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On the Electrical Conductivity of Hydrogen Bonded Biological Systems

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The LCAO MO method with Bloch eigenfunctions has been applied to the imidazole crystal to evaluate the anisotropy of current carriers mobilities. The results obtained for the exponent of 0.45 of the $2p$ hydrogen orbital of the hydrogen bond implied in the calculation are in qualitative agreement with experimental data for electrical conductivity. The possible role of the $2p$ hydrogen orbital of the hydrogen bond for the charge transfer of biological systems is pointed out.

The hydrogen bonded biological systems like DNA [1] and a number of complementary bases [2, 3] show a relatively high electrical conductivity in the solid state. Intermolecular hydrogen bonding resulting in an infinite structure seems to be responsible for the fact that the conductivity of these systems is several orders higher than that of centrosymmetric dimers (Table 1) where conjugation is restricted only to two hydrogen bonded molecules. It should be noted that the activation energies are much lower in the first case. On the other hand the role of hydrogen bridges in the electrical conductivity seems to be distinct in the compounds where the maximal current is observed along the direction of hydrogen bonds [7, 8].

Table 1. *Electrical conductivity* σ *at 15° C and activation energy* E *found by the relation* $\sigma = \sigma_0 \exp(-E/2kT)$ *for some hydrogen bonded biological systems. For the sake of comparison values of* σ *and* E *for some compounds existing as centrosymmetric dimers are given*

Compound	σ_{15} ohm^{-1} cm^{-1}	E eV
DNA	$4.1 \cdot 10^{-16}$ [1]	2.42 [1]
purine	$1.0 \cdot 10^{-11}$ [2]	2.45 [2]
xanthine	$2.5 \cdot 10^{-16}$ [2]	1.34 [2]
hypoxanthine	$2.5 \cdot 10^{-16}$ [2]; $1.0 \cdot 10^{-15}$ [3]	1.59 [2]; 2.20 [3]
thiamine	$1.4 \cdot 10^{-14}$ [2]	2.41 [2]
guanine	$8.8 \cdot 10^{-16}$ [3]	1.96 [2]; 2.20 [3]
adenine	$1.0 \cdot 10^{-15}$ [3]	2.6 [2]; 1.80 [3]
cytosine	$2.0 \cdot 10^{-15}$ [3]	2.4 [2]; 2.80 [3]
thymine	$2.2 \cdot 10^{-15}$ [3]	2.4 [2]; 2.18 [3]
uracil	$2.0 \cdot 10^{-15}$ [2]	2.72 [2]; 2.76 [3]
Centrosymmetric dimers:		
benzoic acid	$5 \cdot 10^{-20}$ [4]	3.66 [4]
salicylic acid	$5 \cdot 10^{-24}$ [5]	5.00 [5]
phthalic acid	$5 \cdot 10^{-27}$ [4]	5.4 [4]
2-naphthoic acid	$5 \cdot 10^{-23}$ [6]	4.2 [6]

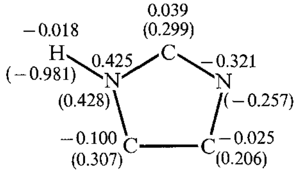

Fig. 1. π-electron densities for the imidazole molecule. (SCF orbitals, $Z_H = 0.45$. In parentheses the results for the excited state are given)

The essence of the problem seems to lie in the hydrogen bonding itself. Among other contributions the empty $2p$ hydrogen orbital may play a role in the charge migration [9]. The role of the $2p$ hydrogen orbital in the electrical conductivity has been studied in this paper within the framework of the tight binding approach which seems to be more adequate than the standard LCAO MO method knowing that the biological systems form periodic three-dimensional structures. As a biological model substance imidazole has been chosen whose crystal structure is fully known [10]. In the approach used here crystal orbitals were constructed as a linear combination of molecular π-orbitals

