

Conjugated one and two dimensional polymers

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The band structures of some existing and hypothetical one and two dimensional conjugated polymers are examined in this work. The aim is to explore how the band gap sizes and the occurrence of partially filled bands are related to unit cell constitution and the geometrical disposition of the atoms in the unit cell. Among the polymers explored are polyacetylene, polydiacetylene, polyphenylene, polyacene, graphite, boron nitride, polynitrile, polycyanonitrile, polypyridinopyridine, paracyanogen, the C_3N net, $(SN)_x$, $(XCNSN)_x$, and $C_2S_3N_6$ net.

INTRODUCTION

Conjugated polymers are potentially important because of the possibility that a variety of semiconducting, photoconducting, and even metallic materials may be made by variation of backbone and side group structures (Meier 1974, Paushkin *et al.* 1974). Unfortunately most conjugated polymers synthesized so far by using conventional techniques are neither pure nor readily soluble, which has severely hindered the characterization of their structures and properties. In recent years highly crystalline conjugated polymers, i.e. polysulphur nitride and polydiacetylene, have been synthesized by solid state reactions, and their structures and properties have been extensively investigated.

The electrical and optical properties of a crystalline material depend upon its electronic structure, and ultimately on the chemical constitution of its repeat unit. In searching for new polymer materials with unusual and useful electrical and optical properties, it is important to build an intuition for understanding this relation, namely how the electronic structure of a material depends on the number of atoms and electrons in the unit cell and the geometrical disposition of the atoms. In the present work, the second of a series, such structure-property relations were investigated by surveying the band structures of several one and two dimensional conjugated polymers. Their band structures were calculated within the tight-binding scheme (André 1974) based upon the extended Hückel method (Hoffmann 1963). When a number of alternative configurations are possible for a given polymer, their relative stabilities were estimated in terms of the total energies per unit cell calculated from the band structures (Imamura 1970, Whangbo & Hoffmann 1978).

Owing to the one electron nature of the extended Hückel method, the important rôle of electron-electron interactions in band structures cannot be assessed in the present work. The termination of the long but finite chains clearly must have an important effect on their conductivity and stability, which we plan to examine in the future. Also we did not examine interchain or interplane interactions whose effects are always present in real polymeric materials. These limitations of the calculations, when combined with the unfortunate fact that the structures and properties of most conjugated polymer materials are not well characterized experimentally, significantly restrict meaningful comparisons between theory and experiment. Nevertheless, we feel it is crucial to lay the groundwork for an understanding of the dependence of band structure upon unit cell constitution and topology. This is explored in what follows in terms of simple ideas of symmetry, overlap, and bonding.

THEORETICAL PROCEDURE

Given a set of basis orbitals $\{\chi\}$ for the atoms of a unit cell, the set of Bloch basis functions $\{b_\mu(\mathbf{k})\}$ is formed as follows

$$b_\mu(\mathbf{k}) = N^{-\frac{1}{2}} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_l} \chi_\mu(\mathbf{r} - \mathbf{R}_l), \quad (1)$$

where \mathbf{k} is the wave vector, and $\mathbf{R}_l = \sum_i l_i \mathbf{a}_i$ with \mathbf{a}_i being primitive vectors. With the Bloch basis orbitals, i.c.a.o. crystal orbitals $\psi_n(\mathbf{k})$ are expressed as

$$\psi_n(\mathbf{k}) = \sum_\mu C_{n\mu}(\mathbf{k}) b_\mu(\mathbf{k}). \quad (2)$$

The corresponding eigenvalues $\epsilon_n(\mathbf{k})$ and coefficients $C_{n\mu}(\mathbf{k})$ are obtained from the eigenvalue equation

$$\mathbf{H}(\mathbf{k}) \mathbf{C}(\mathbf{k}) = \mathbf{S}(\mathbf{k}) \mathbf{C}(\mathbf{k}) \mathbf{e}(\mathbf{k}), \quad (3)$$

where $H_{\mu\nu}(\mathbf{k}) = \langle b_\mu(\mathbf{k}) | H_{\text{eff}} | b_\nu(\mathbf{k}) \rangle$ and $S_{\mu\nu} = \langle b_\mu(\mathbf{k}) | b_\nu(\mathbf{k}) \rangle$. Then band structures are determined by repeating the above calculation for various values of \mathbf{k} (usually within the first Brillouin zone). The atomic parameters of the extended Hückel calculation are detailed in the appendix. Unless stated otherwise, lattice sums (i.e. the summation over l in (1)) were carried out to first-nearest neighbours.

Equation (1) indicates that each Bloch basis $b_\mu(\mathbf{k})$ consists of the atomic orbitals $\chi_\mu(\mathbf{r} - \mathbf{R}_l)$ located at the various unit cells l , and each of them carries the phase factor $e^{i\mathbf{k} \cdot \mathbf{R}_l}$. Thus the nodal properties of a crystal orbital $\psi_n(\mathbf{k})$ at a specific value of \mathbf{k} are constructed once the expansion coefficient $C_{n\mu}(\mathbf{k})$ is known for each $b_\mu(\mathbf{k})$.

