PHYSICAL REVIEW B VOLUME 18, NUMBER 10 15 NOVEMBER, 1978

Electronic structure and transport properties of polypeptides: An *ab initio* crystal orbital study of a periodic polyglycine chain

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(Received 26 July 1977)

The electronic structure of an infinite periodic polyglycine chain is studied in its β conformation with the aid of the *ab initio* Hartree-Fock self-consistent-field crystal-orbital method. The calculated large forbidden band gap indicates absence of intrinsic semiconduction. The calculated wave function, charge-carrier mean free path, and their mobility are consistent with an impurity semiconduction mechanism with delocalized holes, but not electrons. The mobility on the basis of this theory is expected to be very low. Furthermore, a critical comparison with earlier semiempirical band-structure calculations is provided.

I. INTRODUCTION: SEMICONDUCTION IN PROTEINS

The energy transport mechanism in fibrous proteins is a central problem in quantum biology.[1] The Szent-Györgyi-Laki hypothesis[2,3] is still relevant in this respect: their original idea about the collective delocalized states of the periodic peptide units is widely accepted among investigators in this field. However, the mechanism of this transport is still not fully known. The aim of the present paper is to contribute to the enlightenment of this point, with the aid of solid-state and refined quantum-chemical calculations.

The first quantum-chemical calculations[4] were performed on periodic π electron models assuming electron delocalization along the H bonds of a periodic protein model via the simple Hückel method. Periodic models simplify the numerical work by enabling one to use the language of band theory.[5] The values obtained for the forbidden energy gap, E_G (3–4 eV), although strongly dependent on parametrization,[6] were the only theoretical values available for a long time. A large series of experimental measurements of Eley *et al.*[7,8] have been interpreted on the basis of the intrinsic semiconduction hypothesis using $\sigma = \sigma_0 \exp(E_G/2k_BT)$ for fitting σ (measured conductivity) vs. T (temperature). The E_G values were obtained in a relatively narrow region around 3eV. This agreement with the theoretical E_G seemed to verify the idea of an intrinsic semiconduction mechanism in proteins[8] with a large gap around 3 eV.

Thus, around 1960 not only was the Szent-Györgyi hypothesis of semiconduction in proteins verified, but the mechanism of this semiconduction also appeared to be a settled problem: intrinsic band-type semiconduction along the long H-bridged systems present in many proteins. However, later experiments and model calculations directed attention to new viewpoints. Firstly, several independent radiation-biological experiments indicated charge-carrier migration along the main chains of polypeptides.[9–12] Thus, the delocalization along the H bridges appeared in the early sixties not to be the only possible mechanism.

In the early sixties, Brillouin proposed a different model to explain semiconduction in proteins: according to his model[13] conduction takes place along the main polypeptide backbone of the protein, while the amino-acid residues (side chains) serve as sources of impurity levels in the forbidden band. Almost at the same time, due to the development of quantum-chemical semiempirical methods, Suard, Berthier, and Pullman reinvestigated the level structure of the H-bridge-delocalization model with the aid of a self-consistent-field method for π electrons of the peptide units only.[14] They estimated energy gaps about twice those obtained by the experimentalists and concluded, therefore, that the intrinsic semiconduction mechanism along the H-bridge system can be ruled out. In our opinion the most important aspect of their work was to call attention to the fact that the first excited-state energy of polypeptides, E_{ex} (measured as the first optical transition in the 6-eV range[15,16]) is about twice the E_G values of Eley *et al.* This discrepancy indicates that E_G is most probably not a band-to-band gap, since in the simple-band theoretical picture E_{ex} is necessarily smaller than E_{bb} (band-to-band gap). The first strong experimental evidence for the presence of impurity-type semiconduction in proteins was the observation that a dose of 10^5 R of ^{60}Co γ rays did not change the semiconductivity noticeably.[17]

