Theoret. chim. Acta (Berl.) 12, 373—378 (1968)

Electronic Spectrum and π-Electron Delocalization of Imidazole

Their Relation to the Electrical Conductivity

H. CHOJNACKI

Department of Physical Chemistry, Wrocław Technical University, Wyb. Wyspiańskiego 27, Poland

Received July 29, 1968

The electronic spectra of imidazole chains involving one, two, and three molecules have been calculated within the framework of the semiempirical SCF LCAO MO CI method. The first $\pi \rightarrow \pi^*$ singlet transition is in very good agreement with that known from experiment. The results indicate the possibility of existence of band structure, giving a bandwidth of the order of 0.6 eV. There is, however, no correlation between electrical parameters and the spectral data as could be expected from the Evans and Gergely model of delocalization of π-electrons across the hydrogen bonds. Such a delocalization produces only a small extra effect on the system compared with the isolated molecule.

Die Elektronenspektren von Imidazolketten aus ein, zwei und drei Molekülen sind im Rahmen der semiempirischen SCF LCAO MO CI-Methode berechnet worden. Der erste $\pi \rightarrow \pi^*$ Singulettübergang stimmt sehr gut mit dem Experiment überein. Es wird auf die Möglichkeit einer Bandstruktur mit einer Breite von 0,6 eV geschlossen. Allerdings besteht keine Korrelation zwischen elektrischen Parametern und Spektraldaten, wie es das Delokalisationsmodell für π-Elektronen von Evans und Gergely erwarten läßt. Solch eine Delokalisation über Wasserstoffbrücken hinweg zeigt lediglich kleine Rückwirkungen auf das System mit dem isolierten Molekül.

Calcul du spectre électronique de chaînes comportant une, deux et trois molécules d'imidazole, dans le cadre de la méthode SCF LCAO MO CI. La première transition singulet $\pi \rightarrow \pi^*$ est en très bon accord avec celle observée. Les résultats indiquent qu'une structure de bande, de largeur 0,6 eV environ, est possible. Il n'y a cependant aucune corrélation entre les paramètres électriques et les données spectrales comme on aurait pu en attendre du modèle d'électrons π délocalisés à travers les liaisons hydrogène dû à Evans et Gergely. Une telle délocalisation n'introduit qu'une faible perturbation dans le système par rapport à la molécule isolée.

The problem of the possibility of existence of energy bands in hydrogen-bonded molecular solids was started by the Szent-Györgyi hypothesis [21] later applied by Evans and Gergely [5] to the protein structure. They thought that a protein macromolecule may behave as a metal-like structure or a semiconductor so that it is able to transmit energy to some points remote from the apparent reaction site [20].

The essence of this hypothesis is that in such a system delocalization of π-electrons can occur across the hydrogen bonds. The merging of the discrete π-energy levels of a great number of the peptide units give rise to the formation of the energy bands. According to that model only excitation of electrons to the empty band should be responsible for conducting properties of these materials. There is, however, no full experimental spectral data for those systems and the energy gaps being obtained from calculations depend considerably on the approximation used. The most trustworthy theoretical results may be obtained by the use of more advanced quantum chemical treatments which, however, implicate a number of difficulties in the case of macromolecules. Moreover, there is no reliable experimental information concerning semiconductive properties of the above systems. In this case the results are strongly dependent on purity of a material and water traces which are difficult to remove completely from a polycrystalline sample.

It seems that a comparison between experimental or theoretical spectral data and the conducting properties of hydrogen-bonded molecular solids is more suitable when the electrical parameters for single crystals are known [18]. As a model substance for this purpose the imidazole molecule has been chosen. In its crystal lattice molecules are linked with each other by hydrogen bonds of 2.86 Å in length, the angle between π-orbitals of the adjacent molecules being of 61.5° [12]. Thus molecules form infinite chains extending in a crystal along the c-axis. The activation energy for electrical conductivity for polycrystalline pellets [3] as well as for single crystals [17] of finely purified imidazole by zone-melting are well known. The anisotropy studies [17] show that its electrical conductivity is larger along the hydrogen bonds than in the perpendicular directions. The imidazole ring being the constituent part of biologically important compounds like adenine, guanine, and their derivatives, is also of great interest.

To make a correlation between electrical and spectral data, the electronic structure of imidazole has been calculated. The calculation was carried out for a isolated molecule, as well as for two molecules (dimer), and three molecules (trimer) situated within the imidazole chain and the respective systems were treated as one molecule. It will be noted that the similar situation is to be found in a solution where existing finite chains are built up of a number of imidazole molecules. The calculation was made in order to obtain some information on the effect of π-orbital interactions along the hydrogen bond direction in the electronic states. The proton of a hydrogen bond, at least at a first stage, was not taken into account.

