

## Electronic Spectra of Hafner's Hydrocarbons

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Electronic structures and spectra of Hafner's hydrocarbons have been calculated by means of the semi-empirical SCF CI MO method incorporated with the variable bond-length technique. The results are in good agreement with experimental data.

Electronic structures and spectra of acceptylene (I) and aceazulylene (II) have long been of theoretical interest since Hafner and Schneider [1] synthesized their dimethyl derivatives in 1958–1959. Theoretical investigations so far made [2–5] agree that predicted excitation energies and intensities interpret the general electronic spectra of I rather accurately, but the agreement in II is less satisfactory. No unambiguous spectral assignment in II seems to have been made. In this paper, we calculate electronic structures and spectra of I and II using the semi-empirical SCF CI MO method which has proved quite successful for the study of electronic properties of nonbenzenoid aromatic hydrocarbons [6] and discuss the spectral assignment in II in particular.

The method used is the self-consistent formalism of the Pariser-Parr-Pople MO method incorporated with the variable bond-length technique [6]. In order to obtain the energetically most favourable set of bond lengths we examine all the group-theoretically possible bond distortions as the starting geometrical structures [7]. In discussing the properties of excited states, configuration mixing of all the singly excited states is included.

The calculated singlet transition energies and intensities are presented and compared with experimental data in the Table. In both the molecules the predicted transition energies are in good agreement with the absorption peaks of their

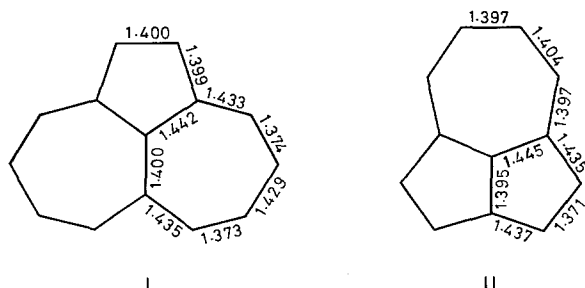


Fig. 1. Bond lengths (in Å) of acceptylene (I) and aceazulylene (II)

Table. Transition types, energies ( $\Delta E$ ) and intensities ( $f$ )

Molecule	Transition type	Theoretical		Experimental <sup>a</sup> $\Delta E$ (eV)
		$\Delta E$ (eV)	$f$ (cgs)	
Aceheptylene, I	$B_2 \leftarrow A_1$	1.52	0.014	1.55
	$A_1 \leftarrow A_1$	2.89	0.009	2.92
	$B_2 \leftarrow A_1$	3.47	0.30	3.33
	$A_1 \leftarrow A_1$	3.82	0.14	3.96 ~ 4.77
	$B_2 \leftarrow A_1$	4.48	0.019	
	$A_1 \leftarrow A_1$	4.57	0.53	
		$B_2 \leftarrow A_1$	4.95	1.44
Aceazulylene, II	$B_2 \leftarrow A_1$	1.73	0.003	1.84
	$A_1 \leftarrow A_1$	2.91	0.001	2.59
	$A_1 \leftarrow A_1$	3.64	0.073	3.37
	$B_2 \leftarrow A_1$	3.86	0.11	3.79
	$B_2 \leftarrow A_1$	4.79	0.39	4.63

<sup>a</sup> The absorption spectra of dimethyl derivatives (K. Hafner, personal communication).

dimethyl derivatives. In case of II the predicted lowest transition is well assigned to the longest wave-length absorption band with  $\lambda_{\max}$  equal to 675 m $\mu$  (1.84 eV), which is so weak that it has been omitted by previous authors in their spectral assignments: Ali and Coulson [2] and DasGupta and Ali [4] have assigned the predicted lowest transition to the second band with  $\lambda_{\max}$  479 m $\mu$  and found that the agreement with experiment in the case of I is very satisfactory but that in the case of II is less satisfactory. Moreover, the transition intensities for II are predicted to increase roughly with transition energies, which is in agreement with experimental facts. In this respect the spectral assignment proposed recently by Julg and François [5] is less satisfactory.

The predicted bond lengths are shown in Fig. 1. It should be noted that in both the molecules the peripheral C-C skeleton is composed of two distinguishable parts, one in which bond lengths are nearly equalized (peripheral bonds belonging to the 5-membered ring in I and those belonging to the 7-membered ring in II) and the other in which a strong double bond fixation exists. Thus, it may be said that there are two regions, one aromatic and the other polyolefinic, in the peripheries of these molecules. Any definition of aromaticity in which it is correlated with the global  $\pi$ -electronic properties, such as the standard deviation of bond lengths [5] is of little importance particularly for these molecules.

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