The geometrical parameters, i.e. bond lengths and bond angles, employed in our study are summarized in the appendix. Unless stated otherwise, standard bond lengths and bond angles were used. Even with those geometrical constraints, a number of different geometries may be conceivable for a given polymer. To estimate the most probable configuration in such cases, the total energies per unit cell were computed from the band structures by using the procedure described in our previous paper (Whangbo & Hoffmann 1978).

RESULTS AND DISCUSSION

(a) *Polymers with a carbon skeleton*

The carbon skeleton provides a number of conjugated polymers, whose basic structure patterns include linear and ladder chains as well as a two dimensional net. Among these polyacetylene has served as a model for extensive theoretical studies, and indeed the problem of whether or not bond alternation should occur in an

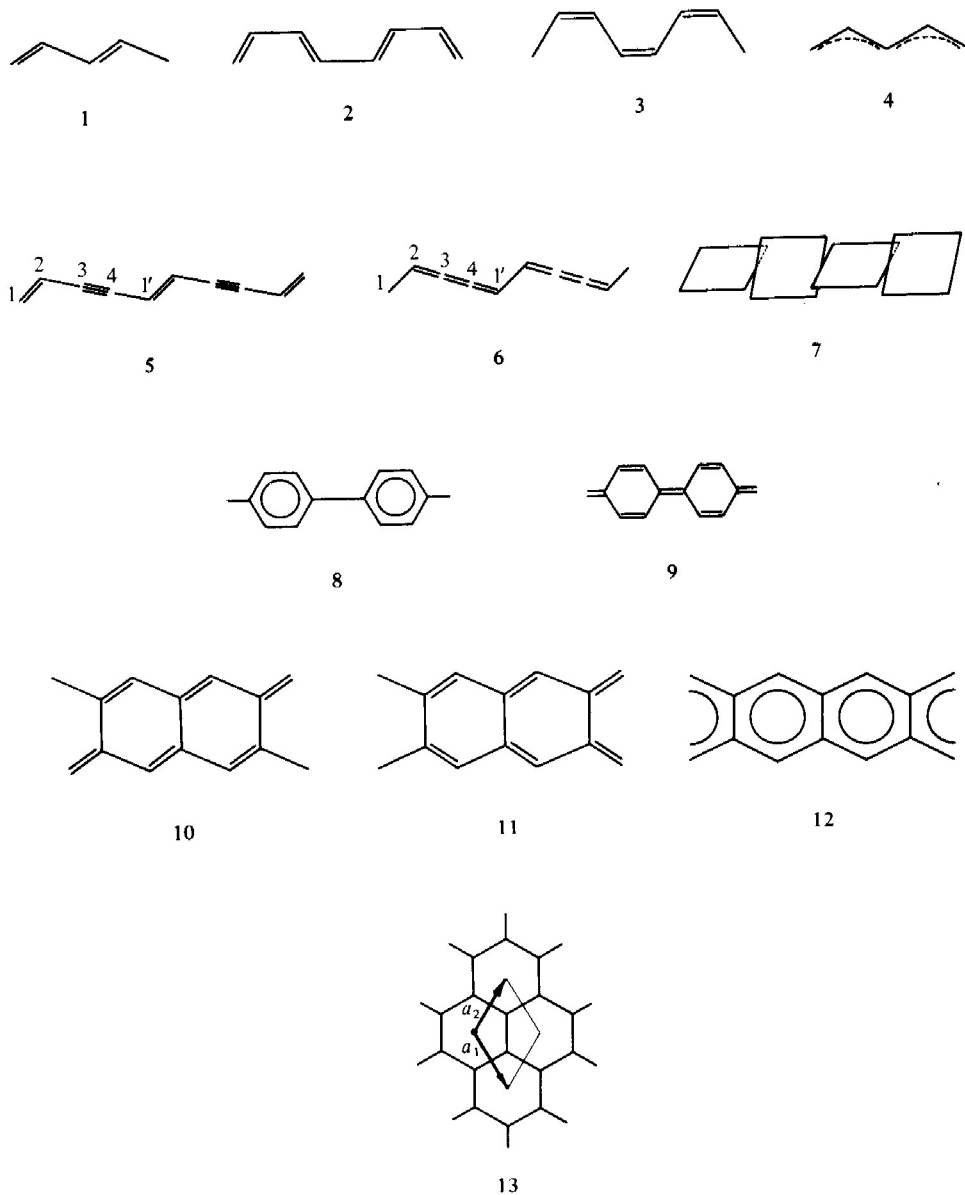


CHART I

infinite polyene has a venerable history (Salem 1966). Currently it is believed that the band gaps in conjugated polymers result not only from bond alternation but also from electron–electron interaction, the latter being more important (Ovchinnikov *et al.* 1973 and references therein). Inclusion of electron interactions within the π -electron approximation, subject to some uncertainties in parametrization, led to the suggestion that the configuration with equal C—C bond lengths is the energetically more favourable one in polyacetylene (Popov 1969, Harris & Falicov 1969). Our discussion is based solely upon the one electron approximation of the extended Hückel method, thereby not accounting for electron–electron interactions.