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \sum_{s} c_{\boldsymbol{n},s} \, \psi_s(\boldsymbol{r} - \boldsymbol{r}_{\boldsymbol{n}} - \boldsymbol{r}_s) \tag{1}$$

where $\psi_s(\boldsymbol{r} - \boldsymbol{r}_{\boldsymbol{n}} - \boldsymbol{r}_s)$ is the highest occupied (for hole) or the lowest empty (for electron) π-orbital described in the crystal by indices $\boldsymbol{n} = (n_a, n_b, n_c)$ and s. The vector $\boldsymbol{r}_{\boldsymbol{n}}$ shows the center of a unit cell with indices n_a, n_b, n_c. The Hückel molecular orbitals (using Pullman's [11] parametrization) or the SCF LCAO MO orbitals (with the Imamura *et al.* [12] parametrization) were used throughout the calculation. The electronic structure of the imidazole molecule calculated with the $2p$ hydrogen orbital is shown in Fig. 1.

By neglecting overlap as well as intermolecular resonance integrals for atoms being more than 5 Å apart, the energy matrix may be expressed [13] as a function of the wave vector $\boldsymbol{k}$ by

$$\begin{pmatrix} E_{us} \\ E_{gs} \\ E_{ua} \\ E_{ga} \end{pmatrix} = 2 \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \begin{pmatrix} H_{11}(0,0) \\ H_{21}(0,0) \cos \boldsymbol{k} \cdot (\boldsymbol{a} - 2\boldsymbol{x} + \boldsymbol{b} - 2\boldsymbol{y} + \boldsymbol{c} - 2\boldsymbol{z}) \\ H_{31}(0,0) \cos \boldsymbol{k} \cdot (0.5\boldsymbol{b} - 2\boldsymbol{y} + 0.5\boldsymbol{c}) \\ H_{41}(0,0) \cos \boldsymbol{k} \cdot (\boldsymbol{a} - 2\boldsymbol{x} + 0.5\boldsymbol{b} + 0.5\boldsymbol{c} - 2\boldsymbol{z}) \end{pmatrix} + 2\boldsymbol{I}\, H_{11}(\boldsymbol{u}, 0) \cos \boldsymbol{k} \cdot \boldsymbol{b} \tag{2}$$

where $\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z}$ are standard coordinates for molecule 1 of the imidazole $C_{2h}^5 - P2_1/c$ space group. The $\boldsymbol{I}$ is the unit matrix and the vector $\boldsymbol{u}$ has the components of $\boldsymbol{u} = (0, 1, 0)$ [13].

The intermolecular resonance integrals $H_{11}(0,0)$, $H_{21}(0,0)$, … $H_{11}(\boldsymbol{u}, 0)$ have been evaluated theoretically using STO's with exponents of 3.08 and 3.69 for carbon and nitrogen, respectively. The proton of the hydrogen bond was either treated as an isolated molecule or was assumed to form the common π-electronic system with the imidazole ring. The whole calculation was repeated for several values of the exponent for the $2p$ hydrogen orbital assumming an orientation of the $2p$ orbital parallel to the $2p\pi$ orbitals in the adjacent imidazole unit.

Table 2. *Calculated anisotropy of current carriers mobilities for imidazole disregarding hydrogen compared with the experimental relative conductivity*

Mobility ratio	Hole	Electron	Relative experimental conductivity
$\mu_{bb}/\mu_{a'a'}$ [a]	4.25	0.94	3.6
$\mu_{cc}/\mu_{a'a'}$	0.06	0.12	3.6
μ_{cc}/μ_{bb}	0.02	0.13	1.0

[a] a' is the axis perpendicular to the (100) plane.

