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Electronic Structure of BF_3-Benzaldehyde

Eduardo A. Castro and O. M. Sorarrain
Facultad de C. Exactas, Dpto. de Fisica, La Plata, CC N°67, Argentina

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Two different models were assumed for BF_3-benzaldehyde: a charge transfer complex and a $\sigma-\sigma$ one. The CNDO/2 and the Mulliken's population analysis were used. From the given numerical results we clearly conclude a $\sigma-\sigma$ model. An electronic migration from benzaldehyde to BF_3 and other results of the population analysis are also discussed.

Introduction

Two structures have been given for the boron trifluoride-benzaldehyde complex: a) charge transfer complex [1] and b) complex of $\sigma-\sigma$ type [2]. The purpose of the present paper is to find the B–O of equilibrium, to study the electronic structure of the complex for the equilibrium distance and to discuss the changes in electronic charges for both components in the complex, respect to the lonely ones. We have used the CNDO/2 approximation [3] as method of calculation, with a Mulliken's population analysis [4].

Method of Calculation and Model Employed

We used a standard programme [5]. The internuclear distances were taken as shows Table 1.

In order to make the conformational analysis we took the BF_3 molecule with a planar configuration [6–10] at a distance of 20Å (distance B–O in the x axe) and then we were changing that distance up to 10Å. This planar configuration was assumed perpendicular to the plane of the benzaldehyde molecule. From 10Å we continued with the variation of the B–O distance, meanwhile we have changed the spatial configuration of the BF_3 molecule from a planar to a tetrahedral one [11–13]; simultaneously the B–F distance was modified up to the tetrahedral equilibrium one.

Table 1. Internuclear distances (see Fig. 1)

Atoms	r(Å)
C–O	1.24
B–F(s) $s=16, 17, 18$	1.30
C(1)–C(2)	1.48
C(p)–C($p+1$) $p=1, \ldots, 6$	1.39
C–H	1.08

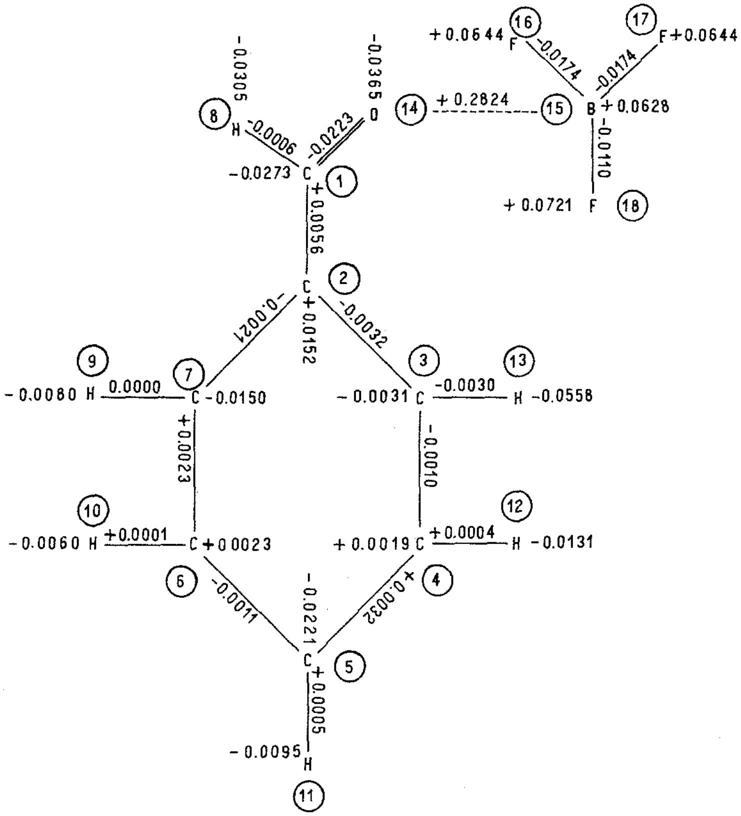
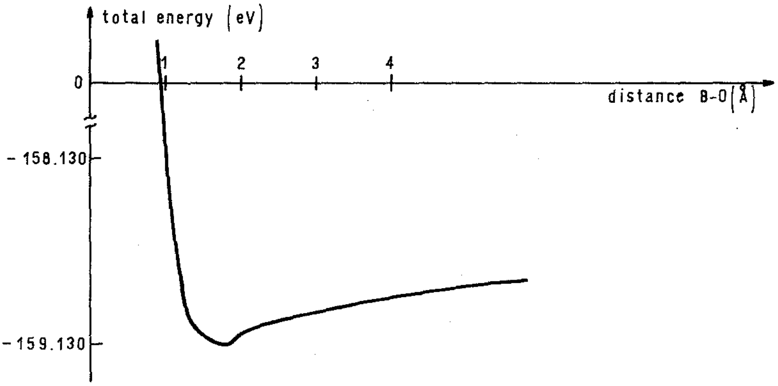


Fig. 1



Total energy as a function of B-O distance

Fig. 2

Numerical Results and Discussion

A) Conformational Analysis

As a criterion for the equilibrium molecular geometry we have taken the absolute minimum for the total energy of the system [14]. In Fig. 2 we give the total energy as a function of the B–O distance; an absolute minimum occurs at 1.8Å, then it is not possible to have a charge transfer complex [15].

In similar compounds, but with a less voluminous substituent, the equilibrium distance between B and O was found to be about 1.5Å [12]. In the actual case the difference in 0.3Å may be due to a steric hindrance between H(13) and F(18) (see Fig. 1).

B) Population Analysis

The F(16) and F(17) are not in the same molecular plane than the remaining elements, so it is not possible to divide their bonds with B in σ and π types. For the other F, B and C atoms we have orbitals of π type. The atomic orbitals in the molecular plane (px and py) have a non-zero overlapping with the $2s$ orbitals of the neighborhood elements, then they give a contribution to σ molecular orbitals.

In Fig. 1 the numerical results are given at the equilibrium distance (differences in electron and overlap populations between the total values for the complex and for the isolated molecules BF_3 and benzaldehyde). We took a tetrahedrical structure for the free BF_3, which is ficticius, but adequate for comparative purposes.

From the numerical results we can see that there are not appreciable variations for the C atoms, except in C(1). For the remaining elements there are weak changes (increase of positive charge) for the H atoms, and remarkable ones for the O, B and F (a decrease for O and an increase for the B and F of negative charge). Then, there is an electronic transfer from benzaldehyde to BF_3 which is in agreement with the experimental results about the pseudo-substituent CHO : BF_3 [2]. For the B–O bond we notice there is an appreciable overlap population at the equilibrium distance. It is due to a lowering in the populations of another bonds such as B–F and mainly C(1)–O, as we can see in Fig. 1. The C–H populations remain practically constant, for the C–C ones only a small change is observed. Then, there are important contributions from C(1) and O to the B–O bond and we can see also contributions from the H atoms for the increased negative changes in the F atoms.

Finally we can say that the B–O bond formation in the benzaldehyde–BF_3 complex imply a whole transference of negative charges from the benzaldehyde to the BF_3 molecule, being the principal donors the C(1), O and H atoms. From this bond formation all the overlap populations in the C–C and C–H bonds remain practically constant, being the C(1)–O and the B–F populations those that change appreciably.

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Dr. Eduardo A. Castro
Facultad de Ciencias Exactas
Departamento de Fisica
La Plata, CC N°67
Argentina