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Electronic Structure of Dioxazines

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The electronic spectra of dioxazines are interpreted by means of the semiempirical Pariser-Parr-Pople method.

Dioxazines are pigments and the study of their optical spectra is therefore of particular interest. These molecules are planar and their structure is shown on Fig. 1.

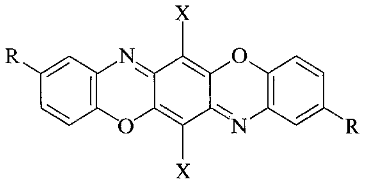

Fig. 1. The structure of symmetrical dioxazines

The purpose of this work is to interpret the electronic spectra of dioxazines having $X = Cl$ and $R = H$ or Cl using the classical semiempirical Pariser-Parr-Pople method [5, 6, 7]. The geometries of the rings were approximated as regular hexagons with all ring bonds equal to 1.4 Å. The parameters used are listed in Tab. 1. The configuration interaction included the four highest occupied orbitals and the four lowest empty ones.

The results are summarized in Tab. 2. It may be seen that the accordance between the experimental and computed transition energies is good.

Chen and coworkers [1] carried out a molecular orbital calculation on the same compounds using the iterative extended Hückel method [2, 3, 4, 8]. Their results differ only slightly from ours. The small differences between the observed and computed spectra may be due either to the ideal assumed geometry and to the imperfect parameter values or to solvent shifts, or both.

Table 1. *Semiempirical parameters (eV)*

Atom A	I	γ	β_{C-A}
C	11.16	11.13	−2.39
N	14.12	12.34	−2.39
O	34.75	21.18	−3.00
Cl	24.02	11.27	−1.859

Table 2. *Electronic transition energies (eV) and oscillator strengths*

Dioxazine	orbital jump	calc. ΔE		calc. f		expt. ΔE [1]	
		This work	Chen [1]	This work	Chen [1]	in benzene	in chloro-naphthalene
R = H	14 15	2.338	2.46	2.00	1.68	2.42	2.38
	13 15	2.458		0.0			
	14 16	3.565		0.0			
	12 15	3.884	3.74	0.05	0.11		
	11 15	3.939		0.0			
	14 17	4.387		0.0			
	14 18	4.668	4.56	0.64	0.52		4.67
	13 16	5.182		1.70			
	13 17	5.862		0.16			
R = Cl	16 17	2.319		2.01		2.38	2.33
	15 17	2.444		0.0			
	16 18	3.565		0.0			
	14 17	3.729		0.11			
	13 17	3.857		0.0			
	16 19	4.382		0.0			
	16 20	4.696		0.56			
	15 18	5.174		1.73			
	15 19	5.816		0.14			

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