Ab-Initio Crystal Orbital Study of One-Dimensional Hydrogen Bonded Chain-Formic Acid

M. Kertesz

Central Research Institute Chemistry, Hungarian Academy Sciences, Budapest

J. Koller, E. Zakrajšek, and A. Ažman

Chemical Institute Boris Kidrič, University, Ljubljana

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Ab initio crystal orbital calculations on the β- and α-form are described. The binding energies and charge rearrangement in hydrogen bonded chains are discussed.

Infrared spectroscopy[1, 2] has been a very useful tool to elucidate the form of the crystal phase of formic acid. Two different modifications (Fig. 1) were discovered[1] and one of them was studied by X-ray[3]. This form, known as β-form has been widely studied by IR spectroscopy. The normal coordinate calculation has been done with the assumption that the β-form represents a one dimensional infinite chain.

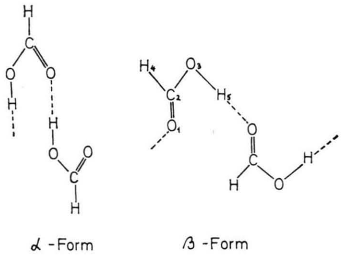

Fig. 1. α- and β-form of formic acid.

The approach we have used in determining the electronic structures of the β- and α-form of formic acid has been described elsewhere[4]. We have used an ab-initio crystal orbital method[5] with one molecule in the unit cell, with next neighbours interaction and with the minimal basis set STO-3G of Pople et alias[6]. The geometry of the β-form was taken from an X-ray study[3] with the O_3H_5 distance as estimated by Mikawa et alias[1]. The geometry parameters of the α-form were taken to be the same as in the β-form, except for the necessary modifications in the angles $(C-O-H)$ and $(C=O...O)$. The charges derived from a Mulliken population analysis and the stabilization energies (ΔE in kcal/mol) are given in Table 1.

Table 1. Charges and stabilization energies (ΔE).

Charges on	monomer [a]	dimer [b]	β-form	α-form
O_1	8.28	8.29	8.37	8.04
C_2	5.73	5.74	5.68	6.15
O_3	8.32	8.36	8.43	8.07
H_4	0.92	0.95	0.91	0.94
H_5	0.75	0.73	0.61	0.80
ΔE	—	7.53	15.37	1.88

[a] geometry from Ref. 7.

[b] geometry as in the β-form; charges on atoms from the proton donor part of the dimer except on O_1 (proton acceptor).

The β-form is predicted to be much more stable than the α-form. The reason for the very small binding energy of the α-form partially comes from the geometry we have used. The stabilization energy of the β-form reflects the large cooperative effect of the hydrogen bonding. In hydrogen bonded systems the rearangement of charges is very pronounced. Since the treated systems are planar the charges can be decomposed into contributions from atomic σ and π orbitals (Table 2).

The charge rearangement influenced by hydrogen bonding is interesting. The σ and π rearrangements on two oxygens directly involved in hydrogen bond-

Table 2. σ and π charges.

$\sigma(\pi)$ charges on	monomer	dimer [a]	β-form
O_1	7.03 (1.25)	6.95 (1.35)	6.96 (1.42)
C_2	4.80 (0.93)	4.83 (0.92)	4.83 (0.85)
O_3	6.49 (1.82)	6.57 (1.78)	6.70 (1.74)

[a] charges on atoms from proton donor part of the dimer except on O_1 (proton acceptor).

