Tetrahedron Vol. 37, No. 21, pp. 3627 to 3634, 1981
Printed in Great Britain

0040-4020/81/213627-08$02.00/0
Pergamon Press Ltd.

LOW ENERGY EXCITED SINGLET STATES OF SOME MONOPHENYL SUBSTITUTED 5-MEMBERED HETEROCYCLES AND THEIR PHOTOISOMERIZATION

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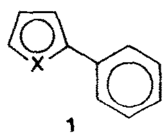
(*Received in the UK* 29 *April* 1980)

Abstract—The two low-lying singlet excited states of 14 mono-phenylated 5-membered heterocycles have been studied with respect to their energy level ordering, the oscillator strengths of the pertinent transitions, the state wave functions and the one-particle density matrices. Two types of lowest energy singlet states could be revealed by means of the configuration analysis (CA) and the similarity analysis (SA). One state (labelled "state A") is characterized by a delocalization over the whole π system, whereas the other (labelled with "state B") is locally excited at the phenyl moiety. An attempt is made to link this classification with the different photoisomerization pathways of the title compounds.

The light-induced rearrangement of conjugated heterocyclic 5-membered ring compounds is a vast field in modern photochemistry.[1,2] Mono-phenylated five-membered heterocycles **1**–**4** photoisomerize as shown in Scheme 1:[3]



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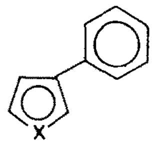
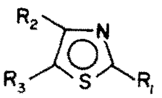


2

1a, 2a: X = S
1b, 2b: X = O
1c, 2c: X = Se
1d, 2d: X = Te



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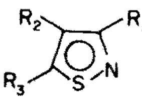
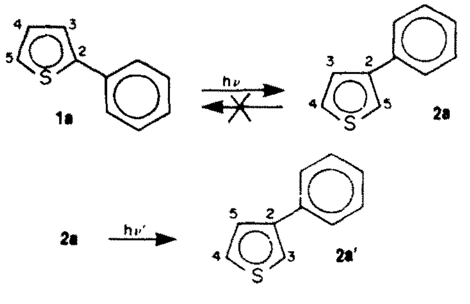


4

3a: $R_1 = Ph$, $R_2 = R_3 = H$ **4a**: $R_1 = Ph$, $R_2 = R_3 = H$
3b: $R_2 = Ph$, $R_1 = R_3 = H$ **4b**: $R_2 = Ph$, $R_1 = R_3 = H$
3c: $R_3 = Ph$, $R_2 = R_1{}^3 = H$ **4c**: $R_3 = Ph$, $R_1 = R_2 = H$



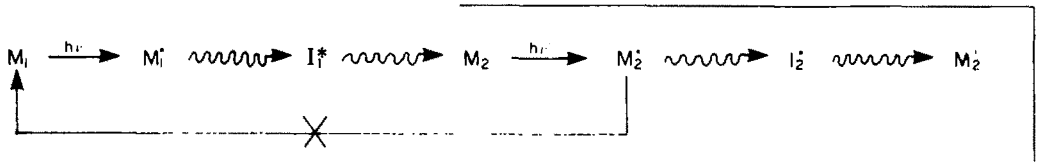
The most interesting detail of this photoisomerization is the irreversible character of the reaction. Thus, being irradiated at the long wavelength absorption band, **1a** is transformed into **2a** with a high quantum yield, whereas irradiation of **2a** has seemingly no photochemical consequences and no traces of **1a** can be isolated.[3,4] Only by means of the deuterium labelling technique combined with a detailed analysis of the NMR spectra could the scrambling of carbon atoms within the five membered ring of excited **2a** be detected.[5] However, all geometrical inversions of **2a** in its excited state lead by chance back to the initial structure **2a**. Therefore, the term "no-reaction reaction" has been introduced for describing this case.[5] A quite similar behaviour is shown by the mono-phenylated thiazoles **3** and isothiazoles **4**. Here **3b** and **4b**, together with smaller amounts of **4a**, all of which can be considered to be azaanaloga of **2a**, are the terminal products after the photochemical rearrangement of all the isomers of **3** and **4**.[6–12]

Although detailed investigations about the photochemistry of alkylated and diarylated furans have been carried out (see Ref. 1 and references therein and[13]) no information about isomerization of the monophenylated furans **1b** and **2b** could be found in the literature.