Those conjugated polymers with a carbon skeleton which we examined are displayed in chart I. They include various conformations of polyacetylene (**1**, **2**, **3**, **4**), polydiacetylene (**5**, **6**, **7**) and polyphenylene (**8**, **9**) as examples of a linear chain, polyacene (**10**, **11**, **12**) as examples of a ladder chain, and finally graphite (**13**) as an example of a two dimensional net. The repeat unit of each of these systems contains an even number of electrons, and the valence (i.e. the highest occupied) band and the conduction (i.e. the lowest unoccupied) band of these polymers are both made up of π orbitals. A restricted range of geometries of a given polymer was examined to estimate its most probable structure and band gap. In particular the latter was considered in some detail by examining the nodal properties of the valence and conduction band crystal orbitals at the Brillouin zone or edge where the band gap occurs.

Polyacetylene (Chiang *et al.* 1978). Configurations **1**, **2**, and **3** are characterized by alternation of single and double bonds, while **4** has equal C—C bond lengths (1.4 Å†). The band structures of **1**, **2**, and **4** are shown in figure 1. Since the general shape of the band structure of **3** is similar to that of **2**, it is not shown.

The total energies per unit cell calculated from these band structures show that the relative energies of **1**, **2**, **3**, and **4** are 0.0, 40.2, 45.6 and 7.5 kJ/mol, respectively, per CH=CH—CH=CH. Thus the *trans*-isomer **1** is more stable than either of the two conceivable *cis*-isomers **2** and **3**. For *cis*-polyacetylene **2** appears to be a better representation than **3**. Of the two *trans*-isomers **1** and **4** the latter, with equal bond lengths, is less stable.

The calculated band gaps of **1**, **2**, and **3** are 0.96, 0.71, and 1.23 eV, respectively, while **4** has the expected zero band gap. The polymer material consisting of *cis*-polyacetylene exhibits a smaller electrical conductivity than that of *trans*-polyacetylene (Shirakawa *et al.* 1973). If this is entirely due to the difference in the band gaps of their individual polymer chains, the above experimental result implies that the *cis*-isomer should have a greater band gap, and thus its configuration should be **3** rather than **2**. This is not consistent with the relative stabilities of **2** and **3** mentioned above. A further study is necessary to resolve this problem.

The π bands are labelled sequentially by lower case letters in figure 1. The nodal properties of the π bands *a* and *b* of **1** at the zone edge are shown below. **1a'** and **1b'** are respectively the out-of-phase and in-phase combinations of the π and π^* orbitals

† 1 Å = 0.1 nm = 10^{-10} m.

of a unit cell ($-\text{HC}=\text{CH}-$). Here and in the following the prime superscript indicates the zone edge, and its absence means the zone centre. If there were no bond alternation, $1a'$ would be of the same energy as $1b'$ thereby leading to overlap of the two bands at the zone edge (figure 1c). With alternating double and single bonds as shown in **1** a band gap results, with $1a'$ at lower energy than $1b'$.

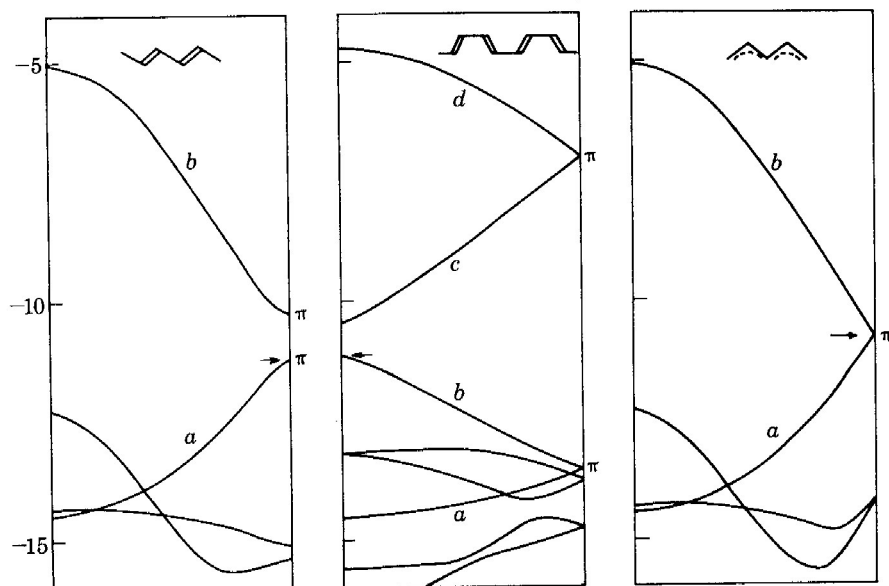
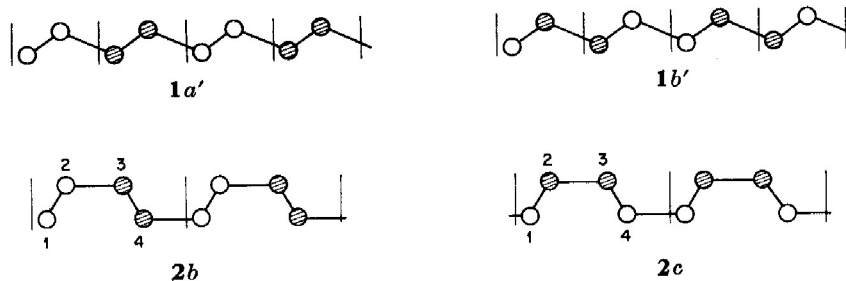


