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The Electronic Structure of Periodic Protein Models
I. CNDO/2 and MINDO/2 Energy Band Structures of a Two-Dimensional Formamide Network

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The energy band structures of a two-dimensional polyformamide network have been calculated with the aid of the CNDO/2 and MINDO/2 crystal orbital method in the first neighbour's interactions approximation. For comparison also one-dimensional polyformamide chains have been computed with the same methods. The features of the obtained band structures are discussed.

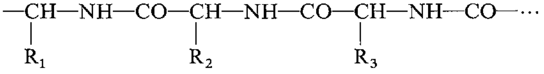
Es wurden die Energiebandenstrukturen eines zweidimensionalen Polyformamid-Netzwerkes in einer Näherung, die die Wechselwirkung der ersten Nachbarn berücksichtigt, mit Hilfe der CNDO/2 und MINDO/2 Kristallorbital-Methoden berechnet. Zum Vergleich wurden auch eindimensionale Polyformamid-Ketten unter Verwendung derselben Methoden berechnet. Die Eigenschaften der erhaltenen Bandenstrukturen werden diskutiert.

Calcul de la structure des bandes d'énergie d'un réseau bidimensionnel de polyformamide à l'aide des méthodes d'orbitales cristallines CNDO/2 et MINDO/2 dans l'approximation d'interaction des premiers voisins. A titre de comparaison les chaînes unidimensionnelles de polyformamide ont été calculées avec les mêmes méthodes. Discussion des caractéristiques des structures de bande obtenues.

Introduction

The electronic structure of proteins is of great importance from obvious reasons. The first approximate Hückel calculation of the π electronic band structure of a H—N—C═O···H—N—C═O··· infinite chain is due to Evans and Gergely [1] back in 1949, who have applied this model to describe the π electrons in proteins following the suggestions of Szent-Györgyi [2], Coulson [3] and Laki [4]. By extrapolating from the semiempirical SCF LCAO MO (PPP) energy levels of a monopeptide, dipeptide and tripeptide, respectively, Suard, Berthier, and Pullman [5] have obtained an approximate band structure of the infinite chain. A similar calculation has been performed by Yomosa [6]. The first proper treatment of the infinite π electron crystal orbitals in the tight binding approximation is due to one of the authors [7], followed by a similar treatment of Suard-Sender [8]. In this paper there is also a calculation of the π electronic structure of an infinite —NCO—NCO— chain.

On the other hand Brillouin [9] has proposed such a periodic model for proteins in which the NH—CO—CH_2 group of a protein forms the elementary cell. Introducing further side chain groups we obtain the



$$-\underset{\underset{R_1}{|}}{CH}-NH-CO-\underset{\underset{R_2}{|}}{CH}-NH-CO-\underset{\underset{R_3}{|}}{CH}-NH-CO-\cdots$$

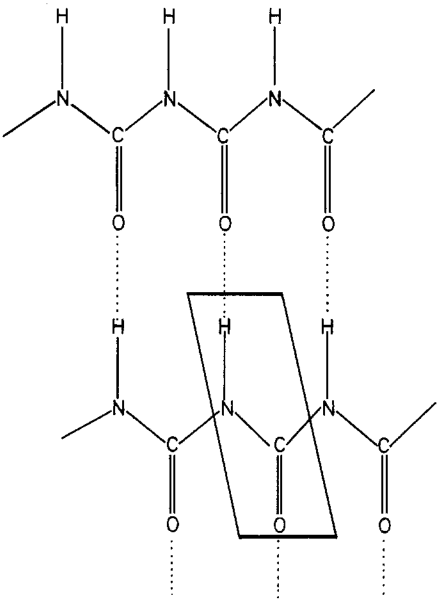


Fig. 1. The two-dimensional polyformamide network. The unit cell is indicated by a quadrangle

chain of the proteins, where the R_1, R_2 and R_3 etc. amino acid residues may play the role of impurities [9]. Following these ideas Fujita and Imamura [10] have performed an CNDO/2 crystal orbital (CO) calculation for the main chain of polyglycine. Most recently a similar calculation has been performed by Beveridge *et al.* for polyglycine in the INDO and MINDO/2 CO approximations [11].