Method and Parametrization

The calculation of the electronic structure of imidazole has been carried out within the framework of the semiempirical Pariser-Parr-Pople method [16]. The approach of zero differential overlap was used, the diagonal and non-diagonal elements of the total π-electron Hamiltonian being evaluated from the following relationships

$$H_{ii} = U_i + 1/2\, P_{ii}(ii|ii) + \sum_{j\neq i} (P_{jj} - n_j)(ii|jj) \tag{1}$$

$$H_{ij} = \beta_{ij} - 1/2\, P_{ij}(ii|jj) \tag{2}$$

respectively. n_j of Eq. (1) is a number of electrons contributed by the atom j to the π-electron system. The U_i's are expressed by the relation

$$U_i = I_i - \sum_{j\neq i} (j|ii) - \sum_{k} (k|ii) \tag{3}$$

where the I_i's are the valence state ionization potentials and the last two terms are penetration integrals. Assuming more appropriate values for U_i [1] than that of $U_i = I_i$ usually taken, allowance is made for penetration integrals. The resonance integrals β_{ij} for a bond between $i-j$ atoms were calculated by the use of the Kon-formula [16], the terms for non-neighbouring atoms being included. For C–C (1.39 Å), C–N (1.34 Å), and N–N (1.33 Å) bonds β_{ij} was assumed to be -2.39 eV, -2.576 eV, and -2.35 eV respectively. The angle dependence of intermolecular resonance integrals was taken into account by the relation

$$\beta_{ij}^{\theta} = \beta_{ij} \cos\theta \tag{4}$$

where θ is the angle between $i-j$ π-orbitals. The Coulomb repulsion integrals $(ii|jj)$ were evaluated by the Mataga-Nishimoto formula [13] corrected by Gołębiewski and Parczewski [9] for non-planarity effect

$$\begin{aligned}(ii|jj) = {} & 1/(R_{ij} + a_{ij}) \times [(2/R_{ij} + 2/(R_{ij}^2 + 4b_{ij}^2))^{1/2}]^{-1} \\ & \times \sum_{m=1}^{2} \sum_{n=1}^{2} \{R_{ij}^2 + b_{ij}^2[\underline{h}_i + (-1)^m \underline{h}_j]^2 \\ & + (-1)^n \cdot 2b_{ij}R_{ij}\underline{e}_{ij} \cdot [\underline{h}_i + (-1)^m \underline{h}_j]\}^{-1/2} .\end{aligned} \tag{5}$$

The one-center terms $(ii|ii)$ and the constant a_{ij} were determined by the Mataga-Nishimoto method [13], the Hinze-Jaffe data [11] being used. The constant b_{ij} is the radius of the charged spheres calculated after the Gołębiewski-Parczewski procedure [9]. $\underline{e}_{ij}$ is the unit vector connecting atoms i and j; R_{ij} is the bond distance. $\underline{h}_i$ and $\underline{h}_j$ are unit vectors perpendicular to the ring planes which include atom i and j respectively. The other empirical parameters used in the calculation are listed in Table 1. The geometry of imidazole molecules was taken from X-ray experimental studies [12].

Table 1. *Semiempirical values of one-center coulomb repulsion integral $(ii|ii)$ and U_i parameters* [1] *(in Units of eV) used in the calculation*

Atom	$(ii\|ii)$	U_i
C	11.13	-9.5
N	12.34	-11.8
NH	12.34	-9.9

The energies of the excited states of imidazole were evaluated by the superposition of a number of singly excited configurations. Interconfigurational matrix elements were calculated after the McWeeny formalism [14]. Singly excited configurations within ca. 4 eV of the lowest excited one were included in the calculation. This leads to 4-th order secular equations for a monomer, 15-th order equations for dimer, and 33-rd order equations for trimer for each of the singlet and triplet states. It was found that multiply-excited configurations as well as those of higher energies had a negligible effect on lower-lying states. The oscillator strengths have been evaluated according to the procedure of Mulliken and Rieke [15].

Results and Discussion

The π-electronic energy levels calculated for isolated molecule, for dimer, and for trimer of the imidazole chain are listed in Table 2. The lowest $\pi \rightarrow \pi^*$ transitions are given in Table 3.

Unfortunately, there is no complete information from an experiment on the spectral data of imidazole. The first singlet excited state known from experiment [2, 6] is in very good agreement with its relevant calculated value. According to the results obtained by the Mataga-Nishimoto for Coulomb repulsion integrals [7] the same should be true for the higher singlet excited states. It is probable, however, that the first triplet excited state lies at higher energy than of our calculation. In general, the π-orbital interactions along the chain result in a rather small red shift of the imidazole absorption bands. For a fuller discussion of the calculated spectral properties more detailed experimental studies of higher excited states as well as the oscillator strengths of absorption bands would be welcome.