2-Phenylselenophene **1c** shows a similar photochemical behaviour as **1a** and undergoes into **2c**, however a competitive photoreactive channel provides elimination of selenium and formation of styrylacetylene. The latter process becomes dominant in the case of the tellurium compounds **1d** and **2d**.[14]

There have been several attempts to interpret the mechanism of these photoisomerizations. From the experimental point of view, the labelling technique with ^{2}H and ^{14}C ensured that the photorearrangement results from drastic geometrical changes within the five membered ring but not from migration of the phenyl fragment.[4,5] Furthermore, quenching experiments with piperylene revealed that the reaction starts from an excited singlet state.[15] After some previous ideas[16] van Tamelen gave the first comprehensive mechanistic model for the molecular rearrangement of conjugated five-membered ring heterocycles[17] based on former suggestions about the irradiation-induced conversion of benzenoid compounds into valence bond Dewar isomers.[18] This general model has been completed and improved by Kellogg, who considered the reaction to lead via intermediates of tight non-planar geometry with antiaromatic $\pi 4_a + \pi 2_s$ character.[19] Following the recent model considerations on photochemical reactions this might indeed represent a stable geometrical situation on the singlet excited potential surface.[20]

Going back to the irreversible rearrangement of singlet excited **1a** into **2a** and the no-reaction reaction of the latter we can conclude (in agreement with the assumption in Ref. 19) that intermediates of different spatial geometry are involved in the photoisomerizations of **1a** and **2a**, respectively. In this connection the question arises whether these different intermediates are also connected with excited states of different character. The crossing of excited states, say S_1 and S_2, during the photoisomerization of **1a**→**2a**→**2a′** seems to be the logical consequence of the irreversible character and the unequivocal course of this photorearrangement. Thus, following this hypothesis, the character of the excited state after a vertical excitation might become representative and decisive for the structure of the intermediate and might play a determining rôle for the course of the reaction, even if the initial geometry is drastically changed along the reaction coordinate. A schematic representation of the irreversible photoisomerization of a molecule M_1 into M_2 via the intermediate I_1^* has then the following form:



The suggestion that excited states of different character are involved in the photoisomerization of **1a** and **2a** was first offered by Wynberg.[4] However, no methods of characterizing excited states having no particular symmetry have been available so far.

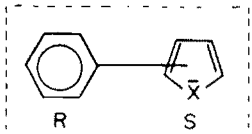
Recently, interpretative methods for the wavefunctions and the charge-bond order matrices have been developed and used to a greater extent to analyze different electronic states and electronic transitions of conjugated compounds.[21] This has been performed by means of comparison with equivalent magnitudes of suited iso-π-electronic reference states. Among these procedures the configuration analysis (CA)[22] and the similarity analysis (SA)[23] particularly enable one to describe the character of ground and excited states of conjugated molecules.

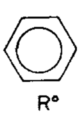
It is the purpose of this paper to check both methods for the mono-arylated five-membered ring heterocycles **1–4** in order to contribute to the mechanistic problem of their photoisomerization by analyzing their initial reactive excited states.

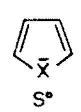
Particularly, the following issues should be tackled: (i) The character of the lowest energy singlet states will be investigated by means of CA and SA. The results of both methods will be compared and their equivalence will be established. Special attention will be paid to the localization of excitation energy in special molecular subunits of the systems **1–4**. (ii) The results obtained will be discussed in correspondence to the photoisomerization of these compounds and an attempt at classification will be made. (iii) The possibility of governing the photochemical behaviour of similar compounds by introducing substituents both in the phenyl ring and the heterocycle will be tested.

Model and methods

The molecular systems **1–4** can be imagined to consist of the two building blocks R and S which are iso-π-topological to the uncoupled reference molecules R^0 (benzene) and S^0 (five-membered ring).




R°



S°

Based on these subunits the ground state of R–S can be expressed by a no bond structure accompanied by a charge transfer term indicating the extent of coupling between R and S.