Table 3. *Calculated anisotropy of electron mobility for several values of the effective nuclear charge of the hydrogen atom considered as an isolated molecule*

Mobility ratio	$Z_H = 0.3625$	$Z_H = 0.45$	$Z_H = 0.575$	$Z_H = 1.0$
$\mu_{bb}/\mu_{a'a'}$	490	27.22	4.85	1.71
$\mu_{cc}/\mu_{a'a'}$	268	27.66	14.10	11.84
μ_{cc}/μ_{bb}	0.55	1.02	2.91	6.94

Table 4. *Calculated anisotropy of mobilities for imidazole when the 2p hydrogen orbital is conjugated with the imidazole ring*

Mobility ratio	Hückel orbitals[a], $Z_H = 0.45$		SCF orbitals[b], $Z_H = 0.45$	
	Hole	Electron	Hole	Electron
$\mu_{bb}/\mu_{a'a'}$	2.38	57.38	2.35	14.02
$\mu_{cc}/\mu_{a'a'}$	0.25	19.39	0.25	12.35
μ_{cc}/μ_{bb}	0.11	0.34	0.11	0.88

[a] Pullman parametrization [11].
[b] Imamura *et al.* parametrization [12].

The calculated anisotropy of current carriers mobilities obtained for the constant relaxation time is listed in Tables 2–4. Disregarding the 2*p* hydrogen orbital the calculated anisotropy of mobilities (Table 2), especially along hydrogen bridges (*c*-axis) is lower than that of electrical conductivity. Therefore it seems that the method does not consider the role of hydrogen bonding satisfactorily. There is an improvement of the results of the anisotropy for the electron when the 2*p* hydrogen orbital is involved in the calculation (Table 3 and 4). The results depend, however, on the exponent of the 2*p* hydrogen orbital, and the qualitative agreement with the experimental anisotropy of conductivity is obtained for the hydrogen effective nuclear charge of 0.45. According to the symmetry of the imidazole unit cell the bands are splitted into four (or eight) Davydov components and the bandwidths are of the order of 1 eV. It should be noted that the role of the three-center integrals involving those of the HB potential is not significant.

The model used involves some crude simplifications as well as great uncertainty in the evaluation of the intermolecular resonance integrals contributed from the 2*p* hydrogen orbital. Thus, the results obtained here should be considered as rather qualitative. They allow, however, to understand the relatively high electrical conductivity of hydrogen bonded systems (Table 1) and to explain the higher conductivity along the hydrogen bonds [7, 8]. Furthermore, according to the Pullman concept [9] our results corroborate a possible role of the $2p$ hydrogen orbital in a charge transport of molecular solids.

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References

1. Eley, D. D., Spivey, D. I.: Trans. Farad. Soc. **58**, 411 (1962).
2. Basu, S.: J. physic. Chem. **67**, 1563 (1963).
3. Mesnard, G., Vasilescu, D., Mathon, Y.: Phys. stat. sol. **11**, K 137 (1965).
4. Gravatt, C. C., Gross, P. M.: J. chem. Phys. **46**, 413 (1967).
5. Gumiński, K., Wolter, K.: Roczniki Chem. **36**, 713 (1962).
6. Grzybowska, B., Gumiński, K.: Roczniki Chem. **34**, 1771 (1960).
7. Pigoń, K., Chojnacki, H.: Acta physica polon. **31**, 1061 (1967).
8. — — Acta physica polon. **31**, 1069 (1967).
9. Pullman, A.: Modern quantum chemistry, O. Sinanoğlu Ed., Part 3, p. 283. New York-London: Academic Press 1965.
10. Martinez-Carrera, S.: Acta crystallogr. **20**, 783 (1966).
11. Pullman, A.: C. R. Acad. Sci. Paris **256**, 5435 (1963).
12. Imamura, A., Fujita, H., Nagata, Ch.: Bull. chem. Soc. Japan **40**, 522 (1967).
13. Chojnacki, H., Gołębiewski, A.: Molecular Crystals **5**, 317 (1969).
14. Cardew, M. H., Eley, D. D.: Discuss. Farad. Soc. **27**, 161 (1959).

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