There was an attempt by Rosenberg and Postow[18] to re-establish agreement between experimental gaps and the new theoretical gap. By simple considerations they estimated the static polarization energy P due to an excess hole or electron in the specimen to be around 1.2 eV,[18] a reasonable value for organic semiconductors.[19] The difference between the theoretical and experimental band-to-band gaps is expected to be $2P$, thus agreement could be re-established.[18] However, on the basis of their careful ac and dc measurements with varying water content,[18,20] Rosenberg and Postow could not exclude any other mechanisms of conduction,[18,20] e.g., (i) the small-polaron model[21]; (ii) the intermolecular tunneling model[21,22]; and (iii) electron (hole) injection from the electrode via the surface states of the proteins.[22]

It is worth noting that Rosenberg and Postow could not choose between the intrinsic and the extrinsic mechanisms (surface impurities or bulk impurities),[18] though they claim that their experiments might exclude the possibility that water would be the impurity,[20] as proposed by Eley and Leslie.[23] On the other hand, Miyoshi and Saito[24] claim that what they themselves measured was a kind of impurity conduction in proteins and other H-bonded substances. A further important contribution of their work seems to us that they provided some arguments, on the basis of the effect of the adsorbed molecules, that the majority carriers in their polypeptide sample were holes.

From a theoretical band-structure calculational view point, the situation is equally unsettled. In the early seventies there appeared several all-valence-electron calculations on simple periodic polypeptide models (including some unrealistic ones in Ref. 28). E_{bb} values in the very wide range of 3.1 to 16.7 eV have been obtained[25-30] using different semiempirical parametrizations. One of the most interesting results of these all-valence-electron band calculations was the insensitivity of E_{bb} to the chain's conformation, and the presence or absence of long hydrogen-bonded systems in the conformers. These theoretical results indicated the important role of the conduction along the main polypeptide chain. Most recently a "simulated *ab initio* molecular orbital" (SAMO) calculation has been done for a planar polyglycine model.[31] However, relatively few results are available by this method for infinite periodic systems, and since previous results for polyethylene[32] showed strong dependence on the number of included neighbors, presently this should also be considered a kind of adjustable method.

This somewhat inconsistent situation prompted us to perform energy-band-structure calculations with the most sophisticated *ab initio* crystal orbital method.[33] On the basis of the results of these calculations, we describe our attempt to estimate some physical parameters characterizing the charge-carrier motion in a periodic β-polyglycine chain.

II. METHOD AND RESULTS OF BAND-STRUCTURE CALCULATIONS

We have applied the linear combination of atomic orbitals (LCAO) Hartree-Fock method in its nonlocal-exchange crystal-orbital form,[34] evaluating all integrals over atomic orbitals within a finite interaction radius ρ.[35] As in all our previous *ab initio* band calculations, we have used our BLOCH program.[35] We have applied a minimal Slater-type atomic-orbital (AO) basis set expanded in terms of three Gaussian functions (G) to represent a single Slater-type orbital (STO)(STO-3G).[36] Self-consistency with respect to the density matrix has been obtained, but convergence with respect to AO-basis-set enlargement and ρ has not been attempted owing to the high cost of computer time.

The first model system studied was an infinite polyglycine chain in its β-sheet conformation [see Fig. 1(a)]. For the nonhydrogen atoms the geometry was taken from Table IV of Pauling and Corey[37] supplemented[29] by H atoms according to standard bond lengths and angles.[38] The number of K points in the one-half Brillouin zone was 9 and the near-neighbor interaction radius ρ was 5.9 Å, corresponding to the 5th atomic neighbor's interaction approximation along the main chain of the macromolecule.

Furthermore, we have studied an infinite hydrogen-bonded chain in order to obtain band-structure information regarding the H-bond delocalization model at the same level of sophistication. For this we have taken an infinite one-dimensional H-bridge system from the Pauling-Corey antiparallel rippled sheet [Fig. 1(b)]. The interaction radius was here 4.86 Å; the number of K points in the one-half Brillouin zone was 5. The geometry of this model was constructed as for the β-polyglycine chain.

The resulting band structures can be characterized by the band edges collected in Table I for both models. For polyglycine, the band structure is

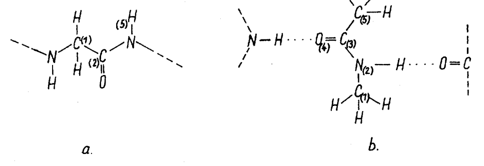

FIG. 1. (a) Polyglycine chain studied (repeat unit is CH_2CONH). (b) Hydrogen-bond model of this paper.

