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Spectroscopy of charge transfer complexes of four amino acids as organic two-dimensional conductors

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Abstract

It is found in this study that four amino acids, namely asparagine, arginine, histidine and glutamine form two-dimensional conducting systems which are charge transfer complexes (CTCs) with organic acceptors like TCNQ, TCNE, chloranil, DDQ, TNF and iodine. It is verified using optical absorption edges that these are 2d conductors like transition metal dichalcogenides obeying absorption functions different from 1d and 3d conductors. This 2d nature is related to the network of intermolecular H-bonding in these complexes, which leads to a global H-bonded network resulting in the absence of local deformation due to the relaxation of strain.

1. Introduction

There has been immense development of biochemistry and a large number of biochemicals are extensively discussed (Lehninger 1984, Volkenshtein 1983, Cerdonio and Noble 1986, Dugas 2000, Slifkin 1971). However, previous studies of electronic transport in biomolecular chemicals have involved just homomolecular biomolecules (Eley 1968). The chemical kinetics and physicochemical properties of charge transfer interactions in biomolecules, discussed elsewhere (Slifkin 1971), led to the present idea of studying charge transfer complexes (CTCs) of biomolecules. There have been only a few reports on the CTCs of important biomolecules (Davis *et al* 1960, Eley and Snart 1966, Birks and Slifkin 1963, Padhiyar and Oza 2003).

High-temperature superconductivity models were suggested for low-dimensional systems on the basis of the exciton mechanism (Little 1964, Davis *et al* 1976, Little 1971). It was suggested that the polyiodide chain complexes of starch–iodine and 2,6-diphenyl-γ–pyrrone–iodine meet the requirements of this model (Little 1969). The iodine chain systems of helical or toroidal inclusion compounds led to the suggestion of circular cyclopeptide based systems having a large number of side chains (Ovichinnikov 1973, Dobler *et al* 1969, Oza 1980, 1998), as required in Little's model.

The model of superconductivity was proposed by Ladik for DNA, but DNA was found to be semiconducting (Ladik *et al* 1966, Gutman and Lyons 1967). Little's model of an excitonic mechanism was also developed for biomolecules like rhodopsin and iodopsin (Dunne 1977,

Mentiene and Pullman 1971). These models have inspired the authors to carry out a study of biomolecular solids.

There are two particular electron systems which reveal in-phase and out-of-phase oscillations of two electrons (Kampas 1970). The out-of-phase mode is due to Coulomb repulsion of two electrons and the in-phase oscillation mode is due to the pairing of two electrons. When there is a red-shift of an electronic band, called the Soret band, associated with in-phase oscillations, the pairing interaction is low-lying and pair formation becomes more probable. A Soret band is found in the occlusion-type CTCs of many polypeptides. Amino acids are the basic units of polypeptides, and this led us to study basic interaction between amino acids with organic electron acceptors.

In the present work, we systematically study CTCs of amino acids with either positively charged side chains or with two or three NH or NH_2 groups which will be more electron donating than those with only one NH or NH_2 group. This criterion reduces to the selection of four amino acids, namely asparagine, arginine, histidine and glutamine, out of all 22 amino acids. Infrared spectroscopy study of the CTCs led to an understanding of electronic conduction on the basis of the relation between the light absorption coefficient and electronic conductivity.

2. Experimental details

The four amino acids, namely asparagine, arginine, histidine and glutamine, were obtained as analytical reagent grades in the form of white powders from the Sigma Chemical Company. Organic acceptors such as TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), TCNE (tetracyano-*p*-ethylene), chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone), DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone), TNF (2,4,5,7-tetranitro-9-fluorenone) and iodine were also used, and were highly purified. The amino acids were ground in solid forms in an agate mortar using a pestle after mixing with acceptors in molecular weight proportions of 1:1. These CTCs were reground with dry KBr spectrograde powder to form weakly absorbing and negligibly reflecting or mainly transmitting pellets.

Although the complexes were prepared by simple reactions in the solid state, the final CTC product should be nanocrystalline since one or both starting materials were nanocrystalline. This nanocrystallinity rather than microcrystallinity is concluded on the basis of an apparent powder-like appearance but including visibly shining materials, particularly the amino acids. The TCNQ, TCNE and iodine used here were highly crystalline and chloranil and DDQ were again nanocrystalline. Even if one of the materials was nanocrystalline, lattice formation in one of them would induce lattice formation of the counter-ion because of charge transfer interaction taking place while grinding, e.g. one acceptor molecule will attract one or two donor molecules to become arranged in a similar fashion. If both the materials were amorphous then only an amorphous final product will result. Moreover this depends upon the level of grinding.

The spectra in the range 400–4000 cm^{-1} were recorded using a GXFTIR single beam spectrophotometer manufactured by Perkin-Elmer Co., USA, having a resolution of 0.15 cm^{-1}, a scan range of 15 600–30 cm^{-1}, a scan time 20 scan s^{-1}, an optical phase detector (OPD) velocity of 0.20 cm s^{-1} and mid-infrared triglycine sulfate (MIRTGS) and far-infrared triglycine sulfate (FIRTGS) detectors. A beam splitter of the opt KBr type was used, having a range of 7800–370 cm^{-1}. The spectra were recorded in purge mode.

