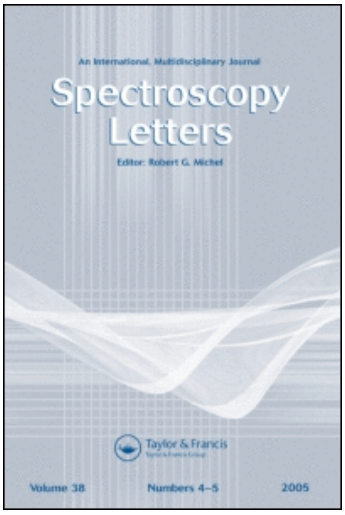

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A CNDO CI Study of the Electronic Structure of Dioxadiene

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A CNDO CI STUDY OF THE ELECTRONIC STRUCTURE OF DIOXADIENE

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I. INTRODUCTION

1,4-dioxadiene (also called p-dioxin) was first prepared by Summerbell and coworkers[1]. The electron diffraction study of this molecule was reported by Beach[2] who made the assumption that the molecule is planar. The ultraviolet absorption spectrum of this compound was reported by Pickett and Sheffield[3] who found it consistent with a D_{2h} symmetry. On the basis of infrared spectra in the liquid and gas phases, Connett et al.[4] concluded that the molecule is planar and is not highly conjugated. Finally, Ray and Narasimhan[5] also predicted a planar structure for dioxadiene as a result of EHT calculations.

II. METHOD OF CALCULATION

The molecule of dioxadiene was assumed to belong to the symmetry group D_{2h}. The geometry used was taken from the work of Beach[2]. The valence shell electronic structure of dioxadiene was computed by means of the modified CNDO CI method of Del Bene and Jaffé[6]. It is known that Pople's original CNDO/2 method[7-9] is not suitable for the calculation of spectra because of the intermingling of sigma and pi orbitals. With too little shielding the pi - electron levels immerge too deeply into the range of the sigma - electron levels. To avoid this kind of mixing, Del Bene and Jaffé used two different β values, β_σ and β_π, which led to a good

agreement with experimental spectral data for a wide range of conjugated molecules.

III. RESULTS

The lowest computed electronic states are listed in Table 1 together with the experimental data. The observed energies of the absorption bands are collected in the last columns irrespectively of whether or not they correspond to the predicted transitions on the left. The theoretical values result from a limited configuration interaction calculation done over the 30 lowest monoexcited transitions. The symbol " // " in the second column of Table 1 means that the corresponding transitions are polarized parallel to the line joining the two oxygen atoms. It may be seen from Table 2 that the excited state geometries are often very different from that of the ground state. It must therefore be noticed that the results presented here, having been calculated by assuming the bond distances fixed during excitations, must not be compared with the observed positions of the O - O bands.

The first band is of much lower intensity than the others and might well correspond to the forbidden $S_o \rightarrow S_1$ transition. The highest allowed transition $S_o \rightarrow S_5$ might clearly be related to the fifth absorption band. The allowed $S_o \rightarrow S_2$ transition might correspond to the second band. Finally, there is some ambiguity with respect to the assignment of the two remaining forbidden transitions $S_o \rightarrow S_3$ and $S_o \rightarrow S_4$ which would occur as weak bands in the observation. To them might tentatively be related the third and fourth bands.

In its chemical reaction 1,4 - dioxadiene is known to behave as an aliphatic unsaturated ether and there is no evidence of aromatic properties such as are found for furan[10]. From a theoretical point of view, dioxadiene is not expected from the Hückel (4n + 2) rule to possess aromatic properties since it is an eight pi - electron system. Our results show (see Table 2) that the C - O pi bond order is very low while the C - C bond order is nearly equal to that of ethylene, thus indicating a poor conjugation of the oxygen atoms. On the other hand, the pi - electron density on O atoms is near from 2. , which justifies the use of Hückel (4n + 2) rule.

Table 1. Electronic spectrum

state	energy (ev)	osc. strength	type	Expt. values[3]	
				liquid phase	vapour phase
S_1	4.051	0.	$\pi \rightarrow \pi^*$	3.72 - 4.6	3.83–4.15
S_2	5.795	0.14 //	$\pi \rightarrow \pi^*$	4.96	4.69 - 5.08
S_3	7.081	0.	$\pi \rightarrow \sigma^*$		5.39 - 5.72
S_4	7.111	0.	$\pi \rightarrow \sigma^*$		6.20 - 6.86
S_5	7.146	0.41 //	$\pi \rightarrow \pi^*$		7.05 - 7.44
T_1	2.484		$\pi \rightarrow \pi^*$		
T_2	2.810		$\pi \rightarrow \pi^*$		
T_3	5.992		$\pi \rightarrow \pi^*$		

Table 2. Electron densities and bond orders

state	electron densities on atoms					π bond orders	
	O		C		H	C - O	C - C
	total	π	total	π			
S_o	6.196	1.903	3.930	1.048	0.972	0.209	0.952
S_1	5.991	1.700	4.032	1.147	0.973	0.382	0.559
S_2	6.029	1.762	4.015	1.139	0.971	0.272	0.593
S_3	5.938	1.888	4.079	1.279	0.952	0.212	0.694
S_4	6.023	1.701	3.936	0.908	1.053	0.380	0.800
S_5	6.024	1.699	3.946	0.901	1.042	0.383	0.804
T_1	6.040	1.748	4.008	1.126	0.972	0.328	0.539
T_2	6.094	1.802	3.982	1.099	0.972	0.254	0.534
T_3	6.143	1.844	3.957	1.070	0.972	0.238	0.506

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