Table 2. *Calculated π-electronic energy levels for molecules within the imidazole chain (in units of eV)*

Single molecule	Dimer	Trimer
+ 2.60	+ 2.74 + 2.39	+ 2.81 + 2.54 + 2.33
+ 1.28	+ 1.46 + 1.07	+ 1.52 + 1.25 + 1.01
− 8.28	− 8.12 − 8.47	− 8.05 − 8.31 − 8.54
− 9.34	− 9.17 − 9.56	− 9.10 − 9.38 − 9.63
−13.62	−13.42 −13.81	−13.35 −13.61 −13.88

Table 3. *The lowest theoretical $\pi \rightarrow \pi^*$ transitions (in units of eV) and oscillator strengths (f) of singlet states for molecules of the imidazole chain*

Single molecule			Dimer			Trimer		
Singlets	*f*	Triplets	Singlets	*f*	Triplets	Singlets	*f*	Triplets
5.99	0.147	2.89	5.96 6.01	0.140 0.153	2.90 2.91	5.95 5.98 6.01	0.145 0.124 0.213	2.91 2.92 2.93
6.38	0.179	3.66	6.36 6.42	0.133 0.231	3.66 3.66	6.36 6.39 6.43	0.239 0.051 0.399	3.66 3.66 3.67
7.92	0.215	5.43	6.92 7.64	$0.87 \cdot 10^{-6}$ $0.72 \cdot 10^{-4}$	5.38 5.42	7.04 7.05 7.50	$0.76 \cdot 10^{-6}$ $0.26 \cdot 10^{-5}$ $0.33 \cdot 10^{-4}$	5.37 5.37 5.42

Table 4. *Comparison of the lowest electronic states of imidazole with its activation energy for electrical conductivity calculated by the relation* $\sigma = \sigma_0 \exp(-E/2kT)$ *(values in units of eV)*

$\pi \to \pi^*$ transitions			$n \to \pi^*$ transitions		Activation energy for conductivity	
Singlet		Triplet	Singlet	Triplet		
5.92 [2]	5.99 [6]	2.89[a]	4.98 [2]	—	2.2 [3]	2.0 [17]

[a] Calculated.

The results of our calculations point out the possibility of the existence of band structure in the imidazole crystal giving the bandwidth of the order of 0.6 eV. There is, however, a lack of correlation between electrical and spectral data as it could be expected from the Evans and Gergely model of delocalization of π-electrons across the hydrogen bonds [5]. It has not been established so far whether it is justified to evaluate the activation energy E for conductivity from the relation of $\sigma = \sigma_0 \exp(-E/2kT)$ instead of $\sigma = \sigma_0 \exp(-E/kT)$ [17]. It will be noticed that even for the first more favourable case neither the first singlet nor the first $\pi \to \pi^*$ triplet state agree with the thermal activation energy (Table 4). Up to now there have been no data in the literature on the possibility of participation of the $n \to \pi^*$ states in the dark electrical conductivity. In our case the first experimental $n \to \pi^*$ singlet transition lies at 4.98 eV [2] and it does not correspond to the energy gap