Among the excited states of R–S the following prototypes can be distinguished: (i) a delocalized excitation over the whole π system without considerable redistribution of charge; (ii) a delocalized excitation accompanied by a charge transfer from R to S or *vice versa*; (iii) a localized excitation within one of the fragments R or S. The CA and SA analyses provide quantitative estimation for a certain molecular excited state to approach to one of the three extreme cases.

Therefore, the two lowest excited singlet states of all molecules mentioned above have been checked in respect to the localization of the excitation within the fragments R or S. In order to link the results with the photochemical behaviour of the systems studied, we assume that the different reaction pathways (see Scheme 1) are caused by excited states of different character.

The configuration analysis originally proposed by Baba *et al.* and applied for new examples by Fabian has been described more detailed in Refs. 24 and 25 and can therefore be characterized very briefly.

The electronic wavefunction of the state I, $\Psi(I)$, can be expressed by the product of the transformation matrix **M** and the linear combination of the wavefunctions $\Psi^0(J)$ characterizing the electronic states J of the reference system

$$\Psi(I) = \mathbf{M}\Psi^0(J) \qquad (1)$$

M can be derived from the transformation matrix of the MO's and the eigenvector matrices of the configuration interaction for both the system under study and the reference system. If we define wavefunctions $\Psi^0(J)$ to be basis functions of the subunits R^0 and S^0 the squared elements of the **M** matrix, $m^2_{I,NB}$, $m^2_{I,A}$ and $m^2_{I,CT}$ represent the weights of the no bond configuration, the local excited configurations and the charge transfer configurations respectively, which describe state I of the molecule investigated. Consequently, if state I can be, for example, overwhelmingly expressed by a state J being traceable to a local excitation within the subsystem R^0 or S^0, $m^2_{I,A}$ represents the local character of the excited state I within the molecular region R or S.

The principle of similarity analysis was described in Ref. 23. The similarity of electronic structures belonging to the system under study in its state I and the reference system in its state J is based on a truncated Euclidean distance function, d(I, J),[26] of the charge-bond order matrices **P**(I) and **P**(J):

$$d(I,J) = \left[\sum_{\substack{\mu>\nu \\ \mu,\nu\in R}} (P_{\mu\nu}(I) - P^0_{\mu\nu}(J))^2\right]^{1/2}. \qquad (2)$$

From (2) the similarity s(I, J) of the two electronic structures can be derived either to:[21]

$$s(I,J) = [1 + d(I,J)]^{-1} \qquad (3)$$

or[27]

$$s(I,J) = \exp\cdot[-1.61\, d^2(I,J)]. \qquad (4)$$

The relations (3) and (4) provide completely equivalent results. In this paper (3) will be used.

Following this general connection, we can define an index of partial similarity between the electronic structures of the fragments R and S with those of the corresponding reference system R^0 and S^0, where the partial distance functions $d_R(I,J)$ become

$$d_R(I,J) = \left[\sum_{\substack{\mu>\nu \\ \mu,\nu\in R}} (P_{\mu\nu}(I) - P^0_{\mu\nu}(J))^2\right]^{1/2} \qquad (5)$$

and the partial similarities $s_R(I,J)$ are defined such as in eqn (3).

A high similarity of the excited electronic substructures of the subsystem R and the reference system R^0 can be considered to be an equivalent of a localized excited state.

Although derived on different mathematical framework $m^2_{I,A}$ and $s_R(I,J)$ reflect the situation of a localized excitation in a corresponding way.

The wavefunctions and charge-bond order matrices needed for both kinds of state analysis have been obtained from PPP calculations. The core parameter and resonance integrals had been proposed in a previous paper.[28] The Mataga–Nishimoto formula served for the approximation of the two centre gamma integrals. The geometry of the system was defined to be idealized (all lengths 1.40 Å, regular polygons), except the bond distance for C–S, S–N, C–Se, and C–Te which have been assumed to be 1,7, 1.7, 1.85 and 2.05 Å, respectively.

