A Molecular Orbital Treatment of the Electronic Spectra of Linear and Cross Conjugated Systems. Thienyl Phenyl Ketones and *N*-Thenylideneanilines

R. Abu-Eittah* and R. Hilal

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Cairo, Egypt

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The electronic absorption spectral measurements as well as MO calculations have been conducted on representatives of a cross conjugated system, thienyl phenyl ketones, and a linear conjugated system, *N*-thenylideneanilines. Results have proved that, although the two systems may be "π"-isoelectronic yet, their electronic spectra differ substantially. The nodal properties of the molecular orbitals of the two systems explain nicely their differences in conjugation. Steric factors play no roll concerning the differences in the spectra of the two systems.

The conformational analysis of composite molecules is a subject of increasing importance yet, the difficulties encountered in the experimental determination of their structure[1-3] turn the attention to the theoretical procedures. Most composite molecules possess a "complex-type" of orbital interactions[4] which are not treated explicity in most theoretical treatments; one such complicated interaction is the cross-conjugation[5] in these molecules.

The aim of the present investigation is to examine the effect of cross and linear conjugation on the electronic spectra of a series of typical composite molecules, namely, 2-thienyl phenyl ketones and *N*-thenylideneanilines.

Qualitative interpretation of the spectra of 2-thienyl phenyl ketone was reported by Koper and Boer[6,7] whereas the spectra of *N*-thenylideneanilines have not been investigated before, although they were synthesized and showed wide applicability.[8]

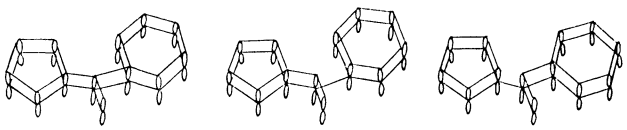
Experimental

Solvents and apparatus used are described before.[9] 2-Thienyl phenyl ketones were prepared by stirring thiophene and the appropiate aroyl chloride in the presence of anhydrous aluminum chloride at low temperature.[10] The mixture is then refluxed, cooled and poured on ice and extracted with ether. Vacuum distillation and crytallization from petroleum ether gave pure products with melting points identical to those reported.[10]

N-(2-Thenylidene)anilines were prepared by azeotropic condensation of thiophene-2-aldehyde with the corresponding aniline. The products were purified by vacuum distillation.

Results and Discussion

I. Electronic Absorption Spectra. (A) 2-Thienyl Phenyl Ketones: In the composite molecule 2-thienyl phenyl ketone, a competition is assumed to exist between the thienyl and phenyl moieties for conjugation with the carbonyl group. If the two moieties interact equally with the carbonyl group *e.g. via* both the resonance and electron repulsion integrals, then Conformer I will predominate and the electronic spectrum of the composite molecule should differ substantially from that of its subsystems. On the other hand, if one moiety enjoys greater overlap with the $2p_z$ orbital of the carbonyl carbon atom then conformers II or III will predominate. In the latter case the interaction of the phenyl ring with



I II III

the thienyl ketone (II) or the thienyl ring with the phenyl ketone (III) will be *via* electron repulsion terms only. Rotation about the sigma bond joining the two subsystems (in Conformers II and III) could lead to a nonplanar conformation for the composite molecule.

Figure 1 shows the electronic absorption spectra of 2-thienyl phenyl ketone, which consists mainly of two overlapping transitions. This spectrum is very much similar to that of 2-acetylthiophene indicating that the interaction of the phenyl group with the thienyl ketone group is not substantial. Consequently, Conformer II is a predominant one. If the phenyl ring aquires a plane perpendicular to the plane of the rest of the molecule, the n_0 electrons would be conjugated with the "π"