It seems obvious to try to take into account simultaneously the interactions through the hydrogen bonds and along the main chain of polypeptides. Such a calculation requires the treatment of a polypeptide as a two-dimensional system. If we want to treat polyglycine as a two-dimensional periodic system from simple geometrical considerations it is clear that four glycine molecules form the elementary cell. The same difficulty arises in the case of other homopolypeptides. Therefore as a first step of this series of investigations on periodic protein models we have investigated as a very simple model system a two-dimensional formamide network in the CNDO/2 and MINDO/2 approximation. In this case as we can see from Fig. 1 a single formamide molecule forms the unit cell.

Method

It was shown [12] that in the case of a two-dimensional periodic system to obtain the band structure we have to solve the matrix eigenvalue equation

$$\boldsymbol{F}(k_1, k_2)\, \boldsymbol{c}_i(k_1, k_2) = \varepsilon_i(k_1, k_2)\, \boldsymbol{c}_i(k_1, k_2) \tag{1}$$

for different components k_1 and k_2 of the crystal momentum $\vec{k}$. Here if we introduce first neighbour's interactions only[1],

$$\begin{aligned} \boldsymbol{F}(k_1, k_2) &= \boldsymbol{F}(0,0) + \boldsymbol{F}(+1,0)\,e^{ik_1a_1} + \boldsymbol{F}(-1,0)\,e^{-k_1a_1} \\ &\quad + \boldsymbol{F}(0,+1)\,e^{ik_2a_2} + \boldsymbol{F}(0,-1)\,e^{-ik_2a_2}, \\ \boldsymbol{F}(-1,0) &= \boldsymbol{F}(+1,0)^{\mathrm{tr}}, \qquad \boldsymbol{F}(0,-1) = \boldsymbol{F}(0,+1)^{\mathrm{tr}} \end{aligned} \tag{2}$$

where a_1, a_2 are elementary translations along the main chain and the hydrogen bonds, respectively. The matrix $\boldsymbol{F}(0,0)$ belongs to the reference cell and the matrices $\boldsymbol{F}(+1,0)$, $\boldsymbol{F}(-1,0)$, $\boldsymbol{F}(0,+1)$ and $\boldsymbol{F}(0,-1)$ contain the interactions between the reference cell and its four different first neighbours.

The CNDO/2 form of the method has been described elsewhere [13]. In the MINDO/2 version of the method

$$\begin{aligned} F_{\mu,\mu}(0,0) = {} & U_{\mu,\mu} + \tfrac{1}{2} p_{\mu,\mu}(0,0)\,\langle\mu\mu|\mu\mu\rangle \\ & + \sum_{\substack{\nu\neq\mu \\ (\nu\in \mathrm{A})}} p_{\nu,\nu}(0,0)\,[\langle\mu\mu|\nu\nu\rangle - \tfrac{1}{2}\langle\mu\nu|\mu\nu\rangle] \\ & + \sum_{\mathrm{B}\neq\mathrm{A}} [p_{\mathrm{B,B}}(0,0) - z_{\mathrm{B}}]\,\gamma_{\mathrm{A,B}}(0,0) + \sum_{\mathrm{B}} [p_{\mathrm{B,B}}(0,0) - z_{\mathrm{B}}]\,[\gamma_{\mathrm{A,B}}(+1,0) \\ & + \gamma_{\mathrm{A,B}}(-1,0) + \gamma_{\mathrm{A,B}}(0,+1) + \gamma_{\mathrm{A,B}}(0,-1)], \qquad (\mu\in\mathrm{A}) \end{aligned} \tag{3}$$

$$F_{\mu,\nu}(0,0) = p_{\mu,\nu}(0,0)\,[\tfrac{3}{2}\langle\mu\nu|\mu\nu\rangle - \tfrac{1}{2}\langle\mu\mu|\nu\nu\rangle] \qquad (\mu\neq\nu,\ \mu,\nu\in\mathrm{A}), \tag{4}$$

