_{n'}\langle T_n|\hat{M}|T_{n'}\rangle.$$

The first term was calculated by the usual procedure and the second term was zero unless $n=n'$.

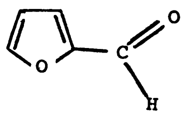
(IV) Comparison with Experimental Results: Table 6 shows comparison of theoretical results with the experimental data. For *N*-(2-furylmethylene)methylamine the correspondence between the theoretical computation using conformer Ia and the experimental results is quite satisfactory. The computed transition energies of 3.36, 4.94, and 5.97 eV favour conformer IIb for *N*-(2-furylmethylene)aniline. Computations on conformer IIa predict the presence of two overlapping transitions in the region of 5.0 eV (at 4.90 and 5.09) and two overlapping transitions in the region of 6.0 eV (at 6.0 and 6.02). Experimentally three transitions were observed at 3.90, 4.40, and 5.44 eV.

Discussion and Conclusion

Many studies have been reported on the electronic structure of the rotational isomers of furfural but none has been reported on *N*-(2-furylmethylene)methylamine. Infrared spectra[24)] show the presence of two carbonyl absorption bands corresponding to two conformers. On the other hand dipole moment measurements[8)] indicate that at room temperature the mixture of the two conformers contains mainly conformer IIIa. The low temperature NMR spectra[25)] indicate that conformer IIIb is energetically favored. The IR spectrum of furfural has been interpreted on the basis that at room temperature conformer IIIa is predominant in carbon tetrachloride.[24)] Calculations by the PPP-CI and DelRe method[26)] of the dipole moments have provided no reason to conclude, as shown previously,[15,26)] that conformer IIIa of furfural is predominant at room temperature.



(IIIa)



(IIIb)

Molecular orbital calculations performed in this work were not *ab initio*, yet some important results were obtained. It was proved that *N*-(2-furylmethylene)-methylamine exists mainly as conformer Ia (oxygen and nitrogen atoms are in the same side).

Molecular orbital calculations on *N*-(2-furylmethylene)aniline were not yet reported. The calculated spectrum for conformer IIb agrees with the experimental data, rather than that for conformer IIa. Although the molecule is rather large, yet the adopted method was shown to be useful for conformational analysis. Figure 2b shows the electronic absorption spectra of the studied *N*-(2-furylmethylene)arylamines. Table 2 gives the numerical values of band maxima. It can be seen that solvent polarity slightly affects the band maxima indicating that the contribution of charge transfer configuration to the state functions is slight (Table 5). Conformer IIa may have a stronger dipole than IIb. Hence an electronic transition from one subsystem to the other would result in a significant change in dipole moment and consequently an apparent shift in the band maxima with solvent polarity. Such a spectral shift was not observed experimentally. It may be interesting to compare the wave functions of the excited states of conformers IIa and IIb of *N*-(2-furylmethylene)aniline (Table 5). For conformer IIa the form of the wave functions indicates extensive mixing between the states of the subsystems (θ's and Y's) to produce the electronic states of the composite molecule. On the other hand the extent of mixing of the states of the subsystems is slight for conformer IIb. Such situation leads to 'localized' transitions of either of the subsystems of the composite molecule. The interaction between the excited states of the subsystems and the charge transfer configurations lowers the transition energies in the composite molecule relative to those in the isolated subsystems. The results of this work indicate that conformer IIb is predominant for *N*-(2-furylmethylene)aniline.

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