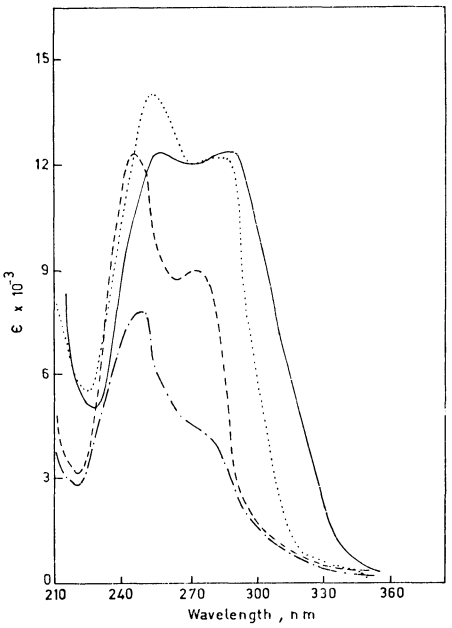


Fig. 1. Electronic absorption spectra.
——: 2-Thienyl phenyl ketone in ethanol, ·····: 2-thienyl phenyl ketone in cyclohexane, ----: 2-acetylthiophene in ethanol, -·-·-: 3-acetylthiophene in ethanol.

system of the benzene nucleus. This explains the absence of an n-π^* transition in the spectra of such a molecule.

To confirm the above results, the spectra of *p*-methoxyphenyl 2-thienyl ketone and *p*-nitrophenyl 2-thienyl ketone were investigated (Fig. 2). The spectrum of the *p*-methoxy derivative is slightly different from that of 2-thienyl phenyl ketone; bands are slightly red shifted and intensified. This effect is expected only if the phenyl ring is not planar with the rest of the molecule. The band at 220 nm most probably corresponds to the ^1L_a of the *p*-methoxyphenyl moiety.[11] Although the ionization potential of anisole[12] (8.4 eV) is less than that of thiophene (9.1 eV) yet, conjugation is still between the carbonyl group and the thiophene nucleus.

The spectrum of *p*-nitrophenyl 2-thienyl ketone (Fig. 2) is different in many respects from that of the parent compound. The first band appears at ≈294 nm (3000) and the second band at 252 nm (21000). These bands compare very well with the corresponding transitions of *p*-nitroacetophenone (297 nm (2300) and 258 nm (16000)). This leads one to suggest that in *p*-nitrophenyl 2-thienyl ketone conjugation extends on the nitro group, the benzene nucleus, and the carbonyl group. It is interesting to remember that this was not the case in either the unsubstituted ketone or in the *p*-methoxy derivative. Rationalization of these results is easily found when considering the symmetry properties of the molecular orbitals of the subsystems, which will be discussed in the next section.

In the case of 2-acetylthiophene, 2-thienyl phenyl ketone and *p*-methoxyphenyl 2-thienyl ketone, the band at 280 nm has a pronounced "charge-transfer" character indicating that in all of them the donor site is the same, *i.e.* the thienyl moiety. For the *p*-nitro derivative this band has a λ_{max} at 294 nm in cyclohexane and 303 nm in methanol indicating that the donor and acceptor sites are different.

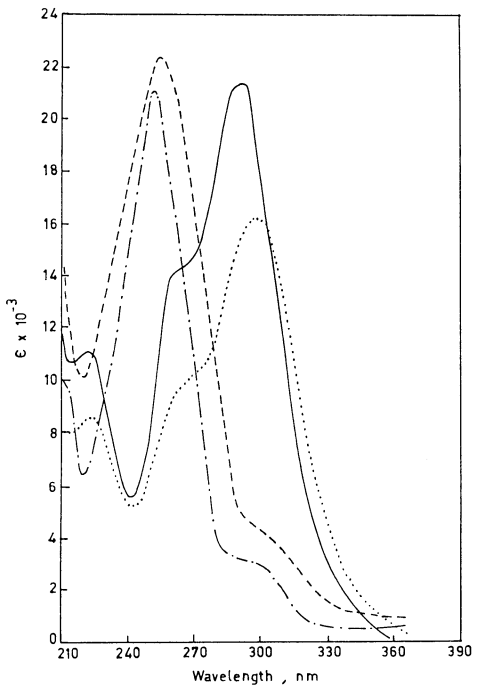


Fig. 2. Electronic absorption spectra.
——: *p*-Methoxyphenyl 2-thienyl ketone in methanol, ·····: *p*-methoxyphenyl 2-thienyl ketone in cyclohexane, ----: *p*-nitrophenyl 2-thienyl ketone in methanol, -·-·: *p*-nitrophenyl 2-thienyl ketone in cyclohexane.