RESULTS AND DISCUSSION

The variety of the transition energies for the different molecules **1–4** is not very high and a complete collection of all data can be omitted for the sake of brevity. Figure 1 demonstrates for the compounds **1a** and **2a** a good fitting of the theoretical results and experimental spectral curves. It can be noticed from Fig. 1 that the long wavelength absorption band of **1a** and **2a** contains two transitions of different oscillator strengths leading to different excited states. The first transition is of high intensity and leads to an excited singlet state labelled with A furthermore; the second one is weak and the resulting excited state will be assigned to the notation B. It can be seen from Fig. 1 that the sequence of both transitions leading to A and B, respectively, is reversed in going from **1a** to **2a**. This will be discussed below.

In order to characterize the ground state and the two excited singlet states having the lowest energy, the CA and SA analyses were carried out for the molecular structures **1–4**. As reference system the uncoupled substructures R^0 and S^0 were used. The values obtained for $m^2_{I,NB}$, $m^2_{I,A}$, $m^2_{I,CT}$ and $s_R(I,J)$, with $I = 0, 1, 2$, are put together in Table 1.

Let us first discuss briefly the results of the CA and SA technique. From Table 1 it can clearly be seen that the ground state can be described mainly by a no bond structure of R and S. This corresponds convincingly to the close similarity of the phenyl π electronic structure with that of the benzene molecule. These equivalent results suggest mono-phenylated five-membered ring heterocycles to be consisting of two weakly coupled

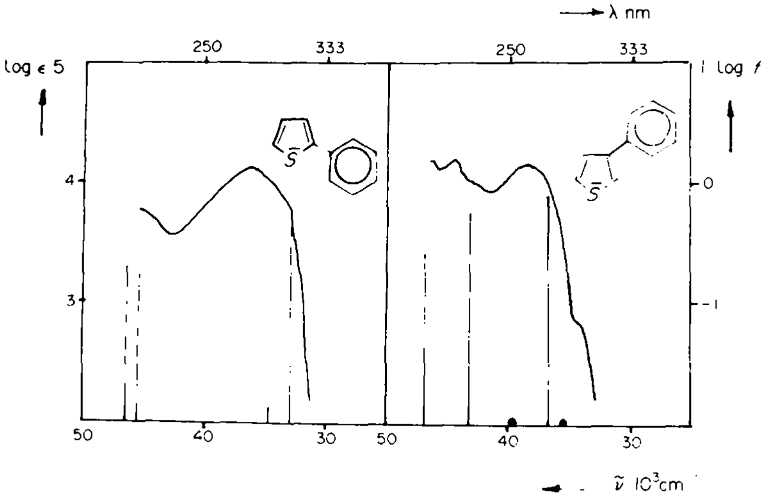


Fig. 1. Electronic spectra of 2-phenylthiophen **1a** and 3-phenylthiophen **2a**[29] with transition energies obtained by PPP calculations.

Table 1. Results of the CA and the SA analyses for the three low-energetic singlet states (S_0, S_1 and S_2) of the compounds 1–4

Compound	configuration analysis [a]											similarity analysis [a]		
	S_0	S_1					S_2					S_0	S_1	S_2
	m^2_{NB}	$m^2\Lambda_R$	$m^2\Lambda_S$	$m^2CT_{S\rightarrow R}$	$m^2CT_{R\rightarrow S}$	Type	$m^2\Lambda_R$	$m^2\Lambda_S$	$m^2CT_{S\rightarrow R}$	$m^2CT_{R\rightarrow S}$	Type	$s_R(0,0)$	$s_r(1,1)$	$s_R(2,2)$
1a	87	-	43	26	11	A	60	-	21	-	B	93	72	86
1b	88	-	42	29	11	A	65	-	18	-	B	94	72	88
1c	87	-	45	23	12	A	61	-	19	-	B	94	73	88
1d	86	-	50	16	-	A [b]	-	42	17	10	A	93	73	74
2a	89	70	-	9	-	B	14	26	16	11	A	95	89	72
2b	90	75	-	7	-	B	31	11	29	-	A	95	92	71
2c	89	70	-	9	-	B	11	30	12	15	A	95	90	74
2d	89	-	64	13	-	A	62	-	9	-	B	95	74	86
3a	87	-	44	36	-	A	63	-	16	-	B	94	73	90
3b	89	70	-	10	-	B	-	42	24	-	A	95	89	72
3c	87	-	44	24	13	A	62	-	19	-	B	94	73	86
4a	89	71	-	9	-	B	-	28	13	15	A	95	85	75
4b	89	72	-	10	-	B	19	15	27	-	A	95	91	74
4c	87	-	33	25	-	A	62	-	15	-	B	94	73	88

[a] All values in %.