FIGURE 1. The band structures of polyacetylene. In all the figures energies are given in electronvolts.



The electronic structure of **2** and **3** is essentially similar to that of **1**. Owing to extension of the unit cell from two to four carbon atoms, a 'folding back' of the bands results with bands a and b of **2** corresponding to a of **1**, and c and d of **2** relating to b of **1**. The degeneracy of the bands of **2** as well as **4** at the zone edge is a consequence of the two-fold screw axis (translation by $\frac{1}{2}a$ coupled with rotation by 180° around the translation axis) (Parry & Thomas 1975). The nodal properties of the π bands b and c of **2** at the zone centre are shown above. Comparison of the 1, 4 interactions within a unit cell of **2** with the corresponding one of **1** indicates that **2b** is less stable

than $1a'$, but $2c$ is more stable than $1b'$. This is the reason for the smaller band gap in **2** relative to **1**. The $2, 1'$ interactions in **3b** and **3c** (below) are greater than the corresponding ones in $1a'$ and $1b'$, respectively. Thus **3** has a larger band gap than **1**.



In figure 1 there appear quite prominently bands of σ symmetry at relatively high energy. The extended Hückel method has a slight tendency to put σ orbitals at too high energy relative to π levels, so that this band placement may be an exaggeration.

Polydiacetylene. Solid state synthesis (Kaiser *et al* 1972, Baughman 1974) has recently been used to obtain polydiacetylenes of a high degree of structural perfection. This in turn has led to the measurement of a number of physical properties of this polymer (Stevens *et al.* 1978) and several theoretical studies (Parry 1976, Boudreaux 1975, Cojan *et al.* 1977, Wilson 1975, Philpott 1977) as well. Experimental studies led to the suggestion that there occurs a phase transition involving two extreme geometries (Iqbal *et al.* 1977) and that an exciton model provides a better description of the excited state properties of this polymer than a band picture (Muller *et al.* 1977, Chance & Baughman 1976, Schermann & Wegner 1974, Reimer & Bäessler 1975).

Two extreme geometries that could be conceived for the polymer are the 'ene-yne' **5** and the 'polybutatriene' **6**. Somewhat arbitrarily these may be defined by the geometrical parameters (D.S. Boudreaux & R. R. Chance, private communication 1977) $r_{12} = 1.34 \text{ \AA}$, $r_{23} = r_{41'} = 1.45 \text{ \AA}$; and $r_{34} = 1.20 \text{ \AA}$ in **5**; and $r_{12} = 1.478 \text{ \AA}$, $r_{23} = r_{41'} = 1.348 \text{ \AA}$, and $r_{34} = 1.26 \text{ \AA}$ in **6**. Intermediate configurations between **5** and **6** may be set up by linear interpolation through a conversion factor δ for each C—C bond length, such that **5** and **6** correspond to $\delta = 0$ and 1 respectively. The band structure of polydiacetylene for $\delta = 0.2$ is given in figure 2.

The total energy per unit cell of polydiacetylene was calculated as a function of δ , which reveals that as δ increases polydiacetylene gradually becomes less stable, **6** being less stable than **5** by about 46 kJ/mol. Thus the phase transition **6** \rightarrow **5** appears to be an energetically favourable process. This is consistent with the recent experimental observation that the low temperature phase of a polydiacetylene crystal with the substituent group $-(\text{CH}_2)_4\text{OCONHC}_6\text{H}_5$ is best described by an ene-yne configuration, while its high temperature phase is a polybutatriene (Iqbal *et al.* 1977).