Table 1. Band maxima and intensities of the studied thienyl phenyl ketones and thenyideneanilines in cyclohexane

Compound	λ_{max}, nm	ε, $m^{-1}\,cm^{-1}$	f
2-Thienyl phenyl ketone	279	12604	0.40
	252	14164	0.42
p-Methoxyphenyl 2-thienyl ketone	288	21452	0.58
	264	14133	0.36
	220	11104	0.39
p-Nitrophenyl 2-thienyl ketone	294	3000	0.05
	252	21170	0.55
N-(2-Thenylidene)-methylamine	273	6266	0.11
	255	9558	0.27
N-(2-Thenylidene)aniline	320	8489	0.22
	288	10033	0.32
	264	8682	0.23
	225	8872	0.28
o-Methoxy-*N*-(2-thenylidene)aniline	340	5829	0.15
	285	11830	0.30
	255	11629	0.39
p-Methoxy-*N*-(2-thenylidene)aniline	336	17018	0.47
	282	17673	0.52
	255	17345	0.52
o-Chloro-*N*-(2-thenylidene)aniline	324	7559	0.19
	288	13837	0.42
	266	13069	0.31
p-Chloro-*N*-(2-thenylidene)aniliee	330	12665	0.31
	294	12892	0.41
	264	11257	0.33
	226	9856	0.32
o-Nitro-*N*-(2-thenylidene)aniline	366	3977	0.09
	270	12263	0.23
	252	16240	0.45
	228	16240	0.57
p-Nitro-*N*-(2-thenylidene)aniline	320	10633	0.25
	282	7733	0.18
	256	6766	0.18

Table 1 gives the values of the molar extinction coefficients, band maxima and oscillator strengths of the observed transitions for the studied thienyl phenyl ketones in cyclohexane as a solvent.

(B) N-*(2-Thenylidene)anilines*: Thenylideneaniline is "π"-isoelectronic with 2-thienyl phenyl ketone. If the two compounds possess the same type of "π" conjugation their spectra would be similar. Comparison of Figs. 1 and 3 shows that this is not entirely the case, though the spectra of 2-acetylthiophene and *N*-(2-thenylidene)methylamine (Fig. 4) are very much similar. Consequently, there must be a substential difference in the degree of interaction of the phenyl group with the rest of the molecule in the two systems, 2-thienyl phenyl ketone and *N*-(2-thenylidene)aniline.

The features of the spectra of *N*-(2-thenylidene)aniline and *N*-(2-thenylidene)methylamine are completely different contrary to the case of 2-thienyl phenyl ketone

and 2-acetylthiophene. The spectrum of *N*-(2-thenylidene)aniline (Fig. 3) is characterized by the presence of overlapping transitions and consists mainly of two band systems whose intensities and positions vary in different ways as one goes from polar to nonpolar solvents. This suggests that they correspond to different electronic transitions. These results confirm a near planar structure for the thenylideneaniline.

The complications of the spectrum of *N*-(2-thenylidene)aniline makes it necessary to examine the spectra of some of its derivatives before any conclusion can be made. The spectra of *o*- and *p*-chloro, methoxy and nitro derivatives of *N*-(2-thenylidene)aniline are examined (Figs. 5—7). The general features of the spectra are similar to those of the parent compound. Substitution has perturbed all the observed transitions. Since the planar conformer is an adequate description of

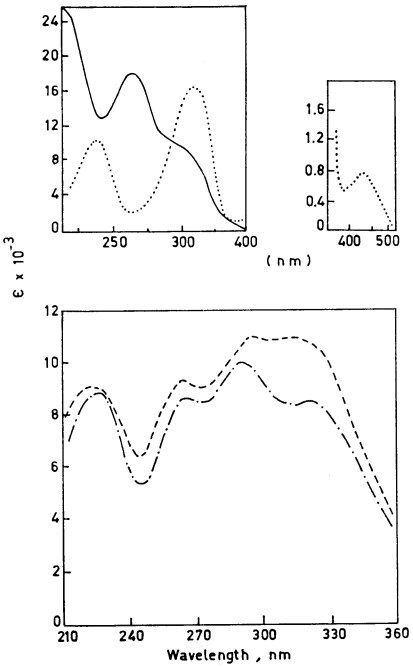


Fig. 3. Electronic absorption spectra of *N*-(2-thenylidene)aniline in methanol (----), cyclohexane (-·-·), and of *N*-benzylideneaniline in ethanol (——), azobenzene in 15% ethanol (·····).