TABLE I. Energy-band edges for the two models studied by the *ab initio* Hartree-Fock crystal orbital method (a.u.).

Band	β-polyglycine chain[a]			H-bonded model[a]		
no.	E_{min}		E_{max}	E_{min}		E_{max}
1		−20.264	(O core)		−20.212	(O core)
2		−15.368	(N core)		−15.435	(N core)
3		−11.257	[$C_{(1)}$ core]		−11.301	[$C_{(3)}$ core]
4		−11.200	[$C_{(2)}$ core]		−11.183	[$C_{(1)}$ core]
5	−1.411		−1.395		−11.095	[$C_{(5)}$ core]
6	−1.270		−1.259	−1.440		−1.439
7	−1.061		−0.930	−1.267		−1.261
8	−0.826		−0.812	−1.065		−1.064
9	−0.773		−0.711	−0.988		−0.987
10	−0.680		−0.632	−0.833		−0.811
11	−0.637		−0.603	−0.722		−0.716
12	−0.568		−0.553	−0.702		−0.702
13	−0.548		−0.526	−0.682		−0.669
14	−0.422		−0.414	−0.663		−0.649
15	−0.370[b]		−0.358[b]	−0.622		−0.618
16	0.250		0.286	−0.597		−0.578
17	0.451		0.491	−0.572		−0.546
18	0.491		0.556	−0.545		−0.535
19	0.621		0.655	−0.410		−0.398
20	0.670		0.696	−0.388[b]		−0.384[b]
21	0.715		0.751	0.292		0.293
22	0.765		0.873	0.522		0.522
23	1.033		1.047	0.575		0.591
24				0.635		0.640
25				0.641		0.652
26				0.672		0.676
27				0.719		0.727
28				0.736		0.775
29				0.785		0.791
30				0.862		0.863
31				0.950		0.956
32				1.171		1.208

[a] See Fig. 1.

[b] Highest occupied band.

depicted in Fig. 2, in the extended-zone scheme, by taking into account the screw axis of symmetry. (Folding back at $\pi/2a$ corresponds to the ordinary unit cell with two glycine molecules.)

We have collected in Table II some most characteristic results of previous band-structure calculations on infinite periodic polyglycine chains in the planar or β configuration (no hydrogen bonding).

According to the results of Morokuma,[26] the charge distribution is not sensitive to the conformational changes of the polyglycine chain, including the presence or absence of H bonds. Comparison of the charge distribution obtained by the intermediate neglect of differential overlap (INDO) and the modified intermediate neglect of differential overlap, version 2 (MINDO-2) methods[7] for the α form and the planar model shows that the differences between the two methods are much larger than the small differences obtained using different models but the same method. (It is to be noted that the applicability of the MINDO-2 parametrization to hydrogen-bonded systems is questionable owing to the special prescription of CH and NH bond "elongation" inherent to this particular form of the MINDO method.) We would like to mention a drawback in the work of Beveridge *et al.*[27] This is connected with the results they obtained for an infinite regular polyene chain, which, in the case of correct integral approximations regarding the intercell interactions,[42] should have a half-filled energy band. Since they obtained a large forbidden energy gap for this system, most probably some of the intercell interactions are not correctly dealt with in their computer program. This deficiency, important for polyene, has, most probably, merely secondary effects on the energy-band structure of insulators, and in our opinion their band structures are essentially correct for polyglycine and polyethylene in the INDO and MINDO-2 schemes.

TABLE II. Forbidden band gaps, charge distributions, and ionization potentials in polyglycine models without H bonds, as calculated by the *ab initio* Hartree-Fock crystal-orbital method and compared with selected semiempirical calculations.