[b] This state is higher in energy for all other compounds.

subunits phenyl (R) and heterocyclic ring (S). The wavefunction and the derived charge-bond order matrix of a subunit, say R, is only slightly perturbed by the presence of S and *vice versa*.

This picture will be considerably modified in the excited states. To begin with we notice only two different kinds of excited states holding through all the compounds considered. (except **1d** see below).

The excited state A caused by the intensive transition is denoted in the CA by a considerable contribution of a local excitation in S accompanied by large charge transfer terms indicating a highly delocalized excited state. In contrast to the ground state the coupling between the two subunits must be considered to be very strong. This is also reflected in the relatively low similarity indices demonstrating a serious deviation of the π electronic structure within the excited subunit R from that of excited benzene.

The excited state B shows quite a different characteristic. Here an overwhelming contribution of a term $m^2_{i,AR}$ indicating a local excitation within the phenyl fragment R has been found, accompanied by a smaller charge transfer term. In good accordance with that, the π electronic structures of the excited phenyl part and that of excited benzene are close to each other in this state. It can be concluded therefore that B is satisfactorily described as an excited state attributed originally from the L_b-transition of benzene. This could be confirmed for **1a** and **2a** by "molecules in molecule (MIM)" calculations.[30]

Summarizing this part we can conclude that the CA and SA methods provide consistent results for all compounds **1–4**, revealing two kinds of excited states, A and B, the character of which has been found to be completely different.

Let us turn to the energy of A and B. In Fig. 2 the sequence and energy differences between the two

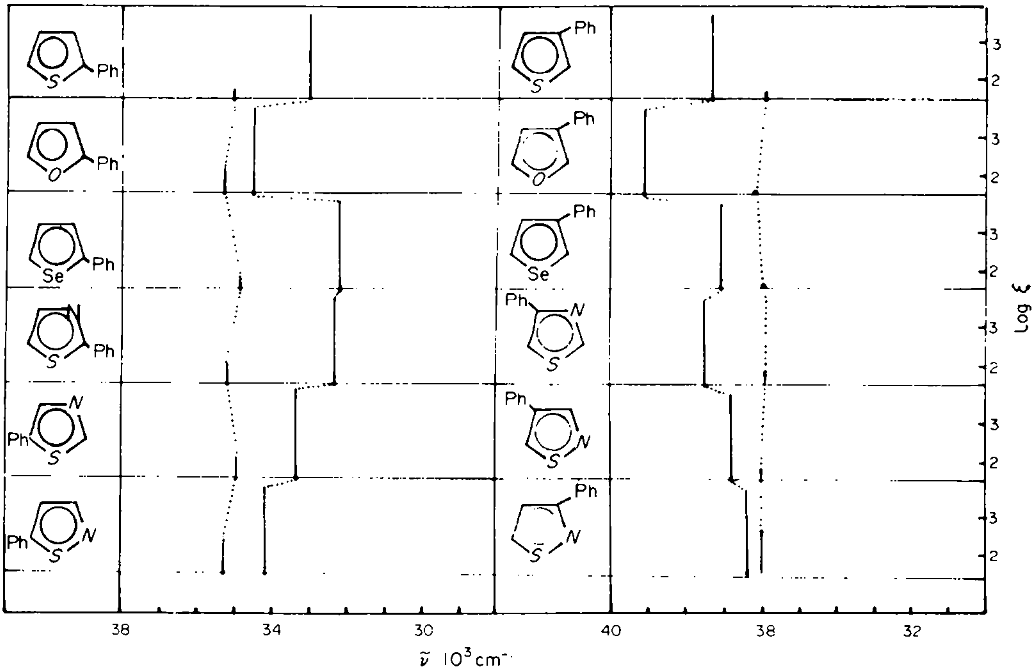


Fig. 2. Level sequence A–B as a function of topology.