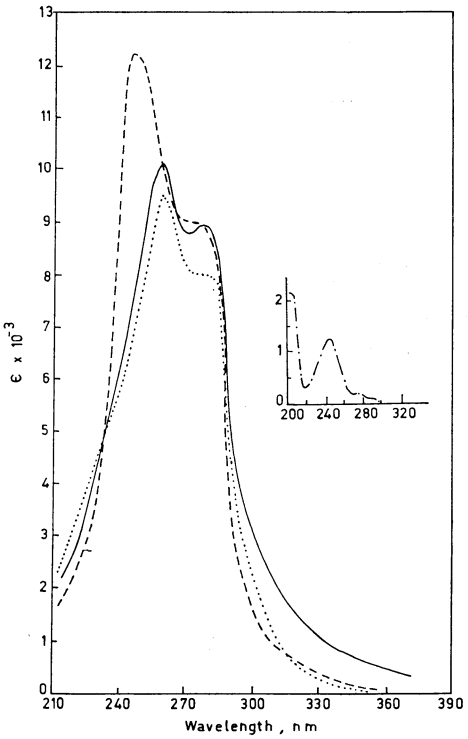


Fig. 4. Electronic absorption spectra of *N*-(2-thenylidene)methylamine in methanol (——) in cyclohexane (·····), and of 2-acetylthiophene in ethanol (----), benzylideneamine in ethanol (-·-·).

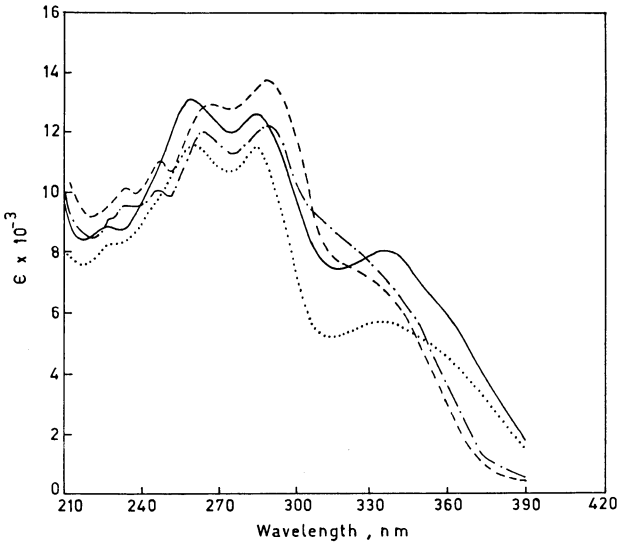


Fig. 5. Electronic absorption spectra of *o*-methoxy-*N*-(2-thenylidene)aniline in methanol (——), cyclohexane (·····), and of *o*-chloro-*N*-(2-thenylidene)-aniline in methanol (----), cyclohexane (-·-·).

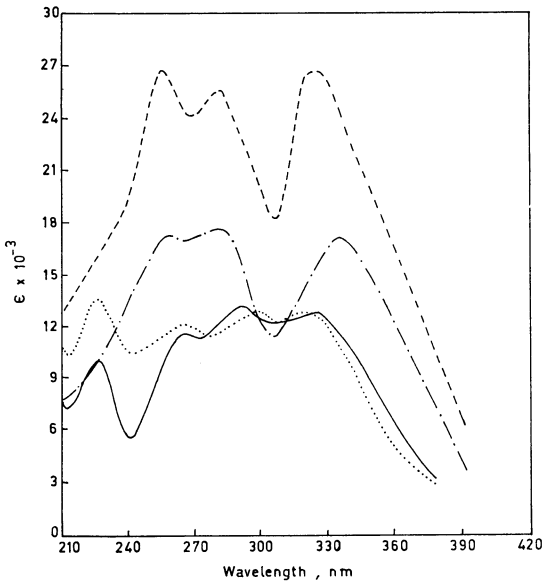


Fig. 6. Electronic absorption spectra of *p*-methoxy-*N*-(2-thenylidene)aniline in methanol (----), cyclohexane (-·-·), and of *p*-chloro-*N*-(2-thenylidene)-aniline in methanol (——), cyclohexane (·····).

