

## Studies of Flavylium Compounds

7. Valence Electron Distribution  
in the Pyrylium Ion\*

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The chemistry of flavylium (2-phenylbenzopyrylium) compounds is to a great extent characterized by the presence of a pyrylium ring in the molecule. Since this group of compounds consists of big molecules, and moreover the conformation of the phenyl group in position 2 is not exactly known, the quantum mechanical calculations carried out in this series of papers (part 1<sup>1</sup> and part 5<sup>2</sup>) have been devoted mainly to the pyrylium ion itself and to benzopyrylium and its hydroxy compounds. In part 5 the atomic charge distribution was obtained from two approaches that include valence electrons, the charge iterative extended Hückel method and the CNDO/2 method. Since the former method includes the overlap integrals between the valence orbitals and gives a realistic charge distribution, it is of interest to study the valence electron distribution obtained by it.

Since this procedure has been described recently,<sup>3</sup> only some additional information is given here. For the Slater hydrogen 1s orbital the "molecular" value 1.2 has been used to calculate the eigenvectors as well as the density itself. The parameters for oxygen in the quadratic charge iterative procedure are in decreasing order of  $q$ : -1.493, 33.265, and -178.143 for oxygen 2s orbitals; -3.487, 57.925, and -236.646 for oxygen 2p orbitals.

The geometry of pyrylium is assumed to be a regular hexagon with all internuclear distance in the ring equal to 1.40 Å. For C-H an internuclear distance of 1.09 Å has been used. The valence angles are 120°.

The contours represent the levels (in electrons per Bohr<sup>3</sup>): 0.1, 0.3, 0.6, ... 0.30, 0.35, ... 0.50, 0.70, ... 1.30.

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Fig. 1 displays the  $\sigma$  charge density in the plane of the ring. Like its isoelectronic nitrogen homologue, pyridine, pyrylium has a lone pair at the oxygen atom which can be observed as a distinct maximum. The relatively strong maximum inside indicates that we probably do not have a pure  $sp^2$  hybridization at the oxygen

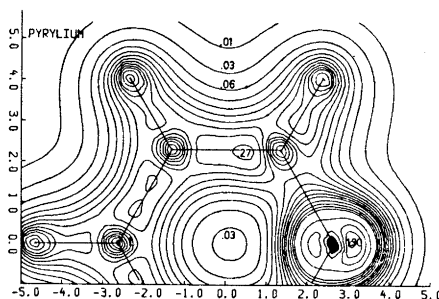


Fig. 1.  $\sigma$ -Charge distribution of pyrylium in the molecular plane.

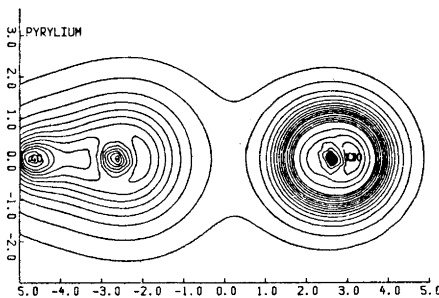


Fig. 2. Valence charge distribution of pyrylium in the symmetry plane perpendicular to the molecular plane.

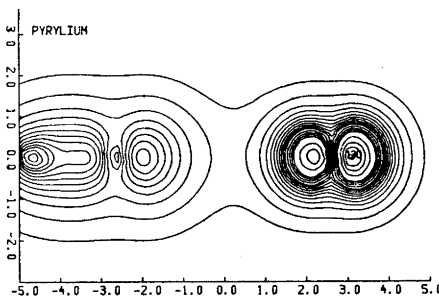


Fig. 3.  $\sigma$ -Charge distribution of pyrylium in the symmetry plane perpendicular to the molecular plane.

atom. The contribution to the occupation of the highest valence orbital from the oxygen atom is also fairly low, or 1.14 electrons as compared to about 1.5 for the nitrogen atom in pyridine.

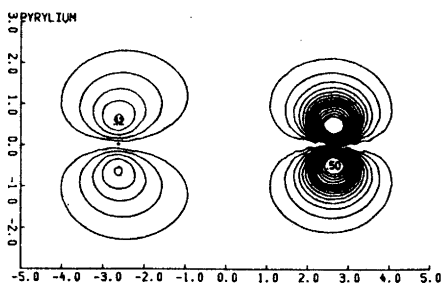


Fig. 4.  $\pi$ -Charge distribution of pyrylium in the symmetry plane perpendicular to the molecular plane.

It is also seen that the inductive effect from the electronegative oxygen atom is a short range phenomenon, the  $C_2-C_3$  and  $C_3-H$  bonds being polarized. The more distant bonds are not influenced. By inspection is observed that all C-C and C-H bonds are straight. How the C-O bonds should be considered is difficult to decide. Intuitively, one perhaps will draw a line slightly bent outwards in the vicinity of the oxygen atomic centre.

Figs. 2, 3, and 4 give the charge distribution and its  $\sigma$  and  $\pi$  parts, respectively, in the symmetry plane perpendicular to the ring. They show how the  $\sigma$  charge predominates. The  $\pi$  charge contours (Fig. 4) are only slightly distorted towards the interior of the ring.

The distribution of the valence charge in a plane 1.5 a.u. above the plane of the ring is shown in Figs. 5, 6, and 7. The

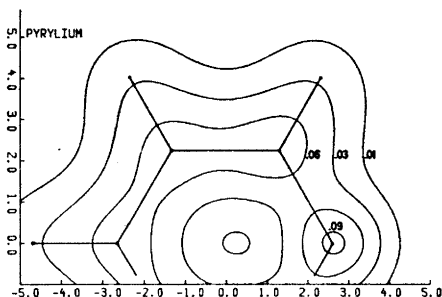


Fig. 5. Valence charge distribution of pyrylium in a section 1.5 a.u. above the molecular plane.

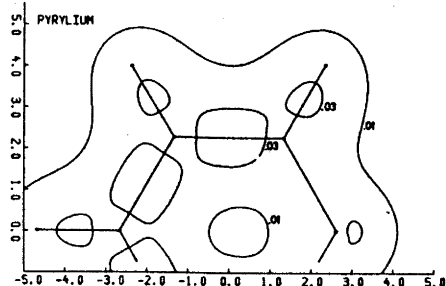


Fig. 6.  $\sigma$ -Charge distribution of pyrylium in a section 1.5 a.u. above the molecular plane.

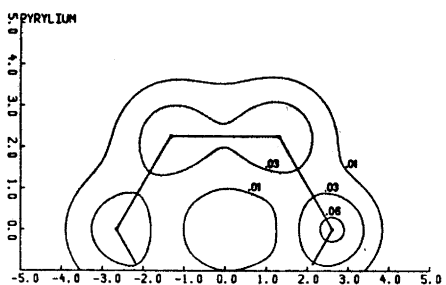


Fig. 7.  $\pi$ -Charge distribution of pyrylium in a section 1.5 a.u. above the molecular plane.

total charge (Fig. 5) has a maximum band which includes all the carbon atoms but not the oxygen atom which seems to retain a certain degree of individuality. The  $\sigma$  charge distribution (Fig. 6) is characterized by maxima over all C-C and C-H bonds but not over the C-O bonds. The individuality of the oxygen atom is also seen from the  $\pi$  charge distribution (Fig. 7). In spite of the fact that the density is highest over the oxygen atom, this is little utilized in conjugation. We see also that the conjugation between the carbon atoms  $C_1$  and  $C_2$  is stronger than between  $C_2$  and  $C_4$  which, of course, also can be read from corresponding bond orders (0.55 against 0.44).

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