With respect to the symmetry operation of inversion **5b** is antisymmetric, but **5c** is symmetric. For the geometrical distortion **5** \rightarrow **6**, **5b** becomes destabilized because of a decrease in bonding and an increase in antibonding. However, the opposite is the case for **5c**. Therefore a band gap narrowing is expected in the course of the geometry distortion **5** \rightarrow **6**. Figure 3a shows the top of the valence band and the

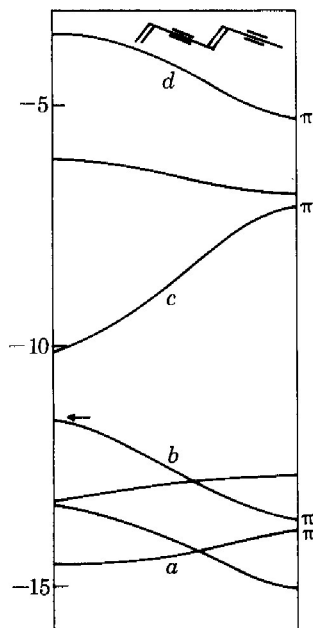


FIGURE 2. The band structure of polydiacetylene ($\delta = 0.2$).

bottom of the conduction band of polydiacetylene as a function of δ . As expected, the band gap becomes narrower with increasing δ . A crossing of the two levels occurs at $\delta \approx 0.87$, where the two π bands b and c touch each other, giving a zero band gap. According to this result, the change in polydiacetylene backbone from an ene-yne to a polybutatriene configuration should cause a red shift in the absorption edge of the electronic excitation spectrum. This appears to be the opposite to the above cited experimental information, which led to the suggestion that the excitation of polydiacetylene is excitonic.



Because of π delocalization in polydiacetylene, the excitation is expected to be of the Wannier-Mott type (Philpott 1977). In a band calculation the lowest exciton level E_{ex} of this type can be estimated by evaluating the effective mass of the top of the valence (m_v^*) and the bottom of the conduction (m_c^*) band as

$$E_{ex} = -13.6 m^* / \epsilon^2 \text{ eV}, \quad (4)$$

where E_{ex} is measured with respect to the bottom of the conduction band, ϵ is the dielectric constant of a crystalline system under consideration, and $1/m^* = 1/m_c^* + 1/|m_v^*|$. The effective masses were calculated from the band structures as a

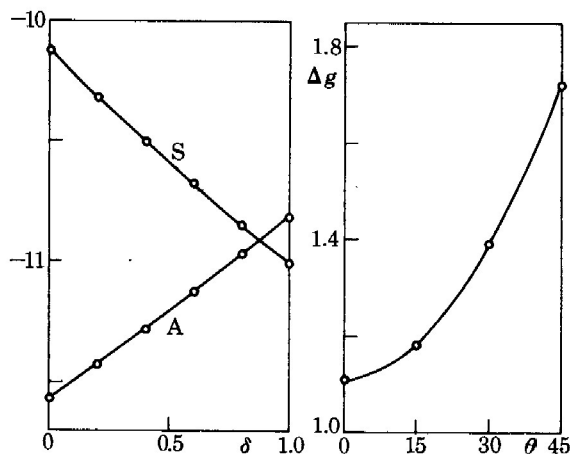


FIGURE 3. (a) The bottom of the conduction band and the top of the valence band in polydiacetylene as a function of δ . (b) The band gap of polydiacetylene as a function of θ .

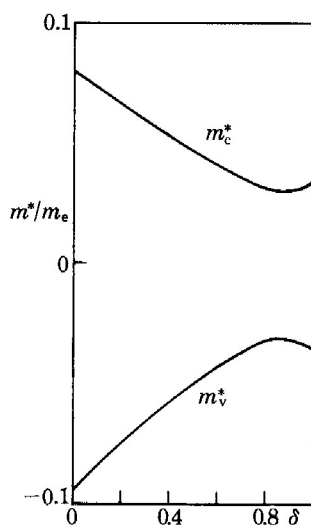


FIGURE 4. The effective mass at the bottom of the conduction band and at the top of the valence band in polydiacetylene as a function of δ .

function of δ , and are summarized in figure 4. With these data and the experimental values of ϵ for polydiacetylene (Cojan *et al.* 1977) the magnitude of E_{ex} turns out to be smaller than 0.1 eV for all δ , so that the main characteristic of the band gap variation shown in figure 3a remains essentially unchanged.

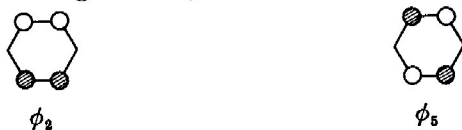
Polydiacetylenes that have been subject to experimental studies have bulky substituents such as



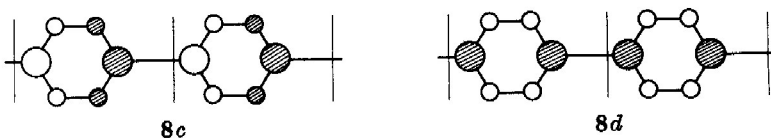
Thus it is of interest to probe the effect of the rotation of such side groups upon the band structure. In the present work $-\text{CH}_2\text{OH}$ was chosen as a model side group R and a complete range of side chain rotamer conformations of the repeat unit $\text{CR}=\text{CR}-\text{C}\equiv\text{C}$ was studied. In general side chain rotation does not affect the band gap in any appreciable way. The top of the valence band and the bottom of the conduction band vary by less than 0.2 eV over the entire range of conformations, both lowered slightly in energy due to $\pi-\sigma_{\text{C}^*}^*$ hyperconjugation when the C—O bond is perpendicular to the polydiacetylene backbone plane.