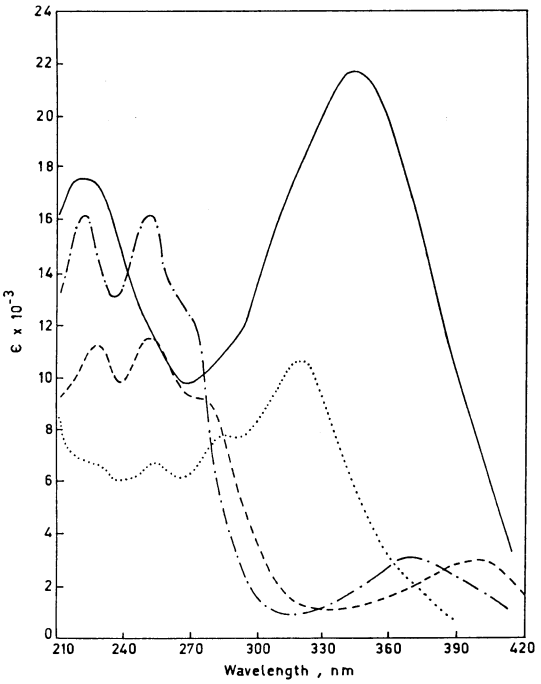


Fig. 7. Electronic absorption spectra of *o*-nitro-*N*-(2-thenylidene)aniline in methanol (----), cyclohexane (-·-·), and of *p*-nitro-*N*-(2-thenylidene)aniline in methanol (——), cyclohexane (·····).

thenylideneanilines; the observed bands correspond to transitions to "mixed-states" of the subsystems as well as a significant contribution of "charge-transfer" configurations.

II. Molecular Orbital Calculations. (A) 2-Thienyl Phenyl Ketone: The SCF wave functions of the molecule are determined assuming that the participation of the sulfur atom d-orbitals is trivial. The resonance integral terms are calculated using the relation[13]

$$\beta_{uv} = [S_{uv}/(1+S_{uv})][(I_u+I_v)/2]. \quad (1)$$

The electron repulsion terms are calculated using Nishimoto-Mataga[14] equation.

The self-consistent molecular orbitals of the composite molecule A-B are those of the separate constituents A and B. The extent of interaction between the two subsystems is determined by the value of the resonance integral β_{uv} and repulsion integrals γ_{uv} (atom u on A and atom v on B). The general expression for the interaction between two different singly excited configurations $^1\psi_{a-b}$ and $^1\psi_{c-d}$ is given by[15]

$$\langle {}^1\psi_{a-b}|\hat{H}|{}^1\psi_{c-d}\rangle = 2(cd|ab)-(ca|bd),$$

where $\hat{H}$ is the total Hamiltonian for the system.

Application to the Planar Conformer: The SCMO's of benzene are symbolized by the lower case letters (θ's), those of thienyl ketone by (y's). The corresponding states are symbolized by upper case letters (θ, Y). The singly excited states of benzene are

$$\Theta_\beta = (1/2)^{1/2}(\theta_3^{-1}\theta_4-\theta_2^{-1}\theta_5);\ \Theta_\beta = (1/2)^{1/2}(\theta_3^{-1}\theta_5+\theta_2^{-1}\theta_4),$$
$$\Theta_p = (1/2)^{1/2}(\theta_3^{-1}\theta_4-\theta_2^{-1}\theta_5);\ \Theta_\alpha = (1/2)^{1/2}(\theta_3^{-1}\theta_5+\theta_2^{-1}\theta_4).$$

For the 2-thienyl ketone the energies of the different configurations, $y_4^{-1}y_5$, $y_4^{-1}y_6$, $y_4^{-1}y_7$, $y_3^{-1}y_5$, $y_3^{-1}y_6$, $y_3^{-1}y_7$, are computed by the usual procedure[18] and the configuration interaction matrix of 2-thienyl ketone is solved. The form of the wave functions corresponding to the singly excited states of 2-thienyl ketone are available on request.