Method of calculation, reference		*ab initio* (Present work)	SAMO (Ref. 31)	CNDO-2[g] (Ref. 26)	INDO (Ref. 27)	MINDO-2 (Ref. 27)
Model, and geometry used		β chain PC[a]	Planar-model standard geometry	β chain PC[a]	Planar-model glycine optimized geometry	
Forbidden gap (eV)		16.54	15.97	16.1	9.53	6.14[b]
Ionization potential (eV)		9.73	10.9	11.9	~12	c
Net atomic charges	N	−0.758	−0.495	−0.182	−0.270	−0.676
	$C_{(2)}$(=O)	0.554	0.362	0.356	0.435	0.812
	O	−0.4065	−0.373	−0.366	−0.448	−0.710
	$C_{(1)}$	0.194	−0.257	0.039	0.233	0.380
	$H_{(5)}$(−N)	0.324	0.322	0.130	0.179	0.276
	H(−C)	0.104	0.219	0.018	−0.060	−0.041
	H(−C)	−0.010	0.219	0.016	−0.060	−0.041
Width of highest valence band (eV)		0.32	0.3	0.21[d] 2.13[e]	~1.0	1.68[f]
Width of lowest conduction band (eV)		0.99	c	0.21[d] 2.65[e]	~2.4	1.23[f]
Total width of valence bands (eV)		28.65	27.5	~44[d]	40.8	c

[a] Pauling-Corey geometry supplemented with hydrogens at standard (Ref. 38) bond lengths and angles.

[b] Suhai reported a different value: 7.015 eV (cited in Ref. 29 as an unpublished calculation).

[c] Value not available.

[d] From Ref. 25 (α helix).

[e] From a two-dimensional calculation Ref. 29.

[f] From a two-dimensional calculation with strongly modified geometry Ref. 28.

[g] CNDO-2: complete neglect of differential overlap, version 2.

The E_{bb} values obtained by the different methods in question cover a very wide range. The smaller values have been obtained by π electron methods for the H-bonded model,[4,14] but, as was shown first by Morokuma[26] in the case of polyglycine, these methods are not applicable to this system due to the large σ-π mixing. The all-valence-electron methods not using the σ-π separability hypothesis yielded values between 6.1 and 16.1 eV. The smaller ones were obtained with those parameterizations which use reduced Coulomb integrals (implicitly taking into account in this way the effect of electron screening and correlation). The phenomenon of reduced gaps is well known for molecules and polymers like polyethylene.[43] The SAMO results[31] are most close to the present *ab initio* calculation, but the details differ in some respect. By analogy with other similar band-structure calculations for polyethylene we expect that the valence density of states, as obtainable in electron spectroscopy for chemical analysis (ESCA) experiments, should be closest to our *ab initio* results, but due to lack of such data for polyglycine this point needs confirmation.

The widths of the conduction bands need some comment. These widths are much narrower than those of the valence bands in the case of the INDO and MINDO methods, as noticed by Beveridge *et. al.*[27] These authors have suggested as a possible explanation the neglect of zero differential overlap (ZDO). However, the SAMO method, which is not based on the ZDO assumption, yielded relatively narrow conduction bands, as noticed by Duke *et al.*[31] Our *ab initio* results, however, indicate band widths of comparable magnitude for the conduction and valence bands. We note that especially the calculated conduction bands are

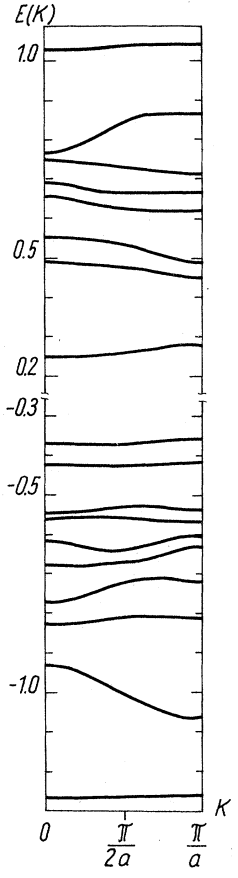

FIG. 2. Energy-band structure of a β-polyglycine chain as calculated by the *ab initio* Hartree-Fock crystal-orbital method. An extended zone scheme is used. 1 a.u. = 27.21 eV.

sensitive to basis-set effects. Nevertheless, it may be concluded on the basis of our results that the band widths and consequently the effective masses should not differ drastically for electrons and holes.

