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SCF CI Calculation of the Electronic Spectra of Cis and Trans Isomers of Stilbene and Azo-Benzene

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SCF CI calculation has been made on cis and trans isomers of stilbene and azo-benzene. It has been shown that the electronic spectra of trans isomer should appear at a shorter wave length than the corresponding cis isomers, although the resonance theory reverses their positions. Experimentally azobenzene agrees with the conclusions of SCF theory while stilbene is better represented by the resonance theory.

Nous avons calculé les spectres électroniques des isomères cis et trans du stilbène et de l'azobenzène. Les spectres des isomères trans devraient apparaître à des longueurs d'onde plus courtes que ceux des cis correspondants. La théorie de résonance donne des résultats inverses. Les spectres des azobenzènes s'accordent aux conclusions de la théorie SCF, tandis que les stilbènes se représentent mieux par la théorie de résonance.

Für die cis- und trans-Isomeren des Stilbens und Azobenzols wird eine Berechnung nach der SCF-CI-Methode durchgeführt. Es wird gezeigt, daß die Elektronenspectren der Trans-Isomeren bei einer kürzeren Wellenlänge als diejenigen der cis-Isomeren liegen sollten, obwohl nach der Resonanztheorie eine umgekehrte Lage zu erwarten wäre. Die experimentellen Ergebnisse stehen beim Azobenzol in Einklang mit den Resultaten der SCF-Methode während sie beim Stilben besser im Rahmen der Resonanztheorie zu deuten sind.

It is a usual experimental observation that the cis and trans isomers of an unsaturated organic compound have different electronic spectra with respect to the maximal wave length and the intensity of the absorption band due to an allowed electronic transition [2]. It has been argued that since the chromophoric system of a trans isomer is more elongated than that of the corresponding cis isomer, the λ and ε for the N—V band is expected to decrease in the latter as is generally the case with carotinoids and polyenes. It is known, however, that such physical arguments may some times lead to completely wrong conclusions. All such physical arguments must be backed by proper theoretical calculations so as to enable one to use the physical picture with more confidence. The object of the present investigation was to make a complete SCF calculation with π-electron approximation of the long wave length electronic spectra of cis and trans isomers of stilbene and azo-benzene. Experimentally the trans isomer of stilbene absorbs at a longer wave length than the corresponding cis isomer, while the reverse is the case with azo-benzene.

Method of Calculation

The method of calculation is too well known to be reproduced here. The procedure for machine computation has been described in a previous communication [1]. No less than 32 iterations were necessary to get complete self-consistency. The calculation, however, converged very rapidly over the first 12 iterations and thereafter the convergency was very slow. To get accuracy up to four decimal places 12 iterations were found to be good enough. All the results recorded in the present communication were obtained after 12 iterations.

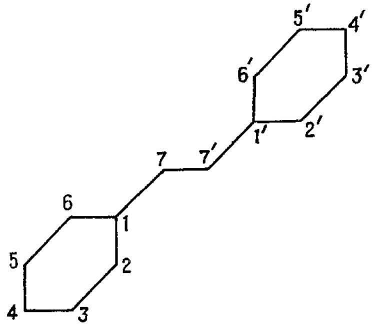

Fig. 1. Stilbene and Azobenzene [5]
For Azobenzene 7—7' N—N 1.23 Å
1—7' C—N 1.46 Å
rest 1.39 Å
For Stilbene 7—7' C—C 1.33 Å
1—7' C—C 1.45 Å
rest 1.39 Å
All bond angles equal to 120°

Selection of the parameters: Following values were used for Coulomb and resonance integrals in the Hückel calculations on stilbene and azobenzene:

$$\alpha_N = \alpha_C + 0.25\,\beta_{CC};$$
$$\beta_{NN} = .96\,\beta_{CC} \text{ and } \beta_{CN} = 0.66\,\beta_{CC}\ .$$

The mono-centric electron repulsion integrals were estimated from the valence state ionization energy and electron affinity of the respective atom [3]. The two-center integrals were calculated by point-charge approximation [4]. The core resonance integrals were given the following values in the SCF calculation:

$$\beta_{CC} = 2.39\,\text{ev};$$
$$\beta_{CN} = 1.60\,\text{ev and } \beta_{NN} = 2.30\,\text{ev}\ .$$

Since the $7 - 7'$ C $-$ C bond in stilbene is almost an isolated double bond, the core resonance integral for this bond was set equal to 2.92 ev in stilbene.

In the CI calculation levels lying within 10 ev were mixed symmetrywise. This led to mixing of the configuration wave function $\chi^{7,8}$ with $\chi^{7,9}$.

Results

The results of the calculation of the longest wave length $\pi - \pi^*$ singlet by SCF and SCF CI methods for stilbene and azo-benzene are summarised in the Tab. 1 along with the experimental values.