In the planar conformer the resonance integral β_{uv} is not zero and will mix together configurations which differ by the position of just one electron. The integrals to be evaluated are

$$\int \psi_o \hat{H}_{core}\psi_a^{-1}\psi_b \quad d\tau = (2)^{1/2}\int \psi_a(i)\hat{H}_i^{core}\psi_b(i)d\tau_i,$$
$$\int \psi_c^{-1}\psi_a\hat{H}_{core}\psi_c^{-1}\psi_b \quad d\tau = \int \psi_a(i)\hat{H}_i^{core}\psi_b(i)d\tau_i,$$
$$\int \psi_a^{-1}\psi_c\hat{H}_{core}\psi_b^{-1}\psi_c \quad d\tau = -\int \psi_a(i)\hat{H}_i^{core}\psi_b(i)d\tau_i.$$

The above integrals will be zero unless ψ_a belongs to one subsystem and ψ_b to the other. To calculate the electronic states of 2-thienyl phenyl ketone one has to consider the interaction between (1) ground state and "charge-transfer" states, (2) "charge-transfer" states to produce "charge-resonance" wave functions, (3) locally excited configurations and charge-resonance, and (4) locally excited configurations of the two subsystems.

To begin with, the charge-transfer (CT) configurations, $y_4^{-1}\theta_4$, $\theta_3^{-1}y_5$, $y_4^{-1}\theta_5$, $\theta_2^{-1}y_5$, are combined to produce the charge-resonance wave functions (CR's)

$$CR_I = (1/2)^{1/2}(\theta_3^{-1}y_5+y_4^{-1}\theta_4),$$
$$CR_{II} = (1/2)^{1/2}(\theta_3^{-1}y_5-y_4^{-1}\theta_4),$$
$$CR_{III} = (1/2)^{1/2}(\theta_2^{-1}y_5+y_4^{-1}\theta_5),$$
$$CR_{IV} = (1/2)^{1/2}(\theta_2^{-1}y_5-y_4^{-1}\theta_5).$$

The interaction terms between the fifteen different states, namely, the ground state, the four CR's, and the ten singly excited states localized on the two subsystems (Θ's and Y's) are computed (mathematical procedure is given before[16]). The interaction matrix is solved and the resultant energies and state wave functions of the ground and first three excited states are

		eV
(1)	$0.9855\psi_o-0.06226CR_I+0.05667CR_{II}$ $+0.1003CR_{III}$,	−0.137
(2)	$0.4948Y_1-0.5946Y_2+0.1434Y_3$ $+0.1958\Theta_\alpha+0.0480\Theta_P+0.0828CR_I$ $-0.4239CR_{II}+0.2136CR_{III}-0.3014CR_{IV}$,	3.375
(3)	$-0.7051Y_1-0.4095Y_2-0.3853\Theta_\alpha$ $-0.1499\Theta_\beta-0.1411\Theta_\beta-0.2313CR_I$ $-0.2094CR_{II}-0.3035CR_{III}-0.2796CR_{IV}$,	3.998
(4)	$0.1232Y_1-0.2018Y_2+0.0887Y_3$ $+0.6519\Theta_\alpha+0.1610\Theta_p+0.4835CR_I$ $+0.3205CR_{II}-0.1500CR_{III}-0.4319CR_{IV}$.	4.050

The calculated value 3.5 eV for the transition energy of the planar conformer of 2-thienyl phenyl ketone is significantly lower than the experimental one (4.4 eV). This is a strong evidence that either the planar conformer is a poor description of the molecule, or the molecule is planar but conjugation is not extending over the entire molecule. The spectrum of the molecule indi-

cates that conjugation extends only on the thienyl and carbonyl groups *i.e.* not including the benzene nucleus.

Application to the Perpendicular Conformer: The interaction between locally excited states Y's and Θ's is computed adopting the ZDO approximation. The matrix elements are computed for the ten states (six Y's and four Θ's) of 2-thienyl phenyl ketone. Solving this matrix, the energies and state wave functions are obtained. The first three are

	eV
(1) $-0.9985Y_1-0.0893\Theta_\alpha-0.0883\Theta_p$,	4.29
(2) $-0.9960Y_2+0.0862\Theta_\alpha+0.0127\Theta_\beta$,	4.59
(3) $0.0870Y_1+0.0870Y_2-0.1325Y_3$ $+0.9829\Theta_\alpha+0.0129\Theta_p$.	4.90

Comparison with experiment is postponed till we consider the "π"-isoelectronic *N*-(2-thenylidene)aniline.