As can be seen from Table III, the wave functions at $K=0$ for the electrons in β-polyglycine, obtained by the *ab initio* crystal-orbital method, are not completely delocalized. It is, therefore, not straightforward to apply the conventional semiconductor theory for the conduction band. For holes, however, the situation is different because the corresponding one-particle wave functions at band edge (Table III) are more evenly distributed among the atoms of the main chain of β-polyglycine. In the H-bonded model both charge carriers are delocalized over the atoms of the conduction chain except for the H atoms in the bridges. This result is also in conflict with the idea of charge-carrier transport in this direction, although AO-basis-set enlargement could change the wave function, especially for the empty bands.

The wave functions obtained in previous calculations are not very well documented, as common in present-day quantum-chemical publications, and comparisons could not be provided here.

III. ESTIMATION OF THE CHARGE-CARRIER MEAN FREE PATH AND MOBILITY

There are a number of phonon modes in a pure periodic polyglycine with which electrons can be scattered—not mentioning the different types of impurities and irregularities present in real proteins. It is, therefore, difficult to predict the electron and hole mean free paths: Λ_e and Λ_h, as well as their mobilities, μ_e and μ_h. Here we follow an oversimplified approach by assuming that conventional semiconductor theory may be applied.

In order to obtain a rough estimate of Λ and μ we have adopted the deformation-potential approach of Bardeen and Shockley.[39] Herewith we neglect all scattering mechanisms except that with longitudinal-acoustical (LA) phonons. Beleznay *et al.*[44] have given the expression for the mobility and the pre-exponential factor σ_0 in the formula for the conductivity for one-dimensional (1D) semiconductors, in this approximation. Their expression

TABLE III. One-particle wave functions at band edges (coefficients of the atomic orbitals in the crystal orbitals at band edge.[a]

β-polyglycine	Conduction band	$-0.2\mathrm{N}(2p_z) - 0.3\mathrm{C}_{(2)}(2p_y) + 0.5\mathrm{C}_{(2)}(2p_z) + 0.2\mathrm{O}(2p_y)$ $-0.4\mathrm{O}(2p_z) - 0.2\mathrm{H}_{(5)}(1s)$
	Valence band	$-0.2\mathrm{C}_{(1)}(2p_y) + 0.3\mathrm{N}(2p_y) - 0.3\mathrm{N}(2p_z) - 0.2\mathrm{C}_{(2)}(2p_y)$ $+0.1\mathrm{O}(2p_y) + 0.5\mathrm{O}(2p_z)$
H-bond model	Conduction band	$-0.2\mathrm{N}(2p_y) + 0.3\mathrm{N}(2p_z) + 0.5\mathrm{C}_{(3)}(2p_y) - 0.8\mathrm{C}_{(3)}(2p_z)$ $-0.3\mathrm{O}(2p_y) + 0.5\mathrm{O}(2p_z) + 0.1\mathrm{H}_{\mathrm{Me},(1)} - 0.2\mathrm{H}_{\mathrm{Me},(5)} - 0.2\mathrm{H}'_{\mathrm{Me},(5)}$
	Valence band	$-0.4\mathrm{N}(2p_y) + 0.6\mathrm{N}(2p_z) + 0.6\mathrm{C}_{(3)}(2p_y) - 0.8\mathrm{C}_{(3)}(2p_z)$ $+0.3\mathrm{O}(2p_y) - 0.8\mathrm{O}(2p_z) + 0.2\mathrm{H}_{\mathrm{Me},(1)} - 0.2\mathrm{H}'_{\mathrm{Me},(1)}$

[a] Coefficients are rounded to one significant figure; those less than 0.1 are omitted. Numbering of atoms according to Fig. 1. (The subscript on the methyl hydrogen refers to the carbon number of the group; the prime to another hydrogen of the same group.)

TABLE IV. Some calculated electronic and transport parameters for an infinite β-polyglycine chain.

