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Relationes

CNDO Calculation of the π-Electronic Structure and Barrier to Internal Rotation in Benzenesulphonic Acid

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The CNDO calculation of the charge densities and bond orders show a distinction between two extreme geometrical configurations of the benzenesulphonic acid, but the barrier to internal rotation of the sulphonic group about the C–S bond, calculated by the same method, has revealed that they are energetically equivalent.

1. Introduction

Some years ago we put forward a model of interaction between the sulphonic group and the benzene ring [1]. This model has been considered in the simple LCAO–MO method [1], as well as in the Pariser-Parr approximation [2–4]. In this model the conjugation between the sulphonic group and the π-electrons of the benzene ring is considered to be due to the presence of a vacant orbital centered on the sulphur atom in the sulphonic group. However, this model, which is similar to the Crawford's hyperconjugation model of toluene, might be valid only in the case the sulphonic group rotates freely about the $C-S$ bond. Such barriers to internal rotation are in general small quantities, and their physical origin is not entirely known [5].

In this paper the charge densities and the bond orders for benzenesulphonic acid (anion) as well as the barrier to internal rotation of the sulphonic group about the $C-S$ bond, were calculated by using the CNDO/2 variant of the CNDO method [6–9].

2. Results and Discussions

For practical calculation the two extreme geometrical configurations of the benzenesulphonic acid with we are concerning with are given in Fig. 1.

In the case of the configuration *A* the projection of one of the $S-O$ bonds lies along the x-axis, while this is rotated an angle of 30° about the $C-S$ bond in the case of the configuration *B*. The Broomhead and Nicol's data [10] were used as starting geometrical parameters. For $C-H$ bond length the standard distance of 1.08 Å was used.

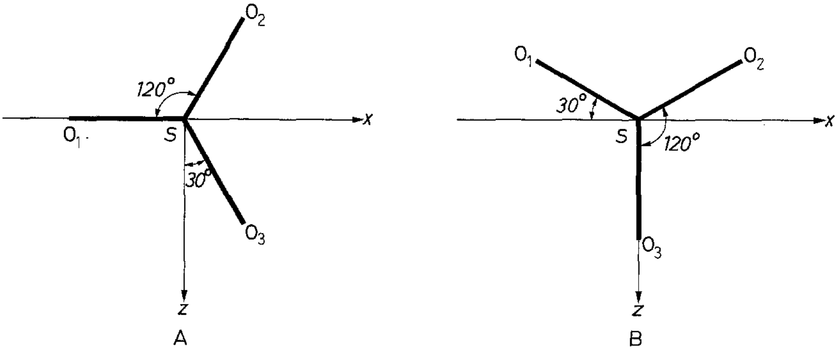

Fig. 1. Configurations A and B of benzenesulphonic acid (anion)

a) Charge Densities and Bond Orders

From the analysis of the charge distribution we observed that these are slightly different in the ring, but significantly modified in the substituent.

The π-electron distribution in the ring was different compared to that obtained in a Hückel MO type treatment [1], but in both cases the meta charge is greater than that located in the ortho position which is in agreement with the chemical nature of the sulphonic group.

From the π-bond order analysis the following conclusions were drawn.

1) The modifications of the bond orders in the ring under the rotation of the sulphonic group were insignificant.

2) The C–S bond has a very weak π-character and a small contribution of the sulphur $3d$ atomic orbitals to this.

3) In the case of the S–O bonds, which are of primarily interest for the present discussion, their physical nature appears to be different both from bond to bond and from configuration *A* to the configuration *B*.

b) Barrier to Internal Rotation

The experimental data [10] show that the three S–O bonds of the sulphonic group are identically, which seems to be contradictory to the above picture of the chemical bonds. But the above CNDO type description of the chemical bonds of the sulphonic group can be brought into the comparison with the experimental evidences if a free rotation of this group about the C–S bond is admitted. This fact suggested us the calculation of the barrier to internal rotation of the sulphonic group about the C–S bond from the configuration *A* to the configuration *B*. The energy difference between the configurations *A* and *B* was calculated as indicated by Pople and its coworkers [6], the calculated barrier being approximately 0.038 kcal/mol. As we know, this barrier has never been measured experimentally. Nevertheless, the magnitude of this barrier is of considerable theoretical importance for the understanding of the physical nature of the chemical bonds in the sulphonic group. So, the smallness of this barrier indicates a free rotation of the sulphonic group about the C–S bond. In view of this remark the three S–O bonds appear as equivalent. This remark is in agreement both with experimental observation and with the interpretation of the interaction between the sulphonic group and the benzene ring [1] in the same manner as in the case of toluene [11].

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