A geometry distortion that polydiacetylene or any other conjugated linear polymer might undergo is an out-of-plane twisting of its backbone. In particular consider **7**, in which each plane contains an $\text{HC}=\text{CH}-\text{C}\equiv\text{C}$ unit, and alternate planes make a dihedral angle θ around the chain axis. For nonzero θ , a unit cell of **7** is twice as large as that of **5**. During the out-of-plane twisting the antibonding interaction between neighbours in **5b** as well as the bonding interaction between neighbours in **5c** becomes smaller. Therefore a band gap widening is expected as θ increases. This is shown in figure 3b for the polydiacetylene structure with $\delta = 0.2$. The total energy per unit cell calculated as a function of θ shows that the out-of-plane twisting gradually makes polydiacetylene less stable. However, the potential surface for this deformation appears to be very soft, the configuration of $\theta = 45^\circ$ being unstable by only 7.5 kJ/mol relative to the planar one. Therefore the out-of-plane twisting appears to be an easy process by which a blue shift in the electronic excitation spectrum might be caused, although the aforementioned blue shift of the polybutatriene configuration may well be a phenomenon explicable only by theory beyond the one electron approximation.

Polyphenylene (Beck 1964, Tyutyulkov & Polansky 1977). Two extreme configurations have been examined by us, the 'aromatic' **8** and the 'quinonoid' **9**. The band structure of **8** is given in figure 5. Two of the π bands, *b* and *e*, are nearly flat. They are composed of the benzene ϕ_2 and ϕ_5 orbitals, respectively, and these have small overlap between neighbouring units.



The benzenoid geometry **8** is calculated to be 40.6 kJ/mol more stable than the quinonoid **9**. **8** has the larger band gap, 1.89 eV, compared to 0.47 eV in **9**. The band gap differential comes from the effect of the distortion that takes **8** into **9** on the frontier bands *c* and *d*. **8c** becomes more antibonding, while **8d** becomes more bonding.



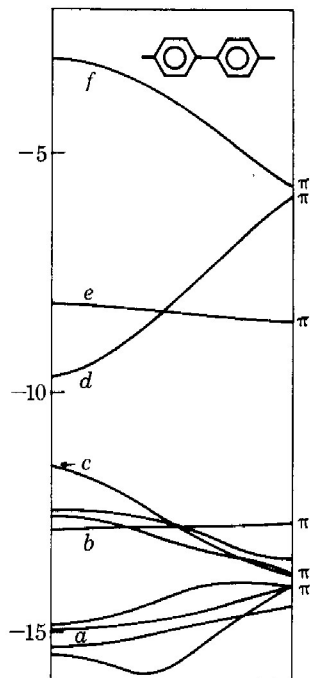
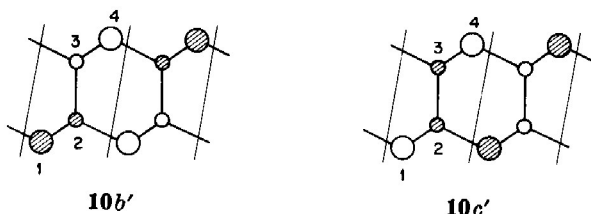
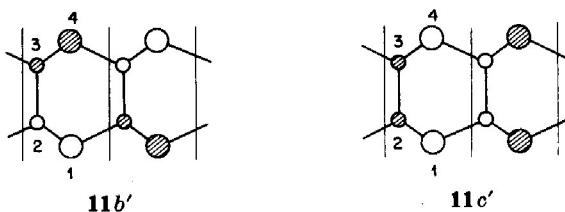


FIGURE 5. The band structure of polyphenylene.

Polyacene (Tyutyulkov *et al.* 1975). We have carried out calculations on three extreme geometries. **10** and **11** consist of localized alternating double and single bonds, with *trans* and *cis* configuration within the unit cell, while **12** is an 'aromatic' structure. The relative energies of **10**, **11**, and **12** are found to be 0.0, 2.1, and 27.6 kJ/mol, respectively. Thus the aromatic configuration is less stable than the non-aromatic configurations, and of the two non-aromatic configurations the *trans* structure appears to be slightly more stable.

The band structures of **10** and **12** are shown in figure 6. The π bands *b* and *c* of **11** or **12** are respectively antisymmetric and symmetric with respect to the twofold rotation around the chain axis. This additional symmetry element allows in principle a crossing of the bands. In **12** these two bands cross, and in **11** (not illustrated) they nearly touch each other at the zone edge. The band gaps of **10** and **11** are 0.45 and 0.002 eV, respectively.





