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A SEMIEMPIRICAL LCAO MO SCF STUDY OF THE ELECTRONIC STRUCTURE OF PHOTOCHROMIC ANILS WITH A VARIABLE β APPROXIMATION

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Abstract—The semiempirical Pariser–Parr–Pople method with a variable β approximation has been applied to salicylideneaniline. The photochromic process is discussed on the basis of energy levels, bond orders and electron charges. In addition, the bond lengths have been computed.

INTRODUCTION

IT HAS been found[1-7] that salicylideneaniline undergoes a photochemical isomerization involving the displacement of an H atom and geometrical changes. A knowledge of the energy levels of the primary molecule and of the reaction products is necessary in order to understand the photochemical processes. Except for the work of Jaffé *et al* on stilbene,[8] no theoretical determination of these electronic states has been done.

The various isomers identified in anils systems [1-7] are: (a) a colorless enol E absorbing in the near ultraviolet, (b) a keto form Q_A generated by displacement of the H atom from the OH group to the N atom in equilibrium with E in polar solvents and absorbing between 400 and 500 nm for which a *cis* configuration is usually postulated and (c) UV excitation of E or Q_A which generates the colored isomer Q_C.

METHOD AND PARAMETERS

The Pariser–Parr–Pople semiempirical SCF ASMO CI method[9] treating π electrons only has been very successfully applied to the calculation of electronic transitions in conjugated molecules. Nishimoto and Forster[10] made a variable β modification to this method, in which each β and bond length for neighbouring atoms was computed by means of a linear relationship from the corresponding bond order at each iteration. It is known[10] that this variable β approximation is insensitive to the assumed geometry. All rings were therefore assigned regular hexagonal structures with equal bond lengths (1·4 Å) and all angles equal to 120°. The two-center repulsion integrals $\gamma_{\mu\nu}$ between non-neighbouring atoms were computed from this conventional geometry. The two-center core integrals $\beta_{\mu\nu}$, the bond lengths $r_{\mu\nu}$ and the two-center electronic repulsion integrals between neighbouring atoms were adjusted at each iteration according to the following equations:

$$\left.\begin{aligned}\beta_{\mu\nu} &= -0{\cdot}51\,p_{\mu\nu} - 2{\cdot}04\\ r_{\mu\nu} &= -0{\cdot}18\,p_{\mu\nu} + 1{\cdot}517\end{aligned}\right\}\quad \text{for the C—C bonds}$$

$$\left.\begin{aligned}\beta_{\mu\nu} &= -0{\cdot}53\,p_{\mu\nu} - 2{\cdot}24\\ r_{\mu\nu} &= -0{\cdot}18\,p_{\mu\nu} + 1{\cdot}451\end{aligned}\right. \quad \text{for the C—N bonds}$$

$$\left.\begin{aligned}\beta_{\mu\nu} &= -0{\cdot}56\,p_{\mu\nu} - 2{\cdot}44\\ r_{\mu\nu} &= -0{\cdot}18\,p_{\mu\nu} + 1{\cdot}410\end{aligned}\right. \quad \text{for the C—O bond}$$

and the classical Nishimoto–Mataga approximation[11]

$$\gamma_{\mu\nu} = \frac{14{\cdot}397}{a_{\mu\nu} + r_{\mu\nu}}$$

The one-center repulsion integrals were estimated from the valence state ionization energies I_μ and electron affinities A_μ:

$$\gamma_\mu = I_\mu - A_\mu$$

The values of these parameters given in Table 1 are the most usual ones.

TABLE 1. PARAMETER SUMMARY

Atoms	I_μ	γ_μ
C	11·16	11·13
Ṅ	14·12	12·34
N̈	26·70	17·44
Ȯ	17·70	15·23
Ö	32·90	21·53

The configuration interaction included the four highest occupied orbitals and the four lowest vacant ones.

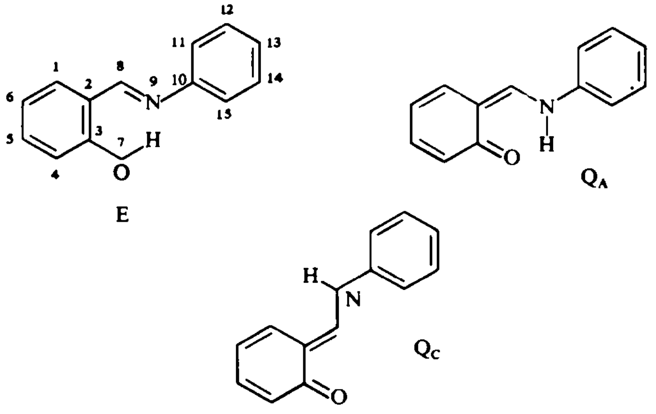

FIG 1. Salicylideneaniline isomers and numbering scheme.