3. Results and discussion

The transmission spectra in the range of 400–4000 cm^{-1}, i.e. 2.5–25 μm of all CTCs of asparagine, arginine, glutamine and histidine, are shown in figures 1–4. These spectra are

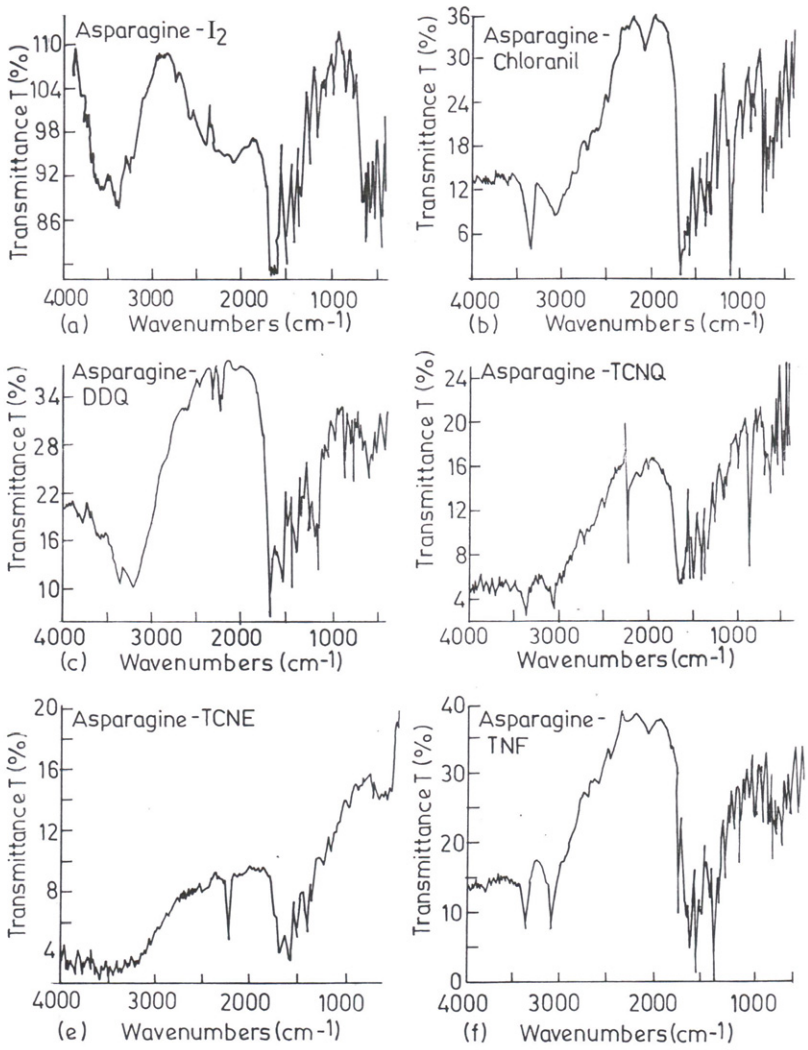

Figure 1. Infrared spectra of (a) asparagine–I_2, (b) asparagine–chloranil, (c) asparagine–DDQ, (d) asparagine–TCNQ, (e) asparagine–TCNE and (f) asparagine–TNF.

compared with the spectra of the amino acids alone (figure 5). The comparison clearly shows that there are interactions of various sites of amino acids with the accepting groups of the acceptor molecules. There are two or three broad dips in the transmission profiles, i.e. formation of absorption envelopes in the infrared range.

Among the asparagine complex, the asparagine–iodine complex shows interaction of iodine with the hydrocarbon lining resulting in changes in $\nu_{C=C}$, ν_{C-C} and δ_{C-H} frequencies of asparagine vibrations. Also ν_{C-H}, ν_{N-H} and ν_{O-H} modes show changes in shape. The δ_{N-H} vibration shows a red-shift. Thus iodine polarizes the aspargine molecules resulting in the formation of H-bonding among asparagine molecules. In the chloranil complex, the interaction arises from C=O vibration and a ring of chloranil molecules with ν_{C-C} and δ_{N-H} modes of asparagine. In the DDQ complex, $\nu_{C\equiv N}$ and ν_{C-O} modes interact with ν_{O-H} and δ_{N-H} modes