Table 2. Classification of mono-phenylated five-membered rings in respect to the sequence of their excited states A and B

Group **1**	Group **2**	Group **3**
The lowest excited singlet state is of the type A being delocalized over the whole π-system: **1a**, **1c**, **1d**, **2d**, **3a**, **3c**, **4c**	The lowest excited singlet state is of the type B being mainly localized at the phenyl moiety: **2a**, **2b**, **2c**, **3b**, **4a**	The states A and B have nearly the same energy. The compounds can belong either to group 1 or to group 2 **1b**, **4b**

excited states of A and B can be observed. The sequence of A and B is clearly dependent on the topology and the heteroatoms in the five-membered ring.

Decrease of the heteroatom core integral and increasing overlap between the heteroatom and the adjacent ring carbon atoms cause a diminution of the energy gap $\Delta E(B-A)$. Thus, whereas in the case of **1a** A has the lowest energy ($\Delta E(B-A) = 0.1762$ eV), replacement of sulphur by oxygen in **1b** contains the possibility of a sequential inversion ($\Delta E(B-A) = 0.0932$ eV with $\beta_{CO} = -2.318$ eV and -0.0649 eV with $\beta_{CO} = -2.666$ eV). On the other hand, heteroatoms with low ionization potentials and weak ability to overlap favour a stabilization of the A state. The effects of the heteroatoms are superimposed by the influence of the topology. Compounds **1b–1d**, **3a**, **3c**, and **4c** can be regarded as iso-π-topologic to **1a**, whereas **2a** can be considered to be the parent compound for **2b–2d**, **3b**, **4a**, and **4b**. In the first group of compounds the delocalized A state is favoured and has the lowest energy of all excited singlet states. Only in the case of **1b** might the sequence be inverse. In the second group the B state being predominantly localized at the phenyl subunit is the excited singlet state with the lowest energy. The only exception is **2d** due to the dominating effect of the heteroatom. Furthermore, the gap becomes extremely small in the case of **4b** and the inverse order of states cannot completely be excluded. Recent experimental findings even revealed that in contrast to all other mono-phenylated S–N heterocycles this compound should isomerize via a triplet state (Ref. 180 g in Ref. 1). Summarizing the results, the compounds under study can be subdivided into three groups as pointed out in Table 2.

This is the point at which to bridge the results of the two analytical methods and the photochemical behaviour of the compounds. All molecules belonging to group 1 undergo a light-induced irreversible photoisomerization into the compounds belonging to group 2. The only exception is **1d** which obviously uses a special competitive reaction channel eliminating tellurium under irradiation.[14] The compounds of the latter group remain seemingly unchanged by light within the framework of a no-reaction reaction. The molecules of group 3 are borderline cases. Whereas the photochemical behaviour of **1b** is obviously unknown **4b** is formed as a relatively stable isomerization product from **3a** and **4c** supporting the level sequence obtained, but further irradiation transfers it into **3b**.[6]

Although the analysis of spectroscopic states does not provide any information about the course of the photoreaction and the character of occurring intermediates, it obviously enables one to systematize the photoreactive behaviour of this class of compounds based on the electronic structures of the initial photoreactive states. It seems therefore that the "fate" of the excited molecule within its radiationless deactivation process, specifically for the class of compounds studied, is strongly determined by the character of the initial reactive excited state. If there exists a crossing of $\pi\pi^*$ electronic states, the photoisomerization becomes irreversible; if no crossing occurs, then no-reaction reaction is preferred.

Figure 3 shows a first qualitative proposal for a state correlation diagram. Because our quantum chemical investigations are carried out in the π approximation the energies of the ground state and the higher excited $(\sigma\sigma^*)^2$ state playing an important rôle for the nonplanar photointermediates are arbitrarily assumed.

Considering the left hand side of the diagram the irreversible character of the photoisomerization should be the more pronounced the greater the energy gap between A and B, the more shanted the potential curve is inclined towards the geometry of the photoproduct and the higher the intermediate I_1^* is stabilized in respect to the initial reactive state. The probability of a no-reaction reaction is not influenced by a barrier within the $\pi\pi^*$ states but only by the tendency of the system to form the intermediate I_2^*.