$$\begin{gathered} F_{\mu,\nu}(0,0) = \Omega_{\mathrm{A,B}}(I_\mu + I_\nu)\,S_{\mu,\nu}(0,0) - \tfrac{1}{2} p_{\mu,\nu}(0,0)\,\gamma_{\mathrm{A,B}}(0,0) \\ (\mu\neq\nu,\ \mu\in\mathrm{A},\ \nu\in\mathrm{B},\ \mathrm{B}\neq\mathrm{A}) \end{gathered} \tag{5}$$

and finally

$$\begin{aligned} & F_{\mu,\nu}(q_1, q_2) = \Omega_{\mathrm{A,B}}(I_\mu + I_\nu)\,S_{\mu,\nu}(q_1, q_2) - \tfrac{1}{2} p_{\mu,\nu}(q_1, q_2)\,\gamma_{\mathrm{A,B}}(q_1, q_2), \\ & (\mu\in\mathrm{A},\ \nu\in\mathrm{B},\ q_1 = \pm 1 \text{ and } q_2 = 0, \text{ or } q_1 = 0 \text{ and } q_2 = \pm 1). \end{aligned} \tag{6}$$

For the one-center core integrals $U_{\mu,\mu}$ and the valence state ionization potentials appropriate values are given by Dewar *et al.* [15]. For all the one-center two electron integrals occurring in (3) and (4) the usual Slater-Condon parameters have been used [16]. The Coulomb integrals $\gamma_{\mathrm{A,B}}(q_1, q_2)$ were computed with the aid of the Ohno-Klopman expression [17]. Finally

$$p_{\mathrm{A,A}}(0,0) = \sum_{\mu\in\mathrm{A}} p_{\mu,\mu}(0,0), \tag{7}$$

$$\begin{aligned} p_{\mu,\nu}(q_1, q_2) = {} & \frac{a_1 a_2}{(2\pi)^2} \int_{-\pi/a_1}^{+\pi/a_1} \int_{-\pi/a_2}^{+\pi/a_2} \sum_{i=1}^{n^*} e^{i(k_1 q_1 a_1 + k_2 q_2 a_2)} \\ & \cdot c_{i,\mu}^{*}(k_1, k_2)\, c_{i,\nu}(k_1, k_2)\, dk_1\, dk_2, \qquad (q_1 = 0, \pm 1,\ q_2 = 0, \pm 1). \end{aligned} \tag{8}$$

The expressions used for the one-dimensional polyformamide systems, can be derived in a trivial way from the formalisms shown here.

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[1] It seems probable that in more accurate calculations at least second neighbour's interactions should be taken into account. Such investigations are in progress.

Table 1. The CNDO/2 and MINDO/2 band structures of an one-dimensional

CNDO/2 No. of band	E_{MO} and type of level	$E_{min}(k_2a_2)$	$E_{max}(k_2a_2)$	δE
		$R_{O\cdots H-N} = 2.66$ Å		
1	13.310 (σ)	13.599 (0)	13.654 (π)	0.055
2	11.890 (σ)	11.782 (π)	12.425 (0)	0.643
3	8.555 (σ)	8.274 (0)	9.414 (π)	1.140
4	4.274 (π)	4.486 (0)	4.529 (π)	0.043
5	1.224 (σ)	1.260 (π)	1.591 (0)	0.331
6	−14.023 (π)	−13.933 (π)	−13.743 (0)	0.190
7	−14.819 (σ)	−14.714 (π)	−14.104 (0)	0.610
8	−19.149 (σ)	−19.657 (π)	−17.863 (0)	1.794
9	−21.590 (σ)	−21.890 (π)	−21.184 (π/2)	0.706
10	−23.045 (π)	−22.109 (0)	−21.947 (π)	0.162
11	−24.611 (σ)	−27.005 (0)	−22.492 (π)	4.513
12	−37.922 (σ)	−39.292 (π)	−36.681 (0)	2.611
13	−44.420 (σ)	−45.173 (0)	−44.230 (π)	0.943
		$R_{O\cdots H-N} = 2.75$ Å		
1	13.310 (σ)	13.558 (0)	13.611 (π)	0.053
2	11.890 (σ)	11.799 (π)	12.375 (0)	0.576
3	8.555 (σ)	8.309 (0)	9.308 (π)	0.999
4	4.274 (π)	4.473 (0)	4.505 (π)	0.032
5	1.224 (σ)	1.271 (π)	1.552 (0)	0.281
6	−14.023 (π)	−13.933 (π)	−13.788 (0)	0.144
7	−14.819 (σ)	−14.742 (π)	−14.237 (0)	0.505
8	−19.149 (σ)	−19.626 (π)	−18.064 (0)	1.562
9	−21.590 (σ)	−22.088 (π)	−21.234 (π/4)	0.854
10	−23.045 (π)	−22.107 (0)	−21.983 (π/4)	0.124
11	−24.611 (σ)	−26.622 (0)	−22.526 (π)	4.096
12	−37.922 (σ)	−39.070 (π)	−36.877 (0)	2.193
13	−44.420 (σ)	−45.051 (0)	−44.255 (π)	0.796