Table 1: *Calculated and experimental spectral transition in e. v.*

Compound	SCF	SCF CI	Experimental [1]
trans-stilbene	4.055	4.038	4.20
cis-stilbene	3.852	3.733	4.42
trans-azo-benzene	4.157	4.147	3.88
cis-azo-benzene	4.032	3.950	3.82

Simple geometric considerations show that in cis compounds steric obstruction will cause the structure to deviate from uniplanarity. If one of the phenyl ring is tilted through an angle θ about the bond $1' - 7'$, the steric strain may be relieved. SCF calculation of the electronic spectra of cis compound with different values of θ were made and the results are summarised in the Tab. 2. For stilbene and azo-benzene following values were used for the core resonance integrals of the $1' - 7'$ bond, about which the phenyl ring was rotated:

$$\beta_{1'-7'} = \beta_{CC} \cos\theta \text{ (Stilbene)}$$
$$= \beta_{CN} \cos\theta \text{ (Azobenzene)}$$

Table 2. *Steric effect on electronic spectra of cis-isomers*

compound	θ	Calculated $\nu_{\max}$ ev			
		singlet		triplet	
cis-azo-benzene	0	4.032	6.422	3.408	5.678
	30	4.041	6.442	3.421	55.710
	45	4.046	6.462	3.431	5.742
	60	4.052	6.477	3.439	5.769
cis-stilbene	0	3.852	5.541	2.749	4.912
	30	3.852	5.565	2.764	4.946
	45	3.854	5.583	2.769	4.975
	60	3.856	5.601	2.771	5.002

Calculations were made for the two long wave length $\pi - \pi^*$ singlet and triplets.

In the Tables 3 – 6 are reproduced the SCF charge and bond-order matrices for cis and trans isomers of stilbene and azo-benzene.

1	2	3	4	5	6	7	1'

Table 3. *Charge and bond-order matrix for trans stilbene (portion of interest in the 14 × 14 matrix)*

1.0000							
0.6206	1.0000						
0.0001	0.6791	0.9998					
−0.3120	0.0000	0.6580	1.0005				
0.0001	−0.3272	−0.0001	0.6654	0.9997			
0.6363	−0.0001	−0.3232	−0.0001	0.6703	1.0000		
0.3518	0.0000	−0.0383	0.0001	−0.0253	−0.0001	0.9998	
−0.0356	0.0000	0.0060	0.0000	0.0073	−0.0000	0.0001	1.0000

Table 4. *Charge and bond-order matrix for cis stilbene (portion of interest in the 14 × 14 matrix)*

1.0000							
0.6169	1.0000						
−0.0000	0.6815	1.0000					
−0.3101	−0.0000	0.6560	1.0000				
0.0000	−0.3280	0.0000	0.6667	1.0000			
0.6239	−0.0000	−0.3212	0.0000	0.6688	1.0000		
0.3622	0.0000	−0.0436	0.0000	−0.0224	−0.0000	1.0000	
−0.0521	−0.0000	0.0143	0.0000	0.0020	0.0000	−0.0000	1.0000

Table 5. *Charge and bond-order matrix for trans azo-benzene (portion of interest in the 14 × 14 matrix)*

0.9895							
0.6406	0.9852						
−0.0002	0.6736	1.0069					
−0.3208	0.0080	0.6620	0.9908				
0.0018	−0.3300	−0.0048	0.6657	1.0068			
0.6440	−0.0051	−0.3272	0.0095	0.6690	0.9810		
0.2552	0.0407	−0.0294	−0.0365	−0.0190	0.0438	1.0401	
−0.0147	0.0124	0.0021	−0.0091	0.0034	0.0129	−0.0751	0.9898

Table 6. *Charge and bond-order matrix for cis azo-benzene (portion of interest in the 14 × 14 matrix)*

1	2	3	4	5	6	7	1′
0.9873							
0.6400	0.9843						
0.0027	0.6743	1.0047					
−0.3202	0.0093	0.6612	0.9902				
−0.0017	−0.3300	−0.0031	0.6664	1.0067			
0.6434	−0.0053	−0.3268	0.0077	0.6684	0.9872		
0.2583	0.0400	−0.0315	−0.0364	−0.0180	0.0430	1.0397	
−0.0244	0.0114	0.0075	−0.0084	−0.0002	0.0137	−0.0745	0.9880

Discussion

From the qualitative physical arguments it has been suggested that cis-trans isomers of azo-benzene behaves rather abnormally with respect to the position of the longest wave length electronic spectra [2]. The SCF calculation, however, suggests that it is stilbene rather than azo-benzene which is abnormal (Table 1). The non-planarity of the phenyl rings cannot explain this discrepancy since the longest wave length singlet and triplet is affected only slightly by tilting one of the phenyl ring with respect to the other through different angles up to about 60°. The bond-orders of 7 — 7′ (trans azo-benzene: 0.9286; cis azo-benzene: 0.9274; trans stilbene: 0.8785; cis stilbene: 0.8754; and 1 — 7 (1′ — 7′) bonds show that they are behaving as isolated double and single bonds respectively (Tables 3 — 6), As there is very little conjugation between the phenyl rings across the central 7 — 7′ bond, tilting of one plane with respect to the other is not expected to affect the energy values appreciably.

The electron densities at various atoms are not very much different in cis and trans isomers, consequently from the point of view of isolated atom approximation the chemical reactivity of the two isomers will be about the same.

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