ACTA CHEMICA SCANDINAVICA 24 (1970) 2745–2750

Studies of Flavylium Compounds

5. On the Charge Distribution in Pyrylium Compounds*

O. MÅRTENSSON and C. H. WARREN**

Quantum Chemistry Group, Uppsala University, Box 518, S-751 20 Uppsala 1, Sweden

The result of CNDO/2 and other earlier calculations on the charge density distribution of the pyrylium ion and of benzopyrylium ion and its monohydroxy derivatives (the corresponding flavylium compounds may be included in this generalization) lead to following points of interest to the chemist.

1. The positive, ionic charge characteristic of the oxonium compounds cannot in these conjugated molecules be ascribed to a particular atom but is distributed over the whole conjugated system. There is a great variation in the charge distribution in the ring containing the oxygen atom.
2. The so called oxonium oxygen atom is slightly negative when all valence electrons are considered. It is distinctly different from the oxygen atom of phenolic type.
3. The carbon atoms at positions 2 and 4 are definitely positively charged and constitute potential targets for nucleophilic attack.
4. A hydroxyl group in position 3 has a stabilizing effect on the system in that it decreases the high positive charges of positions 2 and 4.

The charge distribution of pyrylium compounds is of interest to the chemist from several points of view. Several physical and chemical properties such as nuclear quadrupole coupling constants, NMR chemical shifts, and chemical reactivity can often, to a first approximation, be directly correlated to the net charge ascribed to the various atoms of the molecule.

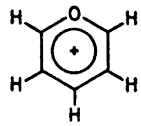
In the pyrylium ion, the oxygen atom is a part of a conjugated system. The positive ionic charge of oxonium compounds is generally ascribed to the oxygen atom, and is often denoted in chemical structure formulas by a + sign at that atom. In molecules containing only σ-bonded oxygen atoms, this assignment of the positive charge to the oxygen atom is a good approximation. However, when the oxygen atom is a part of a conjugated system, this

* Sponsored in part by *King Gustaf VI Adolf's 80-Years Fund for Swedish Culture, Knut and Alice Wallenberg's Foundation* and in part by the *Swedish Natural Science Research Council.*

** National Research Council of Canada Postdoctoral Fellow.

approximation can break down since delocalization of the charge in these systems may be considerable. This question has been previously commented upon in this series of papers in connection with the calculation of the π-charge distribution in benzopyrylium and flavylium compounds by means of the Pariser-Parr-Pople (PPP) method.[1-3]

From the results of these calculations it was suggested that the best way of writing these formulas was by enclosing them in brackets with a + sign outside the bracket.[3] For compounds consisting essentially of a pyrylium ring the + sign may be instead enclosed within the pyrylium ring as the figure indicates.



In the PPP approximation, one first assumes that the σ-π separation is valid and then one has to place the ionic charge in the π-system in order to proceed with the calculation. An all valence electron procedure such as the CNDO/2 method does not require such assumptions. Also one is not required to make a hypothesis as to the valence state of the atoms. We shall therefore report the results of our calculations on pyrylium, benzopyrylium, and some mono-hydroxybenzopyrylium compounds. Charge distributions obtained by other methods [4] for the pyrylium ion have been included for comparison.

The CNDO method [5] may briefly be described as an all valence electron LCAO-MO method with complete neglect of differential overlap. The interactions between all valence electrons are introduced explicitly.

METHOD OF CALCULATION

The CNDO/2 method was applied without modification. In this form, the method has been successfully used to calculate many ground state properties of small molecules. The computations were carried out to a degree of self-consistency of 0.0001 a.u. with respect to the total ground state energy and to 0.005 with respect to the charge density of each atom.

The geometry of the pyrylium ion has not as yet been determined experimentally. Consequently, a hypothetical planar geometry based on the structural parameters of compounds such as benzene and phenol was used in the calculations. At present there is no experimental evidence which suggests that pyrylium and benzopyrylium deviate from a planar conformation. All valence angles have been set equal to 120°. The C–O bond distance in the ring was set equal to the C–C distance, 1.39 Å. The interatomic C–O distance for the phenolic hydroxyl group was taken as 1.36 Å, and 1.09 Å for the C–H bond distance. The O–H bond distance was set equal to 0.970 Å.

Table 1. Charge distribution of the pyrylium ion in various all valence electron, σ-electron, and π-electron approximations.