The criterium of self consistency used in the calculations was

$$|p^{(l+1)}_{\mu,\nu}(q_1, q_2) - p^{(l)}_{\mu,\nu}(q_1, q_2)| \leqq 10^{-3}, \tag{9}$$

where the upper index l stands for the l-th iteration step. To fulfil this we needed usually 18–20 iterations in the CNDO and 12–14 ones in the MINDO case.

To diagonalize the Hermitian complex matrix (2) of order 13 (the number of valence orbitals in formamide) we have rewritten its eigenvalue equation (1) in the usual way [18] into a real form. The eigenvalue problems have been solved with the aid of a fast modified Givens program written by Neszmélyi [19].

Results

In Table 1 we present the CNDO/2 and MINDO/2 band structures of an one-dimensional polyformamide chain in which we have taken into account interactions only through the hydrogen bonds (see Fig. 1). In the Table the first column polyformamide chain (interactions through hydrogen bonds, all energy values in eV)

MINDO/2				
No. of band	E_{MO} and type of level	$E_{\min}(k_2 a_2)$	$E_{\max}(k_2 a_2)$	δE
		$R_{\mathrm{O}\cdots\mathrm{H-N}} = 2.66$ Å		
1	4.569 (σ)	5.079 (π)	5.115 (0)	0.036
2	3.877 (σ)	4.649 (0)	4.681 (π)	0.032
3	2.506 (σ)	2.785 (0)	2.906 (π)	0.121
4	0.389 (π)	0.509 (0)	0.526 (π)	0.017
5	− 1.312 (σ)	− 1.186 (π)	− 1.134 (0)	0.054
6	−11.102 (π)	−10.962 (π)	−10.879 (0)	0.083
7	−11.496 (σ)	−11.065 (π)	−10.919 (0)	0.144
8	−12.783 (σ)	−13.457 (π)	−12.191 (0)	1.266
9	−14.525 (π)	−14.535 (0)	−14.464 (π)	0.069
10	−15.126 (σ)	−15.417 (π)	−14.827 (0)	0.590
11	−17.632 (σ)	−19.535 (0)	−16.191 (π)	3.344
12	−31.779 (σ)	−33.285 (π)	−29.861 (0)	3.424
13	−38.725 (σ)	−43.356 (0)	−38.122 (π)	2.234
		$R_{\mathrm{O}\cdots\mathrm{H-N}} = 2.75$ Å		
1	4.569 (σ)	4.884 (π)	4.933 (0)	0.048
2	3.877 (σ)	4.614 (0)	4.652 (π)	0.038
3	2.506 (σ)	2.753 (0)	2.876 (π)	0.122
4	0.389 (π)	0.500 (0)	0.514 (π)	0.012
5	− 1.312 (σ)	− 1.194 (π)	− 1.150 (0)	0.043
6	−11.102 (π)	−10.965 (π)	−10.903 (0)	0.062
7	−11.496 (σ)	−11.131 (π)	−11.036 (0)	0.095
8	−12.783 (σ)	−13.392 (π)	−12.211 (0)	1.183
9	−14.525 (π)	−14.519 (0)	−14.464 (π)	0.054
10	−15.126 (σ)	−15.449 (π)	−14.834 (0)	0.612
11	−17.632 (σ)	−19.256 (0)	−16.217 (π)	3.039
12	−31.779 (σ)	−33.087 (π)	−30.094 (0)	2.993
13	−38.725 (σ)	−40.072 (0)	−38.102 (π)	1.970