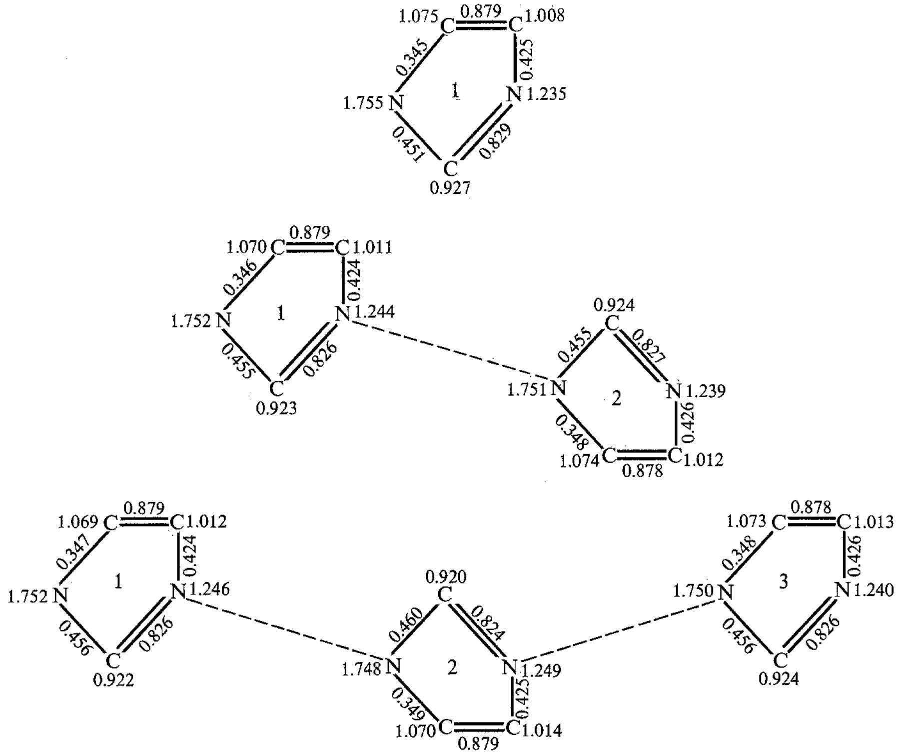

Fig. 1. π-electron densities and bond orders calculated for the imidazole chain. The results are given for monomer ("1"), as well as for dimer ("1–2"), and trimer ("1–2–3") respectively

of conductivity. Knowing the usual magnitude of the $n \rightarrow \pi^*$ singlet-triplet splitting the $n \rightarrow \pi^*$ triplet state should not participate in the conduction mechanism of imidazole either. Thus, similarly to the results of the Pullman calculation [19, 20], our results distinctly show that the model of excitation of electrons to the empty band bringing about intrinsic conducting properties of biological molecular solids seems to be questionable. In such a case another kind of charge transport mechanism may be possible. It is likely to be related to the participation of protons of the hydrogen bonds lowering the barrier height for the charge migration [8].

In Fig. 1 the charge densities and bond orders of imidazole π-electrons are presented. The π-electron dipole moment amounts to 2.44 *D*, 2.40 *D*, and 2.35 *D* for isolated molecule, for dimer, and for trimer respectively. The dipole moment of imidazole including its σ contribution [10] equals 4.35 *D*, 4.31 *D*, and 4.26 *D* for the three cases, whereas the experimental value is 3.99 *D* [4]. The ionization potential obtained from our calculation (Table 2) seems to be a reasonable value as well. In this case, similarly to the other electronic properties calculated for the imidazole chain, the π-orbital interactions along the hydrogen bond direction produce only a small extra effect on the system.

All the numerical calculations have been carried out on the Elliott 803 B digital computer.

Acknowledgment. The author wishes to express his indebtedness to Prof. Dr. K. Pigoń for revision of the manuscript.

References

1. Berthod, H., C. Giessner-Prettre, and A. Pullman: Theoret. chim. Acta (Berl.) **5**, 53 (1966).
2. Braude, E. A.: Annu. Repts. Progr. Chem. **42**, 105 (1945).
3. Brown, G. P., and S. Aftergut: J. chem. Physics **38**, 1356 (1963).
4. Chemical Abstracts **62**, 3494 g.
5. Evans, M. G., and J. Gergely: Biochim. biophysica Acta (Amsterdam) **3**, 188 (1949).
6. Friedel, R. A., and M. Orchin: Ultraviolet spectra of aromatic compounds. New York: J. Wiley 1951.
7. Galasso, V., G. De Alti, and A. Bigotto: Theoret. chim. Acta (Berl.) **9**, 222 (1968).
8. Gołębiewski, A., and H. Chojnacki: Acta physica polon. (in press).
9. —, and A. Parczewski: Theoret. chim. Acta (Berl.) **7**, 171 (1967).
10. Hamano, H., and H. F. Hameka: Tetrahedron **18**, 985 (1962).
11. Hinze, J., and H. H. Jaffé: J. Amer. chem. Soc. **84**, 540 (1962).
12. Martinez-Carrera, S.: Acta crystallogr. **20**, 783 (1966).
13. Mataga, N., and K. Nishimoto: Z. physic. Chem. Neue Folge **13**, 140 (1957).
14. McWeeny, R.: Proc. physic. Soc. A **70**, 593 (1957).
15. Mulliken, R. S., and C. A. Rieke: Rep. Progr. Physics **8**, 231 (1941).
16. Parr, R. G.: The quantum theory of molecular electronic structure. New York-Amsterdam: W. A. Benjamin, Inc. 1964.
17. Pigoń, K., and H. Chojnacki: Acta physica polon. **31**, 1069 (1967).
18. —, K. Gumiński, and J. Vetulani: Półprzewodniki organiczne (Organic Semiconductors). Warsaw: WNT 1964.
19. Pullman, A.: Biopolymers Symposia p. 29, No. 1 (1964).
20. — Modern Quantum Chemistry (O. Sinanoğlu Ed.), Part 3, p. 283. New York-London: Academic Press 1965.
21. Szent-Györgyi, A.: Science **93**, 609 (1941).

Dr. H. Chojnacki
Department of Physical Chemistry
Wrocław Technical University
Wyb. Wyspiańskiego 27
Wrocław, Poland