It would be interesting to investigate if, for the compounds **1–4**, a sequential inversion of A and B could be governed by solvent effects or the introduction of photoinactive substituents. In this way, the modified system could be induced to change its photoreactive channel, being a sound proof of our assumptions. However, the solvent effect was estimated as small for every state and no remarkable energetic shift can be expected by varying the solvent. The introduction of new substituents in the R as well as in the S part of all systems completely

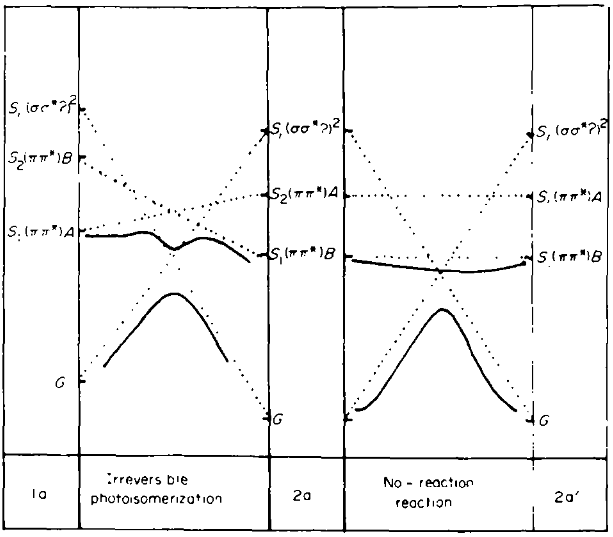
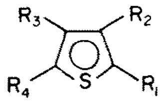


Fig. 3. Qualitative correlation diagram for the photoisomerization of mono-phenylated five-membered heterocycles.

Table 3. CA and SA results of some substituted thiophens (cf footnotes of Table 1)

Compound	configuration analysis a)							similarity analysis a)		
	S_0	S_1			S_2			S_0	S_1	S_2
	m^2_{NB}	$m^2\Lambda_R$	$m^2\Lambda$	$m^2CT_{S\to R}$	$m^2\Lambda_R$	$m^2\Lambda_S$	$m^2CT_{S\to R}$	$a_R(0,0)$	$a_R(1,1)$	$a_R(2,2)$
5	86	-	31	41	41	-	42	92	70	75
6	87	-	17	46	27	-	53	92	69	70
7	87	-	44	35	55	-	- 26	94	77	68
8	87	44	-	30	44	16	12	88	67	70
9	83	42	-	25	74	-	-	88	67	63

changes the character of the low lying excited singlet states (see compounds **5–9**). Due to large charge transfer contributions the states become delocalized and considerably different from A and B. Therefore other channels to deactivate their excited states become available and no prediction can be made within this rough model about the photochemical behaviour of the compounds **5** to **9** the CA and SA results of which are collected in Table 3. Discussing the values in Table 3 it should be emphasized that the modified fragmental parts R and S for **5–9** are weakly coupled in the ground state. However, the character of the excited states is so clearly distinguished from those of the compounds **1–4** that an analogue classification cannot be justified, although **7** and **9** were found to show a similar isomerization.



5: $R_1 = R_3 = OMe$; $R_2 = Ph$; $R_4 = H$
6: $R_1 = R_4 = OMe$; $R_2 = Ph$; $R_4 = H$
7: R_1 = Naphthyl; $R_2 = R_3 = R_4 = H$
8: R_1 = Styryl; $R_2 = R_3 = R_4 = H$
9: $R_1 = p-MeO-Ph$; $R_2 = R_3 = R_4 = H$

CONCLUSIONS

The analysis of different electronic states of monophenylated five-membered heterocycles can be performed equivalently by configuration analysis and the similarity analysis. The uncoupled π-systems of benzene (R^0) and the five-membered heterocycles (S^0) can be regarded as the appropriate reference systems.

Both methods describe the ground state as consisting of the weakly coupled sub-units and differentiate strongly between the two low lying excited singlet states. One of the latter is described as delocalized over the whole molecule whereas the other is found to be mainly localized at the phenyl moiety. The energetic order of both states depends on the molecular topology.

