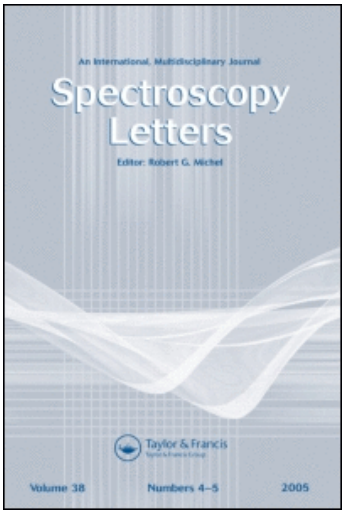

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A CNDO CI Study of the Electronic Structure of Trans- and Cis-Diimide

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A CNDO CI STUDY OF THE ELECTRONIC STRUCTURE OF TRANS- AND CIS-DIIMIDE

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The electronic spectra of cis- and trans-HN=NH have been the subject of a number of studies. The most interesting work in this area is probably that of Robin, Hart and Kuebler[1]. They studied the two isomers both experimentally and theoretically and attempted to correlate their electronic states with that of ethylene.

Most recently, Del Bene and Jaffé[2] introduced a modification of the well-known semiempirical CNDO/2 method in order to better calculate the electronic states of molecules. This new all valence electrons CNDO CI method proved very successful and appears to be very promising in predicting the electronic states of saturated as well as conjugated molecules. It was therefore of interest to apply this new method to the investigation of the electronic structure of diimide. The geometries were taken from the work of Robin et al.[1]. The configuration interaction included all singly excited transitions.

The MO levels of diimide isomers and ethylene are listed in Table 1. In the ground states, all levels with negative energies are doubly filled.

The lowest computed transition energies are summarized in Table 2. The degeneracy of singlet and triplet $n \longrightarrow \pi^*$ excited states is due to the fact that $K_{ij} = 0$ for these states[2].

Table 1. SCF Molecular orbital energies (ev)

character	cis-diimide	ethylene	trans-diimide
σ	-42.50	-34.30	-42.10
σ	-26.21	-29.25	-27.75
σ	-22.43	-20.72	-19.06
σ	-15.64	-15.73	-18.26
π	-14.16	-11.35	-14.12
σ	-12.61	-10.87	-11.96
π	+ 0.45	+ 1.62	+ 0.49
σ	+ 7.53	+ 4.33	+ 7.48
σ	+ 7.76	+ 5.70	+ 7.98
σ	+11.97	+ 6.88	+12.01
σ		+ 7.48	
σ		+11.39	

Table 2. Excited states (ev) and oscillator strengths

cis-diimide		ethylene		trans-diimide	
singlets		singlets		singlets	
3.40 (0.)	$n \rightarrow \pi^*$	4.15 (0.)	$\sigma \rightarrow \pi^*$	2.60 (0.)	$n \rightarrow \pi^*$
5.98 (0.)	$n \rightarrow \pi^*$	6.45 (0.16)	$\pi \rightarrow \pi^*$	7.60 (0.18)	$\pi \rightarrow \pi^*$
7.59 (0.18)	$\pi \rightarrow \pi^*$	6.99 (0.)	$\pi \rightarrow \sigma^*$	8.76 (0.)	$n \rightarrow \pi^*$
11.55 (0.02)	$n \rightarrow \pi^*$	7.32 (0.03)	$\sigma \rightarrow \sigma^*$	10.06 (0.)	$n \rightarrow \pi^*$
triplets		triplets		triplets	
3.40	$n \rightarrow \pi^*$	3.61	$\pi \rightarrow \pi^*$	2.60	$n \rightarrow \pi^*$
4.50	$\pi \rightarrow \pi^*$	4.15	$\sigma \rightarrow \pi^*$	4.50	$\pi \rightarrow \pi^*$
5.98	$n \rightarrow \pi^*$	6.97	$\sigma \rightarrow \sigma^*$	8.76	$n \rightarrow \pi^*$
10.94	$n \rightarrow \sigma^*$	6.99	$\pi \rightarrow \sigma^*$	10.06	$n \rightarrow \pi^*$

Table 3. Atomic valence electron densities

cis-diimide		ethylene		trans-diimide	
N	5.088	C	4.151	N	5.097
H	0.911	H	0.925	H	0.903

The singlet excited states observed at about 3.5 ev in both cis- and trans-azoalkanes[1] are to be associated with the computed $n \rightarrow \pi^*$ states at 3.4 and 2.6 ev in the diimides. The computed transitions at 7.6, 8.76 and 10.06 ev in trans-diimide may also be correlated with the bands I, II and III at 6.7, 7.9 and 8.7 ev in trans-azomethane, since it is observed[1] that a decrease in the size of the substituent R in R-N=N-R results in a blue shift of these bands and an increase of the intensity of band I.

The computed dipole moment of cis-diimide is 3.63 D. which is near the value 3.94 D. obtained by Robin et al.[1]

The trans form of the diimide is computed to be more stable than the cis form by 0.47 ev.

Applying Koopman's theorem[3] we find that the computed ionization potentials of cis- and trans-diimide (12.61 and 11.96 ev, respectively) are somewhat greater than the experimental value (9.85 ev[1]).

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