Method	Carbon atom			Oxygen atom	Hydrogen atom		
	ortho	*meta*	*para*		*ortho*	*meta*	*para*
EHM	+0.60	−0.14	+0.13	−0.69	+0.13	+0.14	+0.13
IEHM	+0.15	+0.06	+0.08	−0.07	+0.13	+0.10	+0.10
$\sigma\pi$IEHM	+0.22	+0.08	+0.14	−0.11	+0.09	+0.07	+0.06
CNDO/2	+0.25	−0.03	+0.19	−0.06	+0.10	+0.09	+0.07
(EHM)σ	+0.33	−0.13	−0.11	−0.94	+0.13	+0.14	+0.13
(IEHM)σ	+0.14	−0.04	−0.10	−0.65	+0.13	+0.10	+0.10
σIEHM	+0.04	−0.03	−0.03	−0.35	+0.09	+0.07	+0.06
σRE	+0.09	−0.02	−0.03	−0.30	+0.04	+0.03	+0.03
(CNDO/2)σ	+0.07	−0.01	−0.09	−0.47	+0.10	+0.09	+0.07
(EHM)π	+0.27	−0.01	+0.24	+0.25			
(IEHM)π	+0.01	+0.11	+0.18	+0.58			
πIEHM	+0.18	+0.11	+0.17	+0.24			
PPPM	+0.22	+0.04	+0.22	+0.26			
PPPO	+0.21	+0.01	+0.26	+0.30			
IPPM	+0.14	+0.08	+0.15	+0.42			
IPPO	+0.11	+0.08	+0.17	+0.45			
(CNDO/2)π	+0.19	+0.03	+0.27	+0.41			

The abbreviations used in Table 1 are as follows:

EHM	Extended Hückel Method for all valence electrons (initial computation of IEHM).
(EHM)σ	σ-part of EHM.
(EHM)π	π-part of EHM.
IEHM	Iterative Extended Hückel Method for all valence electrons.
(IEHM)σ	σ-part of IEHM.
(IEHM)π	π-part of IEHM.
σIEHM	Iterative Extended Hückel Method applied only to σ-electrons.
πIEHM	Iterative Extended Hückel Method applied only to π-electrons.
$\sigma\pi$IEHM	Values obtained when values of σIEHM and πIEHM are added.
σRE	The method by Del Re for σ-electrons.
PPPM	Pariser-Parr-Pople Method with Mataga-Nishimoto's approximation of γ_{ab} (initial computation of IPPPM).
PPPO	Pariser-Parr-Pople Method with Ohno's approximation of γ_{ab} (initial computation of IPPPO).
IPPPM	Iterative PPPM.
IPPPO	Iterative PPPO.
CNDO/2	Complete Neglect of Differential Overlap method 2 for all valence electrons.
(CNDO/2)σ	σ-part of CNDO/2.
(CNDO/2)π	π-part of CNDO/2.

RESULTS AND DISCUSSION

In Table 1, the calculated results for pyrylium by the CNDO/2 and other methods are listed. They have been separated into three cathegories; net total valence electron charge, net σ charge and net π charge for the atoms of the pyrylium ion.

It can be seen that the net total charge distribution varies considerably according to the method by which it is calculated. Extreme values for the

charges are obtained with the Extended Hückel Method (EHM), a method known to give pronounced charge values for molecules containing heteroatoms. Of particular interest is the fact that we have a slightly negative charge at the oxygen atom in all approaches except that of the EHM which yields an unrealistically high negative value. Hence the results of this and other related studies indicate that the structure formula of the pyrylium ion should not be written (as it is often done) with a +sign at the oxygen atom when one is considering all valence electrons. As is mentioned below, only the π-electron charge of the oxygen atom will be positive.

The CNDO/2 scheme leads to *ortho* and *para* carbon atoms which are more positively charged than the carbon atom in *meta* position. The EHM, however, gives an extremely high positive charge at the *ortho* position which seems to indicate that this method overemphasizes the inductive effect.

The charge of the hydrogen atoms, which in the σ-π separation is a pure σ effect, is in the σIEHM (Iterative Extended Hückel Method applied to σ-electrons) and in the CNDO/2 method fairly uniform with a slight decrease of the positive charge from the *ortho* to the *para* positions.

The π-electron charge distribution computed by various semi-empirical methods are mutually consistent with the predominating view of positive charge at the oxygen atom. The *ortho* and *para* positions are calculated to be positive. The positive charge of the oxygen atom, which may be interpreted as the result of a mesomeric effect, is thus opposite to the charge resulting from the σ-electron distribution and the all valence electron distribution. This illustrates the difficulties in the correlation of the charge density to the reactivity and similar phenomena. In simple terms, we have a negative "directing" charge and a positive "mobile" charge for the oxygen atom.

For benzopyrylium and its monohydroxy derivatives, the CNDO/2 calculations give results which complete the picture of the charge distribution of the π-electrons obtained by the PPP method.[3] From the PPP calculations, it is found that the addition of a phenyl group at position 2 of benzopyrylium only moderately perturbs the charge distribution of the parent compound (even when the phenyl group is assumed to be coplanar with the benzopyrylium part of the flavylium compound). Hence the results from the present calculations may also be used to describe the charge distribution of the benzopyrylium part of the corresponding flavylium compounds.

Fig. 1 shows the charge distribution of pyrylium, benzopyrylium, and several of its monohydroxy derivatives. It can be seen that increasing the size of the conjugated system does not change the charge distribution of the pyrylium part of the benzopyrylium ion to any great extent. The absolute values of the charges at positions 2 and 3 increase slightly and this increase is matched with a corresponding decrease in the absolute value of the charges at positions 9 and 10. The charge of the ring oxygen atom is slightly more negative in the benzopyrylium compounds (-0.08 to -0.12) than in pyrylium itself (-0.06).