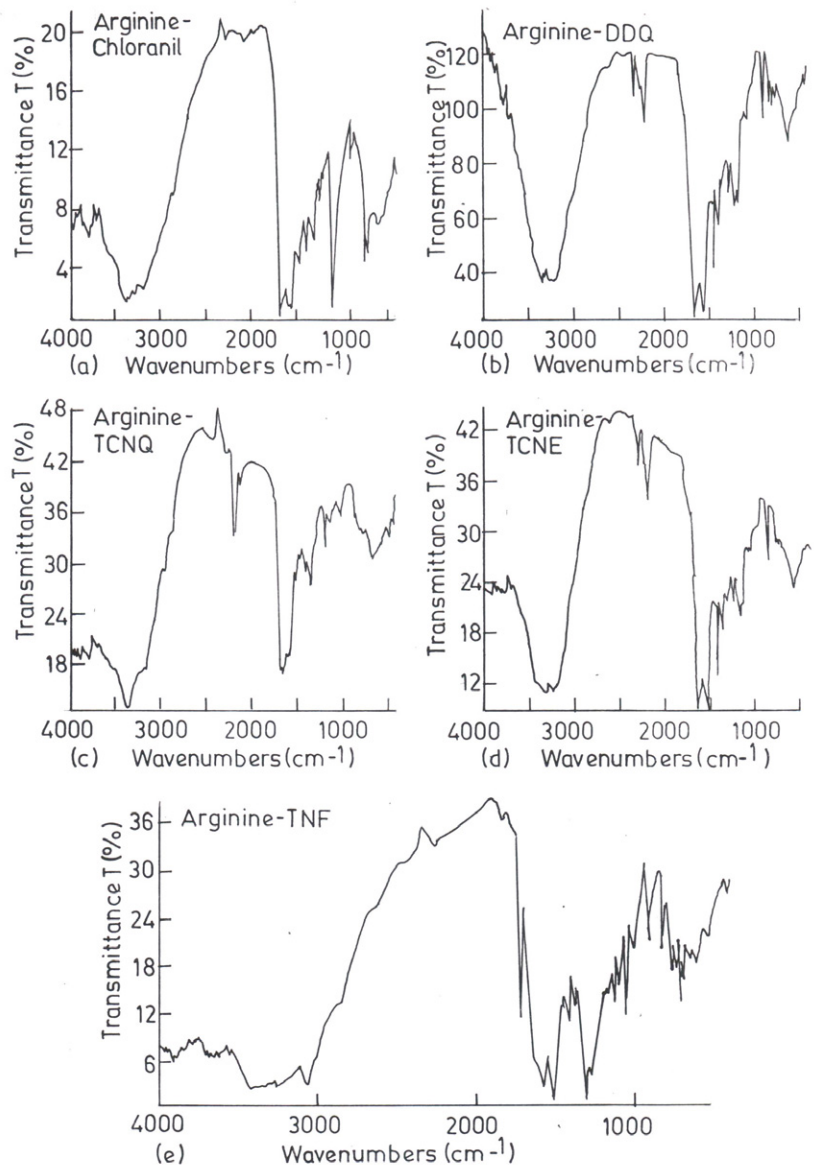

Figure 2. Infrared spectra of (a) arginine–chloranil, (b) arginine–DDQ, (c) arginine–TCNQ, (d) arginine–TCNE and (e) arginine–TNF.

of asparagine. The ν_{C-Cl} mode does not show interaction with asparagine. In the TCNQ complex, $\nu_{C\equiv N}$ and ring vibrations interact with NH and NH_2 groups in asparagine. In the TCNE complex, $\nu_{C\equiv N}$ and $\nu_{C=C}$ vibrations interact. In the TNF complex, $\nu_{C=O}$ and ν_{NO2} of TNF interact with NH and NH_2 groups as well as the hydrocarbon lining. The interaction of accepting group of an acceptor with NH or NH_2 groups is diminished by the formation of H-bonds in O–H–N and N–H–N among asparagine molecules. It seems that the hydrocarbon lining interacts more with acceptors because of the requirement for polarized molecules for consequent H-bonding.

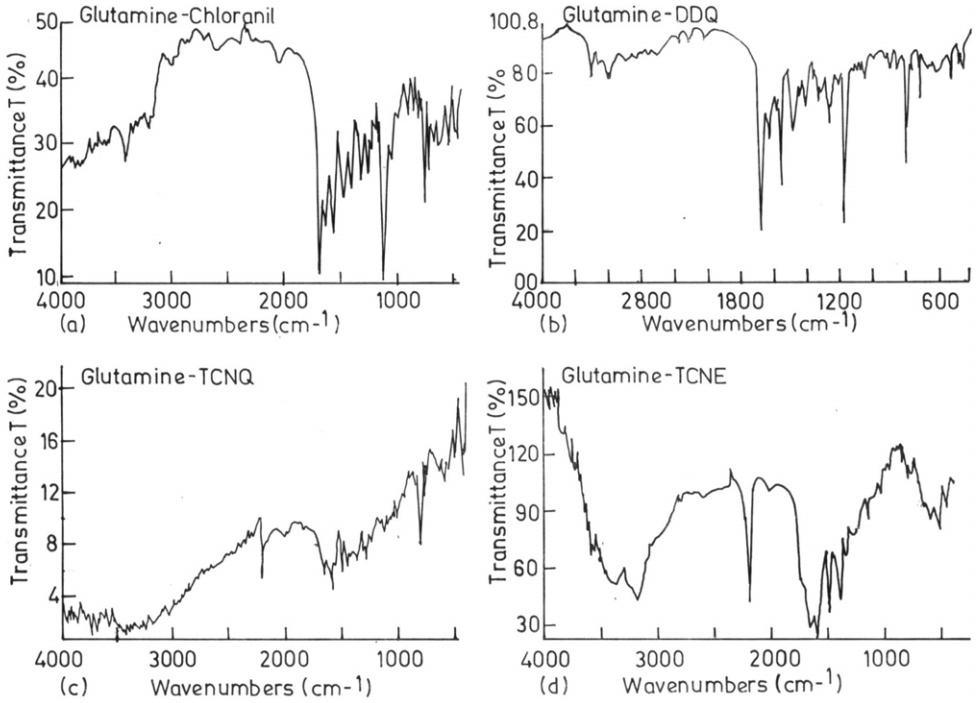

Figure 3. Infrared spectra of (a) glutamine–chloranil, (b) glutamine–DDQ, (c) glutamine–TCNQ and (d) glutamine–TCNE.