Reprint requests to Dr. A. Ažman, Chemical Institute Boris Kidrič, University of Ljubljana, Murnikova 6 — P. O. B. 537, *61001 Ljubljana* (Jugoslawien).

ing are different. Both oxygens gain charges in almost the same amount. The proton accepting atom O_1 looses σ charge but gains π charge. The situation with O_3 is just the reverse. The π charge on O_1 and σ charge on O_3 increase to a very large extent with the formation of the hydrogen bond. Since the basis set does not include p orbitals on hydrogens involved in the hydrogen bonds, the π charge flow through the chain is very small. The rearangements mentioned above appear through $\sigma-\pi$ interaction initiated by hydrogen bonding. The energy bands of the β-form are given in Figures 3, 4. No experimental data are known and therefore only tentative assignments of bands are given:

$$\mathrm{ls}(O_3)\,;\quad \mathrm{ls}(O_1)\,;\quad \mathrm{ls}(C)\,;\quad \sigma(CO_3)+\sigma(CO_1)\,;\quad \sigma(CO_1)+\sigma(CO_3)\,;$$
$$\sigma(CH)\,;\quad \sigma(OH)\,;\quad \mathrm{lp}(O_1)+\mathrm{lp}(O_3)\,;\quad \pi(OCO)\,;$$
$$\mathrm{lp}(O_3)+\mathrm{lp}(O_1)\,;\quad \mathrm{lp}(O_1)+\mathrm{lp}(O_3)\,;\quad \pi(OCO)\,.$$

The assignments of unoccupied bands are:

$$\pi(OCO)\,;\quad \sigma(OH)+\sigma(CH)\,;\quad \sigma(CH)+\sigma(OH)\,.$$

The assignments of all σ and lone pair (lp) bands are very approximative since there is much mixing between them. Both the β- and α-form are insulators. The energy gaps are 0.653 a.u. for the β- and 0.597 a.u. for the α-form at the edges of the zones ($k=\pi/a$).

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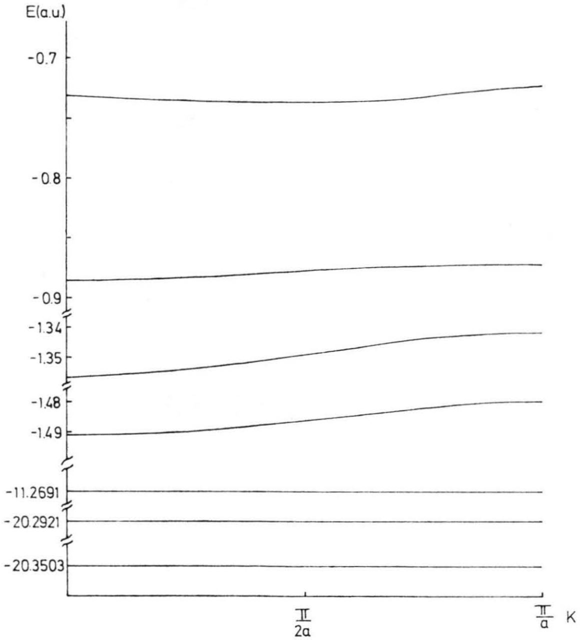

Fig. 2. Energy bands of the β-form.

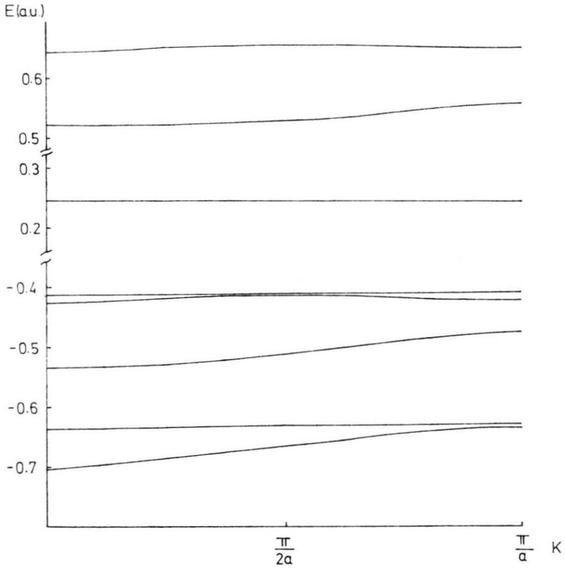

Fig. 3. Energy bands of the β-form (continuation of Fig. 2).

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