contains the corresponding molecular levels, the second and third one, respectively, the lower and upper limits of the bands (their values $k_2 a_2$ are in parenthesis) and finally the last column shows the widths of the bands. The left half of the Table contains the CNDO, the right one the MINDO results. Further the data given in the upper half of the Table refer to O···H—N hydrogen bond distance of 2.66 Å, while the lower one to 2.75 Å.

In Table 2 we give the results obtained again for an one-dimensional polyformamide chain taking into account only interactions along the main chain now. The quantities shown in Table 2 are the same as those in Table 1.

In Table 3 we show our CNDO/2 and MINDO/2 results obtained for the two-dimensional polyformamide model system (see Fig. 1). Here $\varepsilon_{\min}$ and $\varepsilon_{\max}$, respectively, stand for the absolute lower edge and upper edge of the bands (the values $k_1 a_1$ and $k_2 a_2$ belonging to them are again in parenthesis). The results are given here only for the hydrogen bond distances of 2.66 Å.

Table 4 summarizes the forbidden band widths between the valence and conduction bands for all the calculated model systems in both approximations.

Table 2. The CNDO/2 and MINDO/2 band structures of a one-dimensional

No. of band	CNDO/2				
	E_{MO} (type)	$E_{\min}(k_1 a_1)$	$E_{\max}(k_1 a_1)$	δE	
1	13.310 (σ)	13.630 (0)	15.170 (π)	1.540	
2	11.890 (σ)	11.924 ($\pi/4$)	12.686 (π)	0.762	
3	8.555 (σ)	7.412 (0)	9.934 (π)	2.522	
4	4.274 (π)	3.694 (π)	6.953 (0)	3.259	3.259
5	1.224 (σ)	5.572 (0)	6.177 ($\pi/2$)	0.605	
6	−14.023 (π)	−15.516 (π)	−12.922 ($\pi/4$)	2.594	4.211
7	−14.819 (σ)	−15.868 (π)	−11.657 (0)	4.211	
8	−19.149 (σ)	−18.520 (0)	−16.205 (π)	2.315	17.476
9	−21.590 (σ)	−25.241 (0)	−18.796 (π)	7.045	
10	−23.045 (π)	−28.479 (π)	−16.417 (0)	12.062	
11	−24.611 (σ)	−33.681 ($\pi/4$)	−25.350 (π)	8.331	
12	−37.922 (σ)	−43.307 (0)	−37.135 ($3\pi/4$)	6.172	
13	−44.420 (σ)	−53.619 (0)	−43.890 (π)	9.729	

Table 3. The CNDO/2 and MINDO/2 band structures of the two-dimensional

No. of band	CNDO/2				
	E_{MO} (type)	$E_{\min}(k_1 a_1, k_2 a_2)$	$E_{\max}(k_1 a_1, k_2 a_2)$	δE	
1	13.310 (σ)	13.790 (0, $-\pi$)	15.473 (π, 0)	1.683	
2	11.890 (σ)	11.903 (0, $-\pi$)	12.774 (π, 0)	0.871	
3	8.555 (σ)	7.429 (0, 0)	10.126 (π, $-\pi$)	2.697	
4	4.274 (π)	3.441 (π, $-\pi$)	5.997 ($\pi/2$, $\pi/2$)	2.556	
5	1.224 (σ)	6.357 (π, $-\pi/2$)	7.143 (0, $-\pi$)	0.785	
6	−14.023 (π)	−15.308 (π, $-\pi$)	−12.703 (0, 0)	2.605	22.433
7	−14.819 (σ)	−14.753 (π, π)	−11.107 (0, $-\pi$)	3.646	
8	−19.149 (σ)	−17.705 ($\pi/2$, $\pi/2$)	−13.841 (0, 0)	3.864	
9	−21.590 (σ)	−23.857 ($\pi/2$, 0)	−17.581 (0, 0)	6.276	
10	−23.045 (π)	−27.608 (0, 0)	−22.465 (0, $-\pi$)	5.143	
11	−24.611 (σ)	−33.540 (π, $-\pi$)	−26.190 ($\pi/2$, π)	7.350	
12	−37.922 (σ)	−44.960 (0, $-\pi$)	−38.339 (π, 0)	6.621	15.534
13	−44.420 (σ)	−53.873 (0, 0)	−43.490 (π, π)	10.383	