RESULTS

The computed and experimentally observed transitions of the three isomers are summarized in Table 2. The quinoid systems Q_A and Q_C obviously absorb at longer wavelengths than enol E. It may be noted, however that the first computed π → π*

TABLE 2. TRANSITION ENERGIES WITH CALC. OSCILLATOR STRENGTHS (f) OR OBSERVED ABSORBANCES (ϵ)

E			Q_A			Q_C		
Singlets		Triplets	Singlets		Triplets	Singlets		Triplets
Calc. values			Calc. values			Calc. values		
3·72	(0·74)	2·31	3·01	(0·69)	1·22	3·11	(0·97)	1·18
4·36	(0·41)	3·17	4·17	(0·56)	2·69	4·25	(0·39)	2·74
4·51	(0·00)	3·26	4·46	(0·01)	3·16	4·47	(0·02)	3·13
5·35	(0·09)	3·60	5·12	(0·02)	3·70	5·06	(0·01)	3·69
5·73	(0·01)	3·80	5·38	(0·08)	3·83	5·42	(0·06)	3·84
5·77	(0·37)	3·88	5·43	(0·19)	3·95	5·46	(0·17)	3·99
5·86	(0·64)	4·51	5·56	(0·29)	4·52	5·59	(0·21)	4·56
6·30	(0·70)	4·75	5·92	(0·03)	4·87	5·93	(0·04)	4·93
Expt. values[6]			Expt. values[6]			Expt. values[6]		
3·67	(11·5)		2·80			2·58–2·76		
3·90	(1·6)							
4·11	(9·9)							
4·63	(12·9)							
5·44	(19·8)							
5·61	(19·9)							
6·20	(20·0)							

TABLE 3. CHARGES, BOND ORDERS AND MOLECULAR TOTAL ENERGIES (NUCLEAR REPULSION TERMS ADDED)

Molecule	State (ev)	Bond 3–7	Bond 2–8	Bond 8–9	Bond 9–10	Charge on	Charge on	Ground state energy (ev)
	S_0 0·00	0·385	0·369	0·845	0·351	1·857	1·250	−228·75
E	S_1 3·72	0·470	0·565	0·623	0·530	1·755	1·291	
	S_2 4·36	0·412	0·489	0·652	0·498	1·818	1·299	
	S_0 0·00	0·731	0·693	0·554	0·333	1·505	1·620	−223·97
Q_A	S_1 3·01	0·713	0·529	0·499	0·422	1·398	1·558	
	S_2 4·17	0·665	0·673	0·431	0·476	1·561	1·588	
	S_0 0·00	0·761	0·719	0·516	0·329	1·467	1·660	−223·79
Q_C	S_1 3·11	0·719	0·538	0·477	0·402	1·373	1·589	
	S_2 4·25	0·691	0·691	0·416	0·472	1·532	1·620	

transitions are always somewhat higher than the experimental values. This may be due to the lack of accuracy of the geometries used or to solvent effects, or both.

Table 3 summarizes the π bond orders of several bonds in the first excited states of the molecules studied. It appears that in the S_1 state of enol E the bond order of the C—O bond increases, thus indicating a shortening of this bond. Similarly, the length of bond 8–9 decreases whilst that of bonds 2–8 and 9–10 increase, which results in an increase of angles $\angle 2, 8, 9$ and $\angle 8, 9, 10$ and finally in an increase of the distance between atoms O and N. At the same time, the O atom releases 0·1 π electron which is used to strengthen the C—O bond, while the electron charge of atom N increases, thus allowing electrons to form a N—H bond. In this excited state the bond orders and charges exhibit undoubtedly a tendency to become similar to that of the quinoid form Q_A.

It is now established[7] that the formation of Q_C from E or Q_A involves a *cis-trans* isomerization around the 2–8 bond. This geometrical change may proceed via the excited states of Q_A where this bond becomes weaker than in the ground state.

In this scheme, the excited enol singlet E* undergoes a fast proton transfer along the —OH . . . . N— coordinate to form an excited quinoid singlet Q_A^*. Subsequently, competition occurs between a *cis-trans* isomerization leading to Q_C and emission yielding the ground state Q_A. This mechanism was previously suggested by Cohen *et al.*[3] and by Potashnik *et al.*[7]

Table 4 lists the computed bond lengths of the three considered molecules in their ground states.

TABLE 4. COMPUTED BOND LENGTHS (A)

Bonds	E	Q_A	Q_C
1–2	1·407	1·437	1·439
2–3	1·412	1·444	1·448
3–4	1·407	1·443	1·446
4–5	1·393	1·369	1·367
5–6	1·402	1·431	1·433
1–6	1·393	1·371	1·369
3–7	1·341	1·278	1·273
2–8	1·451	1·392	1·388
8–9	1·299	1·351	1·358
9–10	1·388	1·391	1·392
10–11	1·405	1·404	1·404
11–12	1·396	1·396	1·395
12–13	1·398	1·398	1·398
13–14	1·399	1·398	1·398
14–15	1·395	1·395	1·396
10–15	1·405	1·405	1·404

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