(B) N-(2-Thenylidene)aniline. Computations are carried out in a similar way to that followed in the case of 2-thienyl phenyl ketone. Two conformers were considered, the *cis*- and the *trans*- planar ones. The numerical values of the parameters used are[17] (eV)

$$\alpha_C = -11.16;\ \alpha_N = -14.12;\ \alpha_S = -23.12,$$
$$\gamma_{CC} = 11.13;\ \gamma_{NN} = 12.34;\ \gamma_{SS} = 11.19.$$

The wave functions and the corresponding energies are given in Tables 2 and 3.

Comparison with Experiment: Table 4 compares the experimental and theoretically computed transition energies. For the 2-thienyl phenyl ketone values obtained for the perpendicular conformer agree satisfactorily with the experimental ones. On the other hand, planar conformers are good description for the *N*-(2-thenylidene)anilines with the *trans*-configuration nearer to reality than the *cis*-one.

Table 2. State function and energy of the ground and first four excited states for the *cis*-conformer of *N*-(2-thenylidene)aniline

	eV
(1) $0.9901\phi_0+0.0212CR_I-0.0672CR_{II}$ $-0.0702CR_{III}-0.0958CR_{IV}$	−0.112
(2) $-0.8659Y_1+0.1290Y_2-0.2432\Theta_\alpha$ $+0.1950\Theta_\beta+0.1433\Theta_\beta-0.1736CR_I$ $+0.1383CR_{II}+0.2249CR_{III}$	3.835
(3) $0.2761Y_1+0.1697Y_2-0.1203Y_3$ $-0.0138Y_6-0.8735\Theta_\alpha-0.3172CR_I$ $+0.0780CR_{III}+0.0878CR_{IV}$	4.814
(4) $-0.1450Y_1-0.7916Y_2-0.1443Y_3$ $-0.1580\Theta_\alpha-0.3897\Theta_\beta-0.1788\Theta_\beta$ $+0.1360\Theta_p+0.2567CR_{II}-0.1518CR_{III}$ $+0.1450CR_{IV}$	4.90
(5) $0.2037Y_2-0.7386Y_3+0.1011Y_4$ $+0.2305\Theta_\alpha+0.1477\Theta_p-0.2922CR_I$ $+0.1169CR_{II}-0.4364CR_{III}+0.1902CR_{IV}$	5.15

Table 3. State function and energy of the ground and first four excited states of the *trans*-conformer of *N*-(2-thenylidene)aniline

	eV
(1) $0.9902\phi_0+0.0199CR_I-0.0672CR_{II}$ $-0.0702CR_{III}-0.0960CR_{IV}$	−0.112
(2) $-0.8848Y_1+0.0656Y_2-0.1602\Theta_\alpha$ $+0.2161\Theta_\beta+0.1696\Theta_\beta+0.1103CR_I$ $+0.1614CR_{II}+0.1387CR_{III}+0.2239CR_{IV}$	3.811
(3) $0.1786Y_1+0.1815Y_2-0.1165Y_3$ $-0.9015\Theta_\alpha-0.2863CR_I+0.1165CR_{II}$	4.782
(4) $-0.1093Y_1-0.4472Y_2-0.6044Y_3$ $+0.0710Y_4-0.2660\Theta_\beta-0.0897\Theta_\beta$ $-0.2360CR_I+0.3119CR_{II}-0.3950CR_{III}$ $+0.1583CR_{IV}$	5.049
(5) $-0.7605Y_2+0.4093Y_3-0.2441\Theta_\alpha$ $-0.2451\Theta_\beta+0.1913CR_I+0.0865CR_{II}$ $+0.2790CR_{III}$	5.267

Table 4. Calculated and experimental transition energies of 2-thienyl phenyl ketone and *N*-(2-thenylidene)aniline

Compound	Transition energy, eV		*f*	
	Calcd	Obsd	Calcd	Obsd
2-Thienyl phenyl ketone				
perpendicular	4.29	4.42	0.31	0.40
	4.59	4.91	0.22	0.42
planar	3.51		0.06	
	4.13		0.11	
N-(2-Thenylidene)aniline				
cis-	3.95		0.04	
	4.92		0.33	
	5.01		0.65	
	6.26		0.09	
trans-	3.92	3.87	0.33	0.22
	4.87	4.30	0.29	0.32
	5.16	4.70	0.14	0.23
	5.38	5.51	0.07	0.28