Table 4. The forbidden band widths between the valence and conduction bands of the different polyformamide systems (R stands for the O···H—N distance, energies are in eV)

		CNDO/2	MINDO/2
H-bonded one-dimensional chain	$R = 2.66$ Å	15.00	9.69
	$R = 2.75$ Å	15.06	9.75
One-dimensional main chain		16.62	9.20
Two-dimensional network	$R = 2.66$ Å	14.52	8.83

Discussion

As we can see from Tables 1–3 we have always three π bands corresponding to the three π molecular levels and ten σ ones. The bands lie in all cases symmetrical with respect to the molecular levels with the exception of the conduction polyformamide chain (interactions along the main chain, all energy values in eV)

No. of band	MINDO/2				
	E_{MO} (type)	$E_{min}(k_1 a_1)$	$E_{max}(k_1 a_1)$	δE	
1	4.569 (σ)	4.957 (0)	5.232 (π)	0.265	
2	3.877 (σ)	2.930 (0)	3.964 (π)	1.034	
3	2.506 (σ)	2.216 (0)	2.912 (π)	0.696	
4	0.389 (π)	0.228 (π)	1.360 (0)	1.132	2.465
5	−1.312 (σ)	−0.231 (0)	2.214 (π)	2.465	
6	−11.102 (π)	−12.010 (π)	−11.125 (0)	0.885	10.108
7	−11.496 (σ)	−12.364 (π)	−9.427 (0)	2.937	
8	−12.783 (σ)	−12.732 ($3\pi/4$)	−12.163 ($\pi/4$)	0.519	
9	−14.525 (π)	−16.811 (0)	−12.438 (π)	4.373	
10	−15.126 (σ)	−17.240 (π)	−12.789 (0)	4.451	
11	−17.632 (σ)	−19.535 (0)	−16.191 (π)	3.344	
12	−31.779 (σ)	−33.285 (π)	−29.861 (0)	3.424	
13	−38.725 (σ)	−43.356 (0)	−38.122 (π)	2.234	

polyformamide network (all energy values in eV, $R_{O\cdots H-N} = 2.66$ Å)

No. of band	MINDO/2				
	E_{MO} (type)	$E_{min}(k_1 a_1, k_2 a_2)$	$E_{max}(k_1 a_1, k_2 a_2)$	δE	
1	4.569 (σ)	5.940 (0, 0)	6.143 (π, 0)	0.203	
2	3.877 (σ)	3.155 (0, 0)	4.748 (π, $-\pi$)	1.593	
3	2.506 (σ)	3.007 (0, $-\pi/2$)	3.591 (π, $-\pi$)	0.584	
4	0.389 (π)	1.606 (0, 0)	2.522 (π, 0)	0.916	
5	−1.312 (σ)	−0.288 (0, 0)	1.327 ($\pi/2$, $\pi/2$)	1.615	
6	−11.102 (π)	−11.096 (π, $-\pi$)	−9.117 (0, $-\pi$)	1.979	5.822
7	−11.496 (σ)	−11.750 (π, 0)	−11.019 ($\pi/2$, $\pi/2$)	0.731	
8	−12.783 (σ)	−13.235 ($\pi/2$, π)	−11.081 (0, 0)	2.154	
9	−14.525 (π)	−14.939 ($\pi/2$, 0)	−12.092 (0, 0)	2.847	
10	−15.126 (σ)	−16.961 (π, π)	−16.114 ($\pi/2$, π)	0.847	5.611
11	−17.632 (σ)	−21.725 (π, $-\pi$)	−16.373 (0, $-\pi$)	5.352	
12	−31.779 (σ)	−37.676 (0, $-\pi$)	−30.973 (π, $-\pi$)	6.703	16.761
13	−38.725 (σ)	−47.734 (0, 0)	−34.157 (0, $-\pi$)	13.577	