Among arginine complexes, the arginine–chloranil complex does not show much interaction between donor and acceptor on the high-frequency side (above 2200 cm^{-1}) of the spectrum. The ring and $\nu_{C=O}$ modes of chloranil interact with NH and NH_2 groups as well as with the hydrogen lining. In the DDQ complex, ν_{C-Cl}, $\nu_{C=O}$ and $\nu_{C\equiv N}$ interact with ν_{C-H}, ν_{N-H} etc vibrations of the amino acid. In the TCNQ complex $\nu_{C\equiv N}$ and ring modes of TCNQ interact with δ_{N-H} of arginine. In the TCNE complex, more interaction of $\nu_{C\equiv N}$ and $\nu_{C=C}$ is found with the hydrocarbon lining than the interaction with NH or NH_2 groups. δ_{N-H} does not show any shift. In the TNF complex, a symmetric structure arises in the 1200–1700 cm^{-1} range out of the density of states. Again only low- and intermediate-frequency vibrations show changes.

In the case of glutamine complexes, glutamine–chloranil shows interaction of ν_{C-Cl}, $\nu_{C=O}$ and ring vibrations of chloranil with the hydrocarbon lining and δ_{N-H} modes. There is strong smearing of ν_{N-H}, ν_{O-H} and ν_{C-H} vibrations at high frequencies both because of H-bonding and because of interaction with acceptor groups. In the DDQ complex, an interaction exists covering the full infrared range frequencies. $\nu_{C=O}$, ν_{C-Cl} and ν_{C-C} of DDQ interact mainly with the hydrocarbon lining. In the TCNQ complex, $\nu_{C\equiv N}$ and ring vibrations interact with molecular vibrations of glutamine. There is also noise in the full IR spectrum. The electronic absorption envelopes at the intermediate- and low-frequency ranges merge. Glutamine–TCNE shows a transmitting mid-IR range like dyes. $\nu_{C\equiv N}$ of TCNE interact with $\nu_{C=C}$, δ_{O-H} and δ_{C-H} of the glutamine molecule.

In the case of histidine complexes, histidine–chloranil, $\nu_{C=O}$, ν_{C-Cl} and ring vibrations of chloranil show changes due to interaction with histidine. π_{C-H}, δ_{N-H}, ν_{C-N} etc show a red-shift due to interaction with $\nu_{C=O}$ and ν_{C-Cl} of chloranil. In the DDQ complex, the envelopes at intermediate and low frequencies merge. $\nu_{C\equiv N}$, $\nu_{C=O}$ and ring vibrations of DDQ show