	Effective mass (units of m_e)	Deformation potential[a]	Mean free path	Mobility of conduction[b]
Electron	4.25	4.95 eV	0.36 Å	1.4 $\mathrm{cm^2/V\,sec}$
Hole	1.80	4.56 eV	1.0 Å	6.1 $\mathrm{cm^2/V\,sec}$

[a] At 5% dilation. [b] At 300 °K.

is not correct for μ, because it should contain the area of the cross section of the macromolecule f as a multiplicative factor (since the density of states should contain $1/f$, the formula for σ_0 is correct in Ref. 44).

$$\mu^{1D} = 4(2/\pi)^{1/2}(c_L \hbar^2 e/\epsilon_1^2 m^{*3/2}(k_B T)^{1/2})f$$

for both electrons and holes, with ϵ_1 the deformation potential, T the absolute temperature, and c_L the longitudinal elastic modulus. The expression for the charge-carrier mean free path for 1D semiconductors was derived in a straightforward manner. The result for electrons and holes is[45]

$$\Lambda^{1D} = c_L \hbar^2 f/\epsilon_1^2 m^* ,$$

independent of temperature.

Among the parameters entering these formulas, ϵ_1 and m^* can be obtained from band-structure calculations. It is reasonable to estimate f in the 10-Å^2 range; however, for c_L, the problem remains. Since c_L is related to the longitudinal-acoustical sound velocity v_{LA} by

$$f c_L = v_{\mathrm{LA}}^2 (M/L),$$

where M/L is the mass density per unit length of the chain, we decided to estimate v_{LA} instead of c_L. This quantity is also not directly accessible experimentally, but a number of authors have calculated vibrational dispersion curves (phonon dispersion curves) for periodic protein models.[46] These theoretical curves are based on empirical force fields and they are tested by comparing vibrational-spectroscopy experimental results for the optical branches and neutron scattering for the acoustical and low-energy optical branches. Nevertheless, some care must be taken when using these curves for the estimation of v_{LA}, which is related to the first derivative of the LA branch at $K = 0$. We have used the dispersion curves of Ref. 47 and obtained $v_{\mathrm{LA}} \sim 7.1 \times 10^5$ cm/sec, a reasonable value for covalent solids. From this value, we estimate $fc_L \sim 7.8 \times 10^{12}$ (dyn/cm^2)Å^2, which yields $c_L \sim 0.8 \times 10^{12}$ dyn/cm^2 if we estimate $f \sim 10$ Å^2. This latter value is slightly less than that estimated by Suhai[30] in a completely different way. Substituting this fc_L value into our expressions for Λ and μ, together with the effective masses and deformation potential, we obtained the results given for both holes and electrons in the last two columns of Table IV. The mobility values and the mean free paths are small for both electrons and holes, indicating strong electron-phonon coupling in the polyglycine chain considered. We note that Suhai's values[30] are much larger; however, he used the isotropic three-dimensional expressions for Λ and μ,[39] while his model was an extremely anisotropic two-dimensional system. Furthermore, the effective masses used in Ref. 30 seem to be too low as compared to the band width of the same calculations.[29] These two factors account for the unrealistically large (~10^6 cm^2/V sec) drift mobilities obtained in Ref. 30.

IV. CONCLUSION

The following conclusions emerge from the present *ab initio* Hartree-Fock band structure for the most simple polypeptide model, polyglycine. The forbidden energy gap is estimated to be very large, excluding the possibility of intrinsic semiconduction, even if our calculated gap would have been corrected by basis-set and correlation corrections.[40,41] In going to more complicated polypeptide models the following changes may be involved: (1) formation of long H-bridged links (either intrachain or interchain); (2) inclusion of sterical aperiodicity by the occurrence of differently oriented peptide units; and (3) inclusion of aperiodically distributed side chains of different amino acids. We would like to point out that the regular H-bridged chains do not lead to intrinsic semiconduction according to the previous[26,29,30] and present theoretical results involving H-bonded models. Sterical (or orientational) aperiodicity probably does not lead to a drastic change in the density of states of the polymer either. (At least for polyethylene we observed this feature recently by studying large fragments of aperiodic polyethylene models by extended Hückel theory.[48]) Finally the aperiodically distributed side chain may lead, of course, to impurity levels of both donor and acceptor type within the large gap leading to extrinsic semiconduction. An aperiodic surrounding (e.g., water, ions, etc.) may have similar effects. Therefore impurity semiconduction is compatible with the band structure obtained in this work. As mentioned in the Sec. I, this mechanism is compatible with the insensitivity of the energy of the two lowest optical absorption bands to the details of real polypeptides. Values in the 6–7 eV range have been reported by various authors; see, e.g., Refs. 15 and 16. On the basis of these values it is reasonable to anticipate the position of the lowest exciton bands (which are involved in the absorption process) somewhere around 6–7 eV. This value is consistent with the large-gap model, but not with the intrinsic-semiconductor model.