Based on the energetic sequence of the classified excited states the compounds considered can be subdivided in two main groups. The classification corresponds with the photochemical behaviour of these compounds.

Variation of the subunits R and S by introducing substituents results in a considerable change of the excited states electronic structure and does not allow an extended classification of their photochemical reactivity.

REFERENCES

[1] A. Lablache-Combier, *Photochemistry of Heterocyclic Compounds*, (Edited by O. Buchard). p. 123 ff. Wiley, New York (1976).
[2] A. Lablache-Combier and M. A. Remy, *Bull. Soc. Chim. France* 679 (1971).
[3] H. Wynberg and H. van Driel, *J. Am. Chem. Soc.* **87**, 3998 (1965).
[4] H. Wynberg, H. van Driel, R. M. Kellogg and J. Buter, *Ibid.* **89**, 3487 (1967).
[5] R. M. Kellogg and H. Wynberg, *Ibid.* **89**, 3495 (1967).
[6] G. Vernin, J.-C. Poite, J. Metzger, J. P. Aune and H. J. M. Dou, *Bull. Soc. Chim. France* 1103 (1971).
[7] C. Riou, G. Vernin, H. J. M. Dou and J. Metzger, *Ibid.* 2673, 3157 (1972).
[8] G. Vernin, C. Riou, H. J. M. Dou, L. Bouscasse, J. Metzger and G. Loridan, *Ibid.* 1743 (1973).
[9] C. Riou, G. Vernin, J.-C. Poite and J. Metzger, *Tetrahedron* **30**, 879 (1974).
[10] M. Kojima and M. Maeda, *Chem. Comm.* 386 (1970).
[11] M. Ohashi, A. Ilo and T. Yonezawa, *Ibid.* 1148 (1970).
[12] G. Vernin, R. Jauffred, C. Ricard, H. J. M. Dou and J. Metzger, *J. Chem. Soc. Perkin II* 1145 (1972).
[13] A. Padwa and R. Hartmann, *J. Am. Chem. Soc.* **88**, 3759 (1966).
[14] T. J. Barton, C. R. Tully and R. W. Roth, *J. Organomet. Chem.* **108**, 183 (1976).
[15] R. M. Kellogg and H. Wynberg, *Tetrahedron Letters* 5895 (1968).
[16] H. Wynberg, R. M. Kellogg, H. van Driel and G. E. Beekhuis, *J. Am. Chem. Soc.* **89**, 3501 (1967).
[17] E. E. van Tamelen and T. H. Whitesides, *Ibid.* **93**, 6129 (1971).
[18] E. E. van Tamelen, *Angew. Chem.* **77**, 759 (1965).
[19] R. M. Kellogg, *Tetrahedron Letters* 1429 (1972).
[20] N. D. Epiotis, *Theory of Organic Reactions*. Springer Verlag, Berlin (1978).
[21] J. Fabian, A. Mehlhorn and F. Fratev, *Int. J. Quant. Chem.* **17**, 235 (1980).
[22] H. Baba, S. Suzuki and T. Takemura, *J. Chem. Phys.* **50**, 2078 (1969).
[23] F. Fratev, O. E. Polansky, A. Mehlhorn and V. Monev, *J. Mol. Struct.* **56**, 245 (1979).

[24] J. Fabian and G. Tröger-Naake, *Int. J. Quant. Chem.* **11**, 259 (1977).

[25] J. Fabian, *Chimia* **32**, 323 (1978).

[26] B. S. Duran and P. L. Odell, *Cluster Analysis, A Survey* (*Lecture Notes in Economics and Mathematical Systems*, 100). Springer Verlag, Berlin (1974).

[27] F. Fratev, V. Monev. A. Mehlhorn and O. E. Polansky, *J. Mol. Struct.* **56**, 255 (1979).

[28] J. Fabian, A. Mehlhorn and R. Zahradnik, *Theor. Chim. Acta* **12**, 247 (1968).

[29] L. Bruzzi, L. Degani and A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna* **19**, 40 (1961).

[30] J. Fabian and H. Keiper, *Wiss. Z. TU Dresden* **22**, 769 (1973).