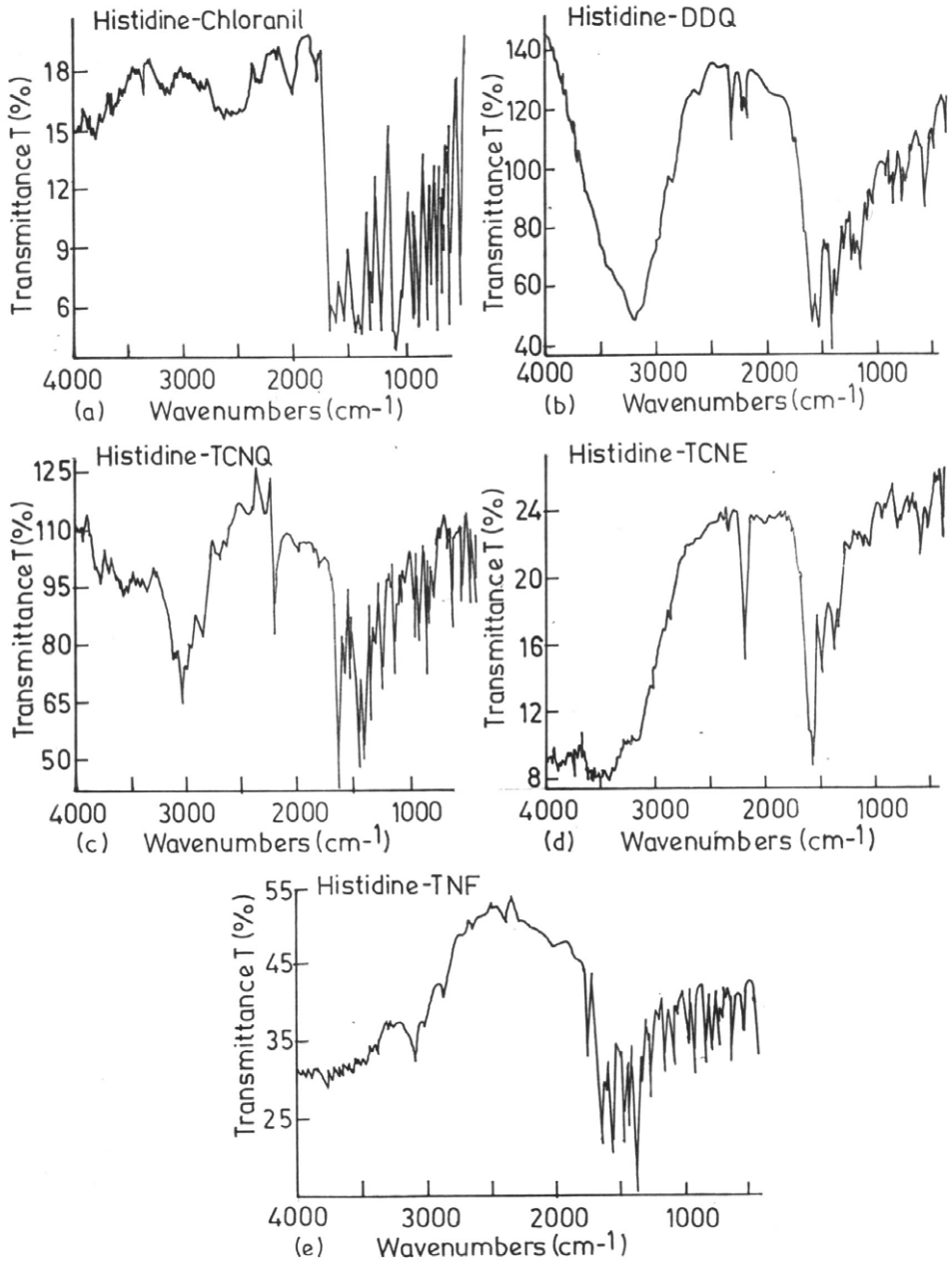

Figure 4. Infrared spectra of (a) histidine–chloranil, (b) histidine–DDQ, (c) histidine–TCNQ, (d) histidine–TCNE and (e) histidine–TNF.

changes due to interaction of NH and NH_2 groups and ring vibrations of histidine. In the TCNQ complex, $\nu_{C\equiv N}$ and ring vibrations interact with NH and NH_2 groups and the ring vibrations of the heterocyclic ring of histidine. In the TCNE complex, $\nu_{C\equiv N}$ and $\nu_{C=C}$ of TCNE interact with NH and NH_2 groups and with the histidine ring.

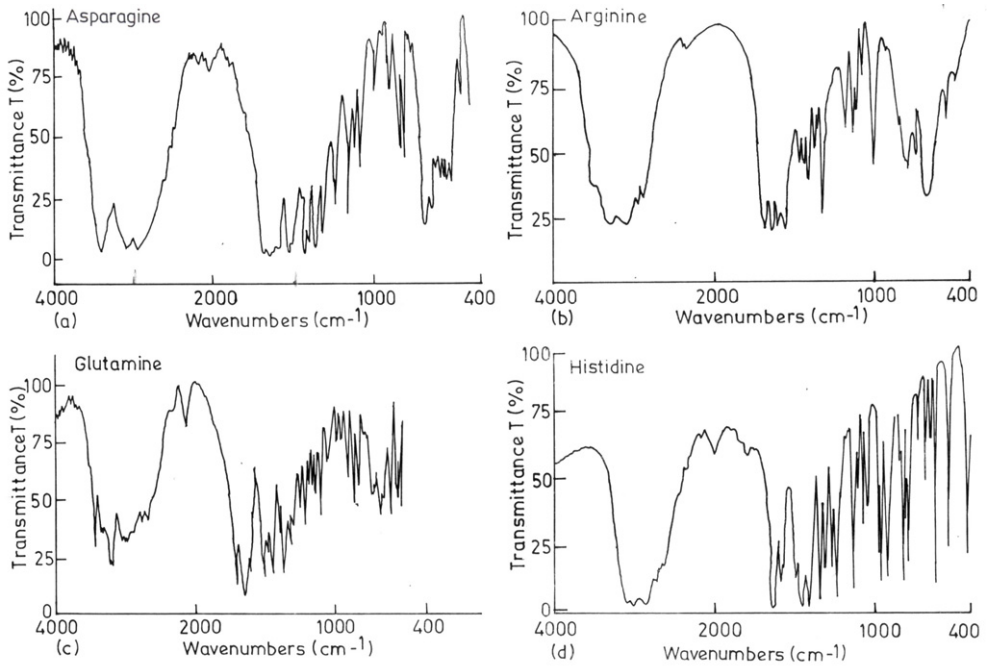

Figure 5. Infrared spectra of (a) asparagine, (b) arginine, (c) glutamine and (d) histidine.

In almost all of the above charge transfer complexes of amino acids, the interaction of acceptors with the hydrocarbon lining leading to an electrical polarization of the amino acid was found to be maximum. The interaction of NH and NH_2 groups with the acceptor was minimized because of the formation of a H-bonded network leading to only a small red-shift of δ_{N-H} vibration. Strong smearing and broadening of ν_{C-H}, ν_{O-H} and ν_{N-H} vibrations in the high-frequency range can be assigned to the formation of the H-bonded network. The compounds, like lipids, have a two-dimensional H-bonded network. This network here also leads to a layered or two-dimensional character of the materials verified by the nature of the transition, i.e. the absorption coefficient as function of frequency.

The absorption function either obeys

$$\alpha = \alpha_0(h\nu - E_g)^r$$

or

$$\alpha h\nu = A(h\nu - E_g)^r$$

depending on whether the material is crystalline (ordered) or amorphous (disordered). The function governed by the exponent r also differs in one-, two- and three-dimensional conductors as summarized in table 1. Here α is the absorbance of the sample depending also upon the sample thickness. $\alpha = 100 - T$ when the reflectance (R) is negligible. T is percentage transmittance. The CTCs of amino acids were classified into four classes on the basis of these dependences of the absorption profiles (table 2). This table shows that all the CTCs obey

$$\alpha = \alpha_0 \frac{(h\nu - E_g)^r}{h\nu}$$

or

$$\alpha = \alpha_0(h\nu - E_g)^r,$$

where $r = 0$ and 1.