Discussion and Conclusions

The spectra shown in Figs. 1 to 7 and the results of molecular orbital calculations (Table 4) indicate that, in 2-thienyl phenyl ketone, "π" conjugation does not extend over the entire molecule. This happens in two situations, (i) the phenyl ring lies in a plane perpendicular to that of the rest of the molecule, or (ii) the whole molecule is planar but the "cross-conjugation" behavior is pronounced; the net result would be the same. Drawing the molecules using Pauling atomic radii shows no sign of steric hinderance. Results at hand can not firmly differentiate between a perpendicular conformer and a planar "cross-conjugated" one. Also computations with a more sophisticated method would not be able to do so. Results of the theoretical treatment of 2-thienyl phenyl ketone shows a good agreement between the perpendicular conformer and the spectra. The wave functions of the excited states are merely those of either the thienyl ketone or the phenyl moieties of the molecule and mixing of states can be considered negligible.

Extensive interaction exists between the thienyl and phenyl groups with the azomethine group in the case

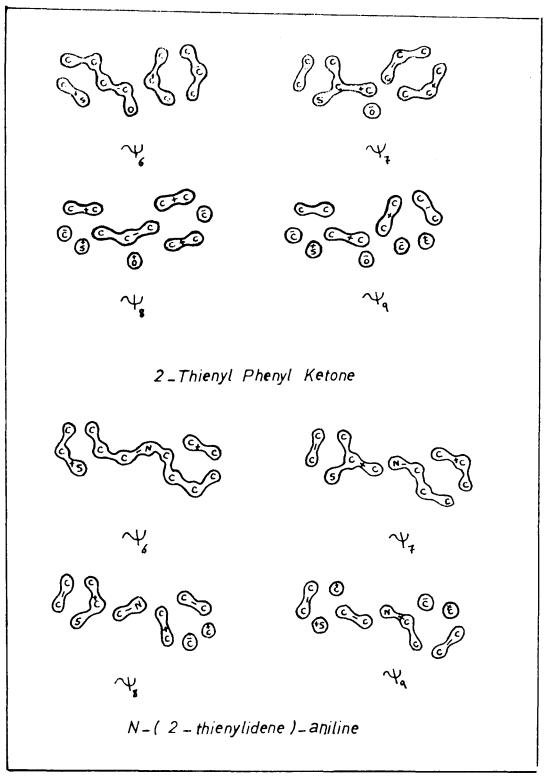


Fig. 8. The nodal properties of the highest two occupied and lowest two vacant MO's of 2-thienyl phenyl ketone and *N*-(2-thenylidene)aniline.

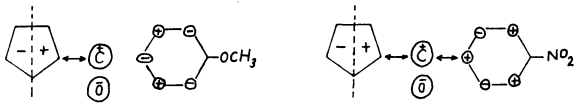


Fig. 9. The nodel properties of the highest two occupied and lowest two vacant MO's of 2-thienyl phenyl ketone.

of *N*-(2-thenylidene)anilines. Examination of Tables 2 and 3 indicates clearly that the wave functions of the excited states of the composite molecule represent mixed-states resulting from extensive interaction between the states of the two subsystems. As a result, the observed transitions can not be assigned to localized ones.

The cross-conjugation behavior is very nicely seen when considering the nodal properties of the molecular orbitals. Figure 8 represents the hieghest two occupied and lowest two vacant SCFMO's of 2-thienyl phenyl ketone and *N*-(2-thenylidene)aniline. Although a planar conformer is considered for both compounds with comparable resonance integrals yet, the antibonding character between the phenyl and carbonyl groups is pronounced in the molecular orbitals of 2-thienyl phenyl ketone as reflected in the values of the mobile "π"-bond order between the carbonyl carbon and the two competing moieties *i.e.* 2-thienyl and phenyl, which are 0.4100 and 0.1964 respectively. On the other hand, bonding character between the azomethine group and both the 2-thienyl and phenyl nuclei is pronounced ("π"-bond orders are 0.3324 and 0.2980 respectively). Hence, classification of the two compounds as cross and linear conjugated ones is reflected quite well in their electronic properties.

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