The 1, 4 interactions within a unit cell are greater in $11b'$ and $11c'$ than in $10b'$ and $10c'$ respectively. Thus $11b'$ is at higher energy than $10b'$, but $11c'$ is at lower energy than $10c'$. This leads to a smaller band gap for 11 than for 10 . The geometry distortion $11 \rightarrow 12$ makes $11b'$ more unstable and $11c'$ more stable, which is responsible for the crossing of bands b and c in 12 .

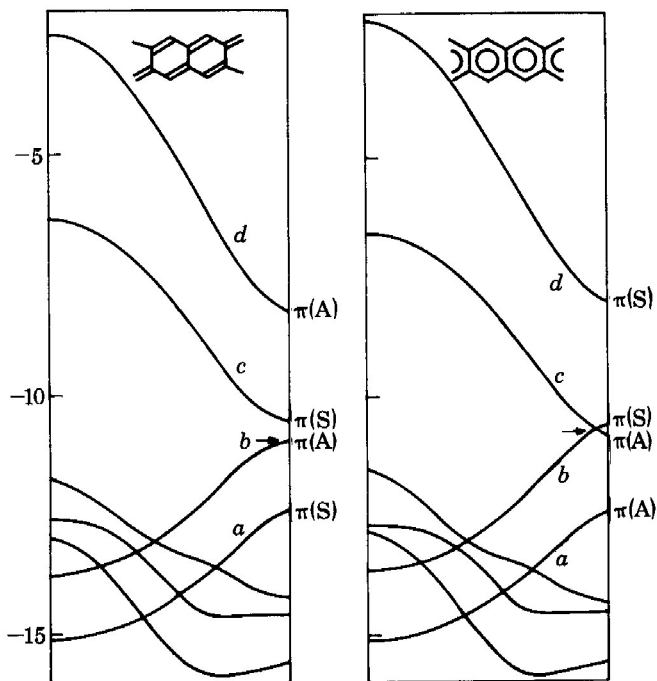
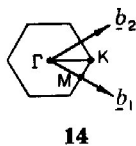


FIGURE 6. The band structures of polyacene.

Graphite. Figure 7 shows the band structure of graphite calculated along the lines joining the symmetry points Γ , K and M of the first Brillouin zone (14) (Slater 1965). There are two π electrons per unit cell in 13, and the π bands a and b overlap at K leading to the



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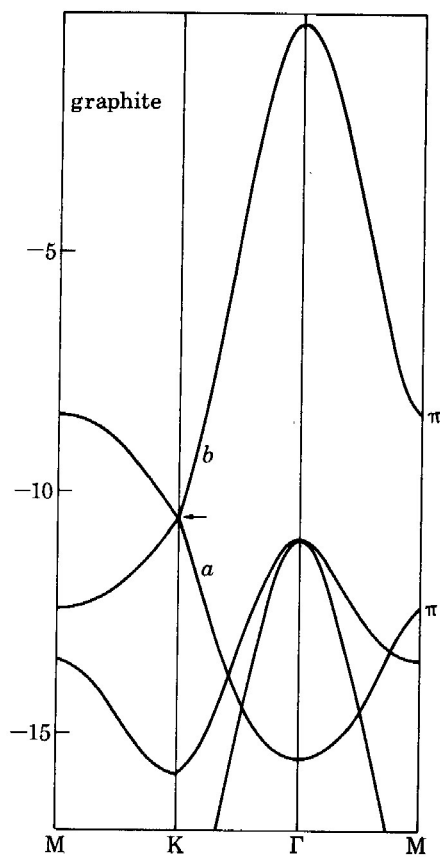
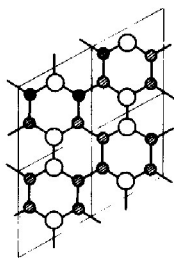
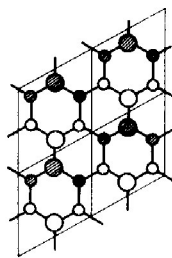


FIGURE 7. The band structure of graphite.

conduction capability of graphite. The degeneracy of the two π bands a and b at K may be analysed in terms of nodal properties of two dimensional crystal orbitals. At K the phase factor $e^{ik \cdot R_l} = e^{-\frac{2}{3}i\pi(l_1+l_2)}$. The nodal properties of a and b at K are constructed by repeating the π and π^* orbitals of a unit cell according to the above phase factor. For example, the real parts of thus constructed nodal properties are shown below:



13a



13b

13a is constructed from the π orbitals in which the repeating orbital pattern (or unit pattern) is one of the $2e$ benzene orbitals. This then is combined in-phase between neighbouring unit patterns. **13b** is constructed from the π^* orbitals, in which a unit pattern is one of the $1e$ benzene orbitals. These are combined out-of-phase between neighbouring unit patterns. Thus the energies of **13a** and **13b** are the same.