Table 1. Dependence of absorption function on dimensionality $\alpha = \alpha_0 \frac{(h\nu - E_g)^r}{h\nu}$ values of exponent r for different types of transition across the band gap. (Note: $\alpha = \alpha_0(h\nu - E_g)^r$ for crystalline material with the same r values.)

	Direct			Indirect		
Types of transition	One dimensional	Two dimensional	Three dimensional	One dimensional	Two dimensional	Three dimensional
Allowed	1/2	0	1/2	2	1	2
Forbidden	3/2	1	3/2	3	2	3

Table 2. Absorption functions for CT complexes of amino acids.

$(h\nu - E_g)^r$ with $r = 0$			
Name of complex	Nature of transition	Nature of transition	Range of α = constant (cm^{-1})
Histidine–TCNE	Allowed direct	$h\nu \uparrow \alpha$ = constant	1700–2400
Glutamine–chloranil			2000–3000
Glutamine–TCNE			1900–2900
Arginine–DDQ			1750–2550
Arginine–chloranil			1800–2300
Asparagine–TCNE			1900–2500
Asparagine–TNF			2000–2500
Glutamine–DDQ			1800–2500
Asparagine–DDQ			1850–2500
$(h\nu - E_g)^r$ with $r = 1$			
Nature of complex	Graph	Nature of transition	Nature of transition
Histidine–chloranil Glutamine–TCNQ Arginine–TNF Asparagine–TCNQ Asparagine–chloranil	α versus $h\nu$	Forbidden direct or allowed indirect	$h\nu \uparrow \alpha \uparrow T \downarrow$
$\frac{(h\nu - E_g)^r}{h\nu}$ with $r = 0$			
Nature of complex	Graph	Nature of transition	Nature of transition
Histidine–TCNQ Arginine–TCNQ Arginine–TCNE	α versus $1/h\nu$	Allowed direct	$h\nu \uparrow \alpha \downarrow T \uparrow$
$\frac{(h\nu - E_g)^r}{h\nu}$ with $r = 1$			
Nature of complex	Graph	Nature of transition	Nature of transition
Asparagine–I_2 Histidine–TNF Histidine–DDQ	$\alpha h\nu$ versus $h\nu$	Forbidden direct or allowed indirect	$h\nu \uparrow \alpha \uparrow T \downarrow$

The function with even $r = 2$ corresponding to forbidden indirect transition in 2d materials was also never found, which may also correspond to a 1d or 3d conductor.

Class I corresponds to $\alpha = \alpha_0(h\nu - E_g)^r$ for crystalline material with $r = 0$ (allowed direct transition in 2d systems), i.e. α = constant. The ranges of wavenumbers of nine complexes in which α = constant are mentioned in table 2. Class II corresponds to $\alpha = \alpha_0(h\nu - E_g)^r$ with $r = 1$ (forbidden direct or allowed indirect transition in 2d systems), i.e. $\alpha = \alpha_0(h\nu - E_g) - \alpha$

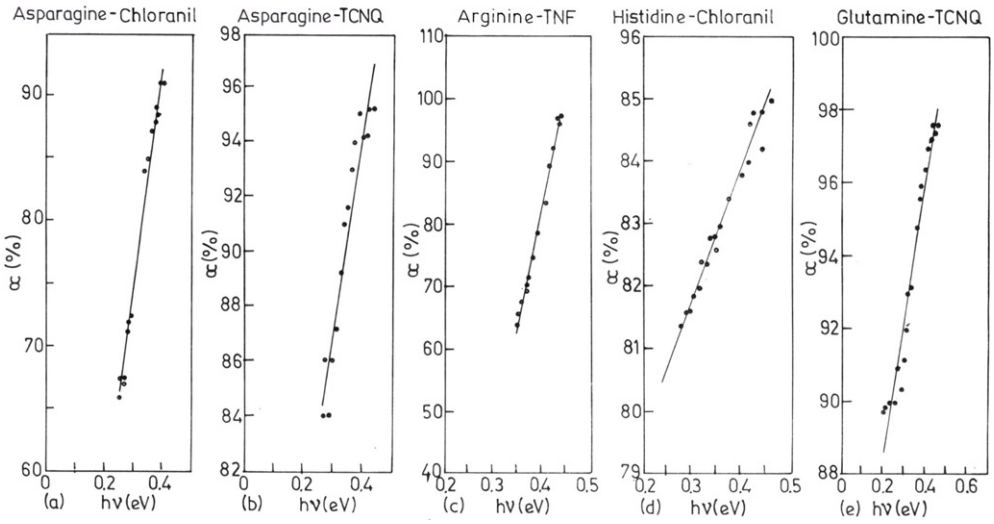

Figure 6. Absorption coefficient (α) versus photon energy ($h\nu$) for (a) asparagine–chloranil, (b) asparagine–TCNQ, (c) arginine–TNF, (d) arginine–chloranil and (e) glutamine–TCNQ.

is linearly proportional to $h\nu$ (or ν). Class III corresponds to $\alpha = \alpha_0(h\nu - E_g)^r/h\nu$ with $r = 0$ (allowed direct transition in amorphous materials having fractal dimension two), i.e. $\alpha = \alpha_0/h\nu$ thus having α versus $1/h\nu$ as rectilinear plots. Class IV corresponds to $\alpha = \alpha_0(h\nu - E_g)^r/h\nu$ with $r = 1$ (either forbidden direct or allowed indirect transition in amorphous materials having fractal dimension two), i.e. $\alpha h\nu = \alpha_0(h\nu - E_g)$ having $\alpha h\nu$ versus $h\nu$ as rectilinear plots.