As to the electron-phonon interactions, it was straightforward to obtain an estimate of the charge-carrier mean free paths and their mobility using the conventional deformation-potential approach. The results of such calculations depend strongly on the choice of the parameters, especially on those of the deformation potential and the longitudinal compressibility. By analogy to the recent successful electron-vibronic coupling-constant calculation (see Table III, column 1 of Ref. 49 for the ν_2 breathing mode which corresponds to the uniform elongation of all C-C bonds of the ring) we are confident in our deformation potentials to a factor of about 2. We have recently performed an analogous *ab initio* molecular-orbital calculation for benzene and obtained linear electron-phonon coupling constants ~2 times larger than the experimental ones for the ν_2 phonon mode. This means an underestimation of μ and Λ of about a factor of 4. There is a furter, and perhaps equally important, uncertainty in the estimation of the electron-phonon coupling: We have used a uniform dilation for the calculation of the deformation potential, which is certainly a crude model due to the presence of different types of bonds (with different stretching force constants) in the main chain of our polypeptide model.

Finally, we reconsider the Fröhlich-Sewell criterion[50] for the applicability of the conventional delocalized charge-carrier mechanism to our model. According to Ref. 50 the criterion for the nonviolation of the uncertainty principle for low-mobility semiconductors is

$$m^*\mu > 20(300/T)\,(^\circ\mathrm{K}^{-1})$$

provided the band width is larger than k_BT (this is fulfilled in our case), where m^* is given in m_e and μ in cm^2/V sec. Since all our data refer to $T = 300\,^\circ$K, we have $m^*\mu$ values of 6 and 11 for electrons and holes, respectively. Considering the above-mentioned uncertainties in the evaluation of the electron-phonon coupling (μ may be larger by a factor up to ~4), we cannot rule out the conventional semiconduction mechanism on the basis of the Fröhlich-Sewell consistency criterion, especially for the holes. However, the calculated mean free paths multiplied by ~4 will lead to a value comparable to the lattice constant for the holes, but not for the electrons. Furthermore, taking into account the partly localized nature of the wave functions obtained for the electrons, but not for the holes, we may conclude that in our periodic protein model the holes can much more probably be considered as conventional delocalized charge carriers than the electrons.

Although it is dangerous to make a direct comparison of our calculation with measurements on real proteins, as, e.g., heavy beef heart mitochondria, it is worth noting that the measured microwave Hall mobilities for this system[51] are not a whole order of magnitude larger than our estimated (conduction and not Hall) mobility for holes. The majority of the charge carriers in Ref. 51 are, in contrast to our results, electrons. Trukhan has found, however, a dependence of the sign of the Hall coefficient on the water content of the sample,[52] which indicates that such a comparison with our idealized model should not be pushed too far. We are convinced that in order to understand the electronic structure and transport properties of biological macromolecules some model systems should be studied, both theoretically and experimentally. For example, in the polymer single crystals of the polydiacethylenes[53] the structure and composition are much better established, and perhaps such systems should be studied more thoroughly in the future.

Note added in proof. Most recently Petrov *et al.*[54] have proposed a new band structure for proteins based on the previous semiempirical band-structure calculations, including the effect of the more loose Rydberg-type atomic orbitals in a heuristic way. Their band-structure model is also of the insulating type with an estimated gap of about 5–8 eV. Although it is difficult to include basis set and particularly correlation corrections to the gap, the larger values of Petrov *et al.* seem to be consistent with our calculated gap, which is not corrected for basis set and correlation effects.

ACKNOWLEDGMENTS

One of us M. K. would like to express his indebtedness to Professor J. Ladik and Dr. S. Suhai for interesting discussions in the early stage of these studies to Dr. F. Beleznay for useful discussions on the mobility and mean-free-path formulas for one-dimensional semiconductors, and to Dr. G. Grüner for useful discussions on organic semiconductors. We also thank Dr. B. J. Duke for sending us some unpublished details of the SAMO studies[31] which enabled us to compare these studies with other calculations.

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