

## Extended Hückel Calculation on the Violuric Acid Radical

SVANTE WOLD and CARL LAGERCRANTZ

University of Umeå, Department of Organic Chemistry, Umeå 6, Sweden and University of Göteborg, Department of Medical Physics, Göteborg SV, Sweden

Extended Hückel calculations<sup>1</sup> have been made on the violuric acid radical. The theoretical spin densities have been compared with experimental spin splittings<sup>2</sup> and a good agreement has been found.

Extended Hückel calculations require specification only of the form of the Hamiltonian matrix elements  $H_{kl}$  and the space coordinates of all atoms in the molecule in question. The diagonal matrix elements  $H_{ii}$  have been taken to be the valence state ionization potentials of the

Table 1. Valence state ionization potentials (eV).

	$H_{ii}(1s)$	$H_{ii}(2s)$	$H_{ii}(2p)$
H	-13.6	—	—
C	—	-21.4	-11.4
N	—	-26.0	-13.4
O	—	-35.0	-17.5

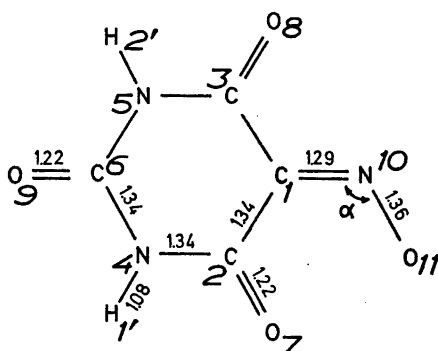


Fig. 1. Geometry and numbering of violuric acid radical. All bond distances in Ångström units.

atomic orbitals (AO) (Table 1) and the off diagonal elements  $H_{ij}$  have been defined by  $H_{ij} = 0.875 (H_{ii} + H_{jj}) S_{ij}$ .<sup>1,3,4</sup> The assumed geometry of violuric acid is shown in Fig. 1.

The spin densities have been calculated using a Mulliken population analysis<sup>5</sup> on the MO containing the odd electron (the highest occupied MO). This method gives separate spin densities on the different AO's ( $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$ ) of each main atom (C, N, and O), and the problem arises how to correlate these spin densities with the experimental splitting constants. Since the theoretical spin densities vary with the angle CNO ( $\alpha$  in Fig. 1) as shown in Fig. 2, no definite correlations between theory and experiment can be made until a reliable value for this angle can be obtained.

Computed spin densities for some different values of  $\alpha$  are shown in Table 2. The extended Hückel method predicts much larger spin densities on atoms situated *syn (cis)* to the iminoxy group than on atoms situated *anti (trans)*. This prediction is confirmed by experiment,<sup>2,6</sup> and the agreement between the ratio of nitrogen splittings and the ratios of nitrogen spin densities is also astonishingly good.

The agreement between theory and experiment found in this investigation might be accidental and further calculations (in progress) will show the value of

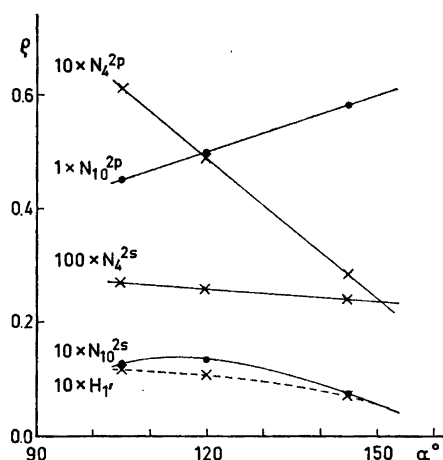


Fig. 2. Spin densities on atoms 4, 10, and  $H_1$  as functions of the angle  $\alpha$ .

Table 2. Computed spin densities and experimental spin splitting constants.

	$\alpha = 105^\circ$	$\alpha = 120^\circ$	$\alpha = 145^\circ$	$a^*$ (from Ref. 2)
$C_1(2s)$	0.0002	0.0002	0.0005	2.48
$(2p)$	0.1691	0.1650	0.1235	
$C_2(2s)$	0.0084	0.0105	0.0110	
$(2p)$	0.1165	0.1201	0.1005	
$C_3(2s)$	0.0021	0.0037	0.0058	
$(2p)$	0.0078	0.0200	0.0385	
$N_4(2s)$	0.0027	0.0026	0.0020	
$(2p)$	0.0613	0.0491	0.0284	
$N_5(2s)$	0.0001	0.0003	0.0006	
$(2p)$	0.0012	0.0024	0.0052	
$C_6(2s)$	0.0001	0.0000	0.0000	31.0
$(2p)$	0.0002	0.0004	0.0005	
$O_7(2s)$	0.0009	0.0004	0.0003	
$(2p)$	0.0606	0.0313	0.0168	
$O_8(2s)$	0.0002	0.0003	0.0003	
$(2p)$	0.0056	0.0079	0.0085	
$O_9(2s)$	0.0000	0.0000	0.0000	
$(2p)$	0.0003	0.0001	0.0000	
$N_{10}(2s)$	0.0127	0.0137	0.0087	
$(2p)$	0.4565	0.4991	0.5833	
$O_{11}(2s)$	0.0001	0.0006	0.0005	1.79
$(2p)$	0.0818	0.0607	0.0560	
$H_1'(1s)$	0.0117	0.0107	0.0070	
$H_2'(1s)$	0.0004	0.0011	0.0020	

the extended Hückel method in predicting spin densities of iminoxy radicals.

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## Mass Spectrometry of Some Carbo-styryls

J. MØLLER and O. BUCHARDT

*Physical Laboratory II and Chemical Laboratory II, The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark*

In connection with the investigation of the photoinduced formation of carbo-styryls,<sup>1</sup> we have recorded the mass spectra of five carbo-styryls (I–V) (Fig. 1).

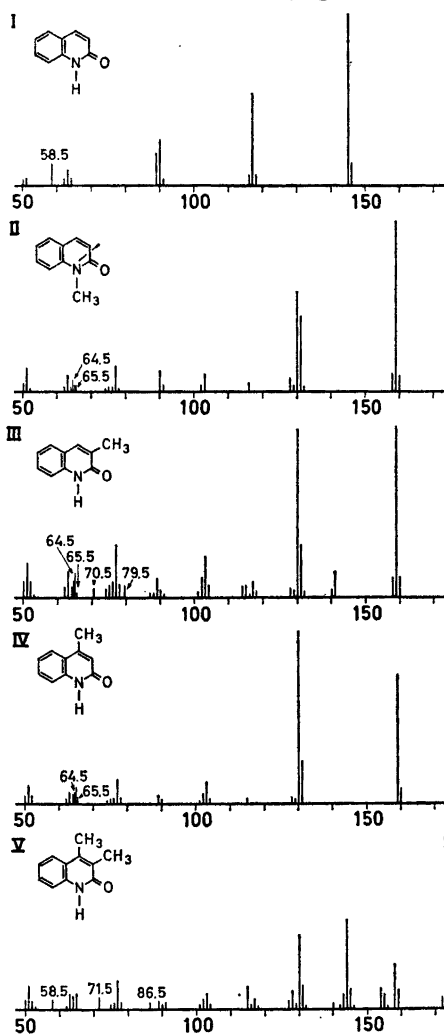


Fig. 1.