Nine complexes of out of 20 were found to obey $\alpha =$ constant for $h\nu > E_g$ with $r = 0$. The ranges of $\alpha =$ constant are also mentioned in table 2. Thus the absorption profile becomes flat above E_g which is a special characteristic of two-dimensional (layered) semiconductors. The electrical resistivity (or conductivity) also becomes constant in its temperature dependence at low temperatures (Nalini 1977). This is found in both inorganic and organic layered materials (Disalvo and Graebner 1977). Only five CTCs obey $\alpha = A(h\nu - E_g)^r$ with $r = 1$, i.e. a rectilinear increase in α with $h\nu$. These plots based on the infrared spectra are shown in figure 6. Thus $9 + 5 = 14$ materials obey functions for crystalline materials.

Only three materials, namely histidine–TCNQ, arginine–TCNQ and arginine–TCNE, obey $\alpha = \alpha_0(h\nu - E_g)^r/h\nu$ with $r = 0$, i.e. α is proportional to $1/h\nu$ (reciprocal to energy). These plots are shown explicitly in figure 7. This is a function for a disordered material.

The last three CTCs, namely asparagine I_2, histidine–TNF and histidine–DDQ, obey $\alpha = \alpha_0(h\nu - E_g)^r/h\nu$ with $r = 1$, i.e. $\alpha = \alpha_0(1 - E_g/h\nu)$. In these cases, $\alpha h\nu$ versus $h\nu$ are plotted in figure 8, which should be straight lines. This is also the absorption function for disordered two-dimensional materials.

The above classification reveals how all of 20 complexes are two-dimensional conductors (table 2). The values of the forbidden energy band gap (E_g) between the top of the valence band and the bottom of the conduction band are obtained from the extrapolation of the absorption profile to zero absorption or to the background value using the concept of optical absorption edges and are tabulated (table 3).

There are two types of H-bonding—intramolecular and intermolecular (Ferguson 1973). There are three types of H-bonded systems which can be classified as: (1) a local

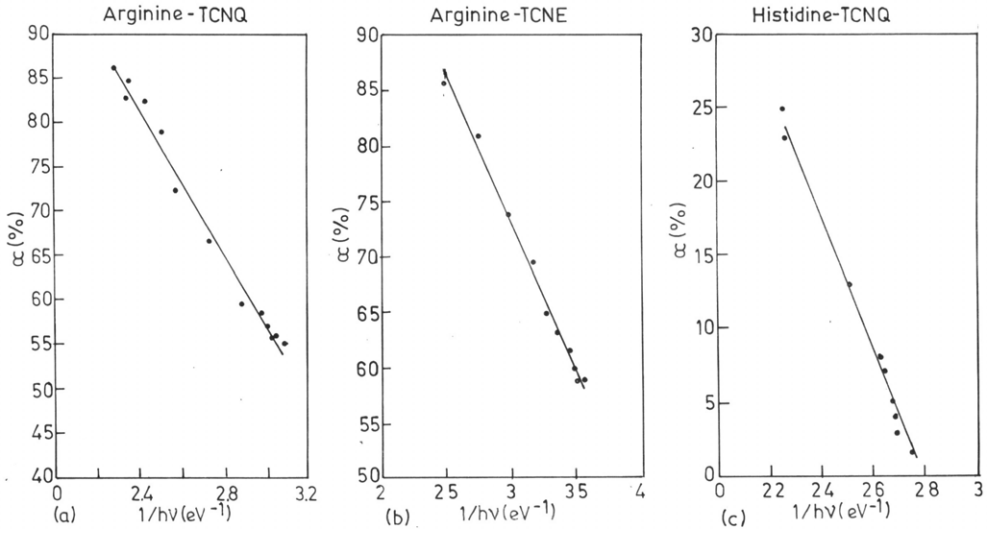

Figure 7. Absorption coefficient (α) versus reciprocal of photon energy ($h\nu$) for (a) arginine–TCNQ, (b) arginine–TCNE and (c) histidine–TCNQ.