Of particular interest is the distinct difference between the charges of the two types of oxygen atoms in the hydroxybenzopyrylium compounds. The charge of the ring oxygen atom is approximately -0.10 whereas the charge of the hydroxyl oxygen atom is approximately -0.25. Preliminary ESCA

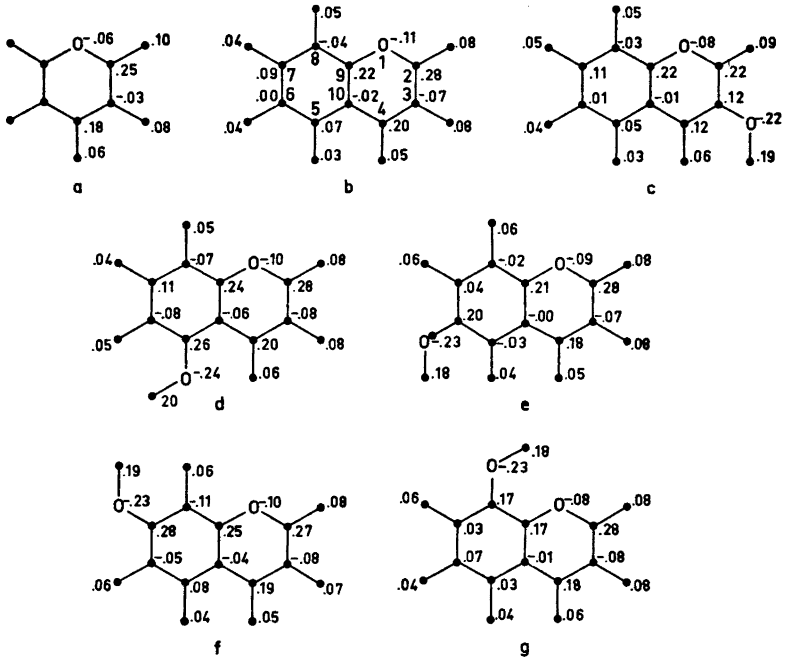


Fig. 1. All valence electron charge distribution of some pyrylium compounds in the CNDO/2 approach: a) pyrylium; b) benzopyrylium; c) 3-hydroxybenzopyrylium; d) 5-hydroxybenzopyrylium; e) 6-hydroxybenzopyrylium; f) 7-hydroxybenzopyrylium; g) 8-hydroxybenzopyrylium.

(Electron Spectroscopy for Chemical Analysis) investigations [6] also indicate that this is the case.

The introduction of a hydroxyl group affects the parent benzopyrylium ion in two ways. A strong inductive effect leads to a positive charge on the carbon and hydrogen atoms adjacent to the hydroxyl oxygen atom and to a strong negative charge on that oxygen itself. The inductive effect more than neutralizes the mesomeric effect which works in the opposite direction. This last effect leads to a strong delocalization of the ionic charge. Of particular interest is the result that the nearest neighbours will be less positive when the hydroxyl group is introduced. This effect is particularly important in the case of 3-hydroxybenzopyrylium. The strongly positive charges at positions 2 and 4 (which to a great extent predominate the chemistry of pyrylium compounds), are damped by the hydroxyl group in the 3 position. This may be the explanation of the relative stability of the 3 hydroxylated flavylium compounds as compared to those lacking the hydroxyl group in position 3.

The positive charge of the hydrogen atoms of the ring system in benzopyrylium is fairly low (0.04 – 0.08) and changes very little with the substitution of the hydroxyl group. The hydrogen atom of this group, on the contrary, has a strong positive charge (0.18 – 0.20).

It should perhaps be pointed out that the twisting of the hydroxyl group about the C–O bond has only a small effect on the charge distribution. For instance, in 3-hydroxybenzopyrylium, the total valence electron energy of the molecule is insignificantly higher, when the hydrogen atom is rotated out from the molecular plane about the C–O bond and placed in the position most distant from the molecular plane (with no change in the C–O–H angle). The net charges of the carbon atoms in positions 3 and 4 change slightly with an increase of 0.1 between the planar and the most distant positions of the hydrogen atom. Other changes are small or none within the third decimal.

Acknowledgement. The authors would like to thank Professor P.-O. Löwdin for generous support.

REFERENCES

1. Mårtensson, O. Uppsala Quantum Chemistry Group, *Prelim. Research Report* QB 37 (1966).
2. Mårtensson, O. and Sundaram, K. Uppsala Quantum Chemistry Group, *Prelim. Research Report* QB 37 B (1966).
3. Bendz, G., Mårtensson, O. and Nilsson, E. *Arkiv Kemi* **27** (1967) 65.
4. Karlsson, G. and Mårtensson, O. *Theoret. Chim. Acta (Berl.)* **13** (1969) 195.
5. Pople, J. A., Santry, D. P. and Segal, G. A. *J. Chem. Phys.* **43** (1965) 129; Pople, J. A. and Segal, G. A. *Ibid* **43** (1965) 136; **44** (1966) 3289.
6. Lindberg, B. J. *Personal communication.*

Received February 5, 1970.