band in the case of the one-dimensional formamide chain (interactions along the main chain) and of the two-dimensional polyformamide network (see Tables 2 and 3).

In that one-dimensional polyformamide chain in which we have the interactions through the hydrogen bonds the σ bands are considerably broader than the π ones (see Table 1), while in the calculated two other model systems the widths of the two types of bands are about the same (see Tables 2 and 3).

The filled σ bands are rather broad already in the first model system (Table 1), and all filled bands and some of the empty ones are quite broad (widths of several eV's, in some cases over 10 eV) in the second and third model systems (Tables 2 and 3).

In connection with the obtained very broad σ bands it should be mentioned that this situation which was found also in other calculations [10, 11] contradicts to the usual picture of localized σ bonds. One could assume that this is the consequence of the different approximations applied in the CNDO/2 and MINDO/2 method, respectively. On the other hand André [20] has obtained similarly broad σ bands in his *ab initio* calculation of a polyene chain. Mathematically it is possible to find such a unitary transformation of the many-electron wave function of a periodic system which would produce localized σ electron wave functions (as it is usually done in the course of *ab initio* molecular calculations). Such a transformation would of course leave unchanged the total energy of the system, but the one-electron description would not be possible any longer.

Returning to the details of the band structures we can see from the Tables that while by the first model system we do not have overlapping bands, by the second and third model systems many of the filled bands (including the valence band) and the two lowest unfilled bands overlap in both approximations. In this way we obtain in some cases allowed regions of 10–22 eV widths (indicated by braces in Tables 2 and 3).

In all cases the highest filled molecular levels are π levels and the lowest unfilled ones σ levels. We can find the corresponding π and σ bands in the band structures though in the second and third models they overlap with other bands. In this way their widths become rather large in these systems (values between ~2.5 eV, and ~22 eV). On the other hand in the first model system the widths of the valence and conduction bands are between ~0.3 eV and 0.05 eV, respectively. It should be further noted that the conduction bands are positive in all models in the CNDO/2 approximation and their upper limits are positive in the second and third model systems also in the MINDO/2 approximation. Therefore the physical meaning of the virtual bands which fell into the ionization continuum is questionable.

The forbidden band widths between the valence and conduction bands are ~15.0 eV by all the three models in the CNDO/2 approximation and they are between 9.2–9.7 eV by the three different model systems in the MINDO/2 approximation (see Table 4).

In the case of the first model system (one-dimensional chain with interactions through the hydrogen bonds) we have used three different hydrogen bond distances, 2.66 Å, 2.75 Å, and 2.96 Å, respectively. As we can see from Table 1 increasing the distance from 2.66–2.75 Å causes only a slight decrease in the band widths. On the other hand increasing the hydrogen bond distance to 2.96 Å we have obtained generally a decrease of the band widths by a factor of two. For proteins the 2.66 and 2.75 Å distances are the usual ones. Since the change of the hydrogen bond distance from 2.66–2.75 Å did not change significantly the band structure, we have performed the calculation for the two-dimensional polyformamide network only by 2.66 Å.

By calculating the total electronic energy of a single formamide molecule and that of the two-dimensional periodic system we have found a delocalization energy per unit cell of ~25 eV in the CNDO/2 and of ~22 eV in the MINDO/2 approximation, respectively.

In the approximation of the electronic structure of periodic protein models as next step we intend to calculate the band structure of a simplified two-dimensional polyglycine model in which we shall not take into account the proper valence angles. In this way it will be enough to put one glycine molecule in the unit cell.

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