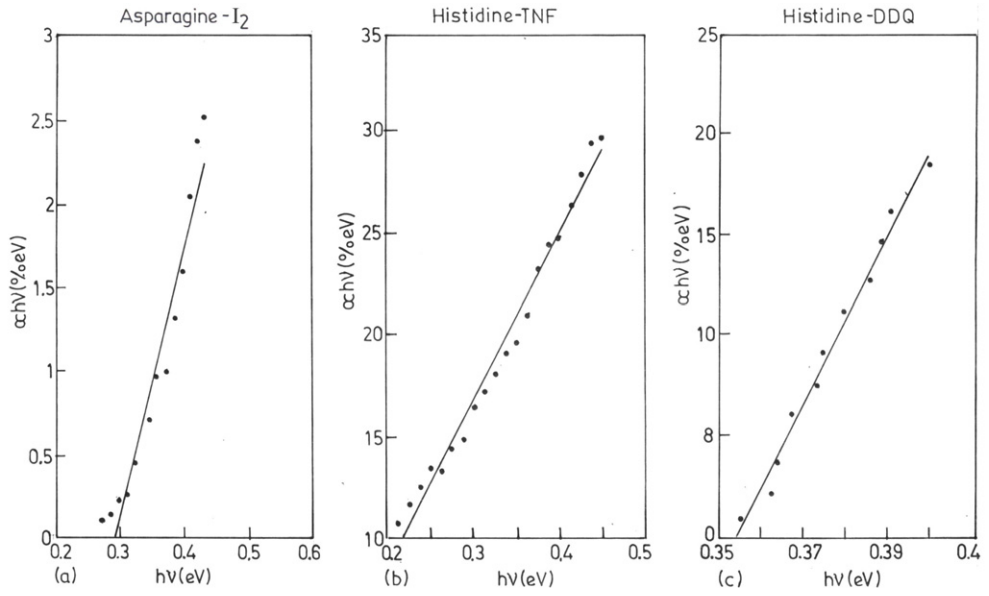

Figure 8. $\alpha h\nu$ versus $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy, for (a) asparagine–I_2, (b) histidine–TNF and (c) histidine–DDQ.

H-bonding having either intramolecular H-bonding or only two molecules joined by a H-bond but remaining discrete in the crystal; (2) an intermediate-range H-bonded network in which a few molecules are involved, forming a macromolecule; and (3) systems having an infinite number of H-bonds forming an extended H-bonded network in one or more directions but spanning the whole crystal. Examples of the first type are $Ni(Hdmg)_2$ where Hdmg = dimethylglyoxime, having an intramolecular H-bond and quinhydrone having a

Table 3. The values of band gaps for CT complexes of amino acids found as optical absorption edges.

Sr. No.	Name of complex	Value of E_g (eV)
1	Histidine–TCNE	0.225
2	Glutamine–chloranil	0.225
3	Glutamine–TCNE	0.225
4	Arginine–DDQ	0.225
5	Arginine–chloranil	0.225
6	Asparagine–DDQ	0.225
7	Aspargine–TNF	0.225
8	Asparagine–TCNE	0.2325
9	Glutamine–DDQ	0.275
10	Asparagine–iodine	0.30
11	Histidine–TNF	0.215
12	Histidine–DDQ	0.354
13	Histidine–chloranil	0.2375
14	Glutamine–TCNQ	0.2331
15	Arginine–TNF	0.2375
16	Asparagine–TCNQ	0.2375
17	Asparagine–chloranil	0.244
18	Histidine–TCNQ	0.225
19	Arginine–TCNQ	0.255
20	Arginine–TCNE	0.2313

H-bond between hydroquinone and *p*-benzoquinone (Trivedi *et al* 2005). Among the second type are polypeptides, polysaccharides and antibiotics forming circular, toroidal or helical molecules. The third type contains systems like benzamide–KI–I_2 and benzamide–HI–I_2 (Reddy *et al* 1964, Robin 1964).

The infrared spectra of CTCs of donor and acceptor molecules normally show a direct interband transition (Oza *et al* 2004). But if H-bonding is present it can show an indirect transition as in the case of quinhydrone (Trivedi *et al* 2005). The phonon involved in an indirect transition can be thus correlated to H-bonding. The transition becomes indirect in systems having regular but direct H-bonding. The present cases of the CTCs of amino acids having an infinite H-bonded network leading to 2d layers show all direct transitions. This means that in the CTCs of quinhydrone there is local deformation or a local phonon mode associated with H-bonding. When an infinite network of H-bonds is formed, there is delocalization or globalization of strain associated with H-bonding, thus again leading to direct transition not involving any phonons. The H-bonds are spread in two directions giving rise to a layered character. Once the system becomes two-dimensional, the probability of the occurrence of Peierls transitions and other 1d localization effects diminishes. Only a commensurate to incommensurate transition can occur, as in the cases of inorganic 2d conductors. Also the probability of a Ginzberg superconducting phase due to an exciton mechanism in layered materials increases (Ginzberg 1972a, 1968, 1970, 1972b).

Purely organic CTCs show direct transitions as compared to CTCs based on organometallic chelates, unless there is intermolecular H-bonding in the former case. The examples are CTCs based on quinhydrone in which *p*-benzoquinone and hydroquinone form quinhydrone with intermolecular H-bonding. Quinhydrone itself shows a forbidden indirect transition which is retained in many of its CTCs. Thus the H-bonding provides emission and absorption of a phonon due to local deformation potential or stress generated due to local binding. The present

study shows that if there is a two- or three-dimensional network of H-bonding and not discrete H-bonding sites the electronic transition becomes direct. Thus when there is a H-bonding network as found crystallographically in benzamide–KI–I_2 and benzamide–HI–I_2, the local stress gets relaxed or spread, quenching the role of phonons in an electronic transition.

All amino acids involved in the present study form two-dimensional conductors with standard organic acceptors because of intermolecular H-bonding of one or more NH or NH_2 groups. This can be concluded on the basis of a comparison with lipids which form a two-dimensional β-structure arising out of a H-bonded network in solid form.

4. Conclusion

The 20 CTCs of four amino acids studied in the present work are all two-dimensional semiconductors. The transitions verified with optical (or electronic) absorption edges reveal a layered nature arising out of H-bonds. The relaxation of the stress associated with the local deformation in H-bonding leads again to a direct rather than indirect transition in these purely organic CTCs.

Acknowledgments

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