Boron nitride is isostructural and isoelectronic with graphite (see below). Yet its properties are quite different from those of graphite. The band structure of BN is given in figure 8, which shows no overlap of the two π bands as was observed for

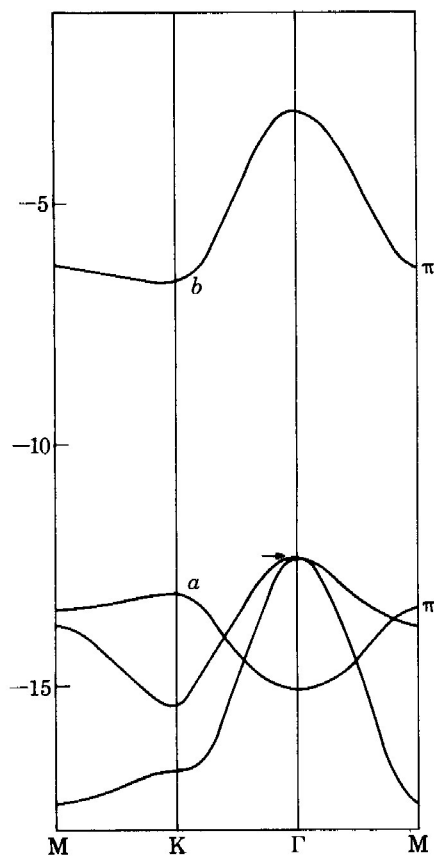
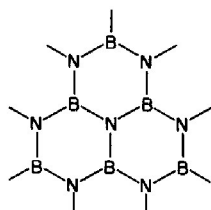
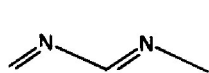


FIGURE 8. The band structure of boron nitride.

graphite (Zunger *et al.* 1976, and references therein). Thus the overlap of the π bands in graphite is not only a consequence of its 'honeycomb' skeleton, but is also due to the additional symmetry resulting from the fact that the two atoms of a unit cell are the same. We will encounter a similar case later.

(b) *Polymers with carbon and nitrogen skeletons*

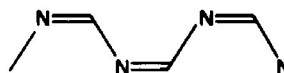
Experimentally known conjugated polymers of carbon and nitrogen atoms include linear and ladder chains. Not many of these are well-characterized materials.



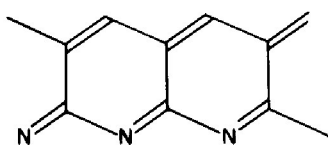
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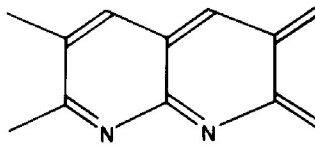
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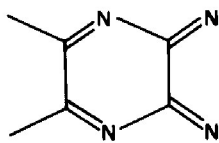
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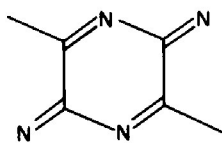
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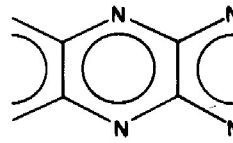
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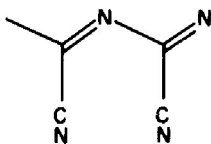
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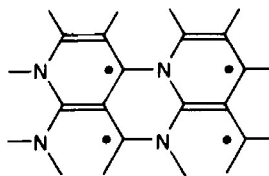
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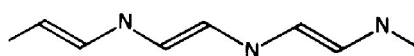
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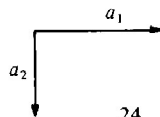


CHART II

There appears to be no strong evidence for a two dimensional net of carbon and nitrogen atoms. Chart II lists the idealized conjugated systems examined by us. These include polynitrile (**15**, **16**, **17**), polycyanonitrile (**23**) and polyenamine (**25**) as examples of a linear chain, polypyrazinopyrazine (**18**, **19**) and paracyanogen (**20**, **21**, **22**) as examples of a ladder chain, and finally the hypothetical two dimensional net **24**. They differ from the conjugated polymers with a carbon skeleton by simple substitution of nitrogen for a CH or carbon atom, and except for **24** all of them contain an even number of electrons in a unit cell.

Our objective in the following discussion is to examine how far the band structures of the carbon polymers, described in the previous section, can be modified by such a replacement. As will be seen, the major change is caused by the high-lying lone pair orbital of nitrogen atoms.

Polynitrile (Kargin *et al.* 1961, Paushkin *et al.* 1965). Three configurations **15**, **16**, and **17** were considered in our calculations for polynitrile. The band structures of **15** and **16** are shown in figures 9a and 9b, respectively. In polynitrile the valence band top is largely composed of nitrogen lone pair orbitals, as shown below. The relative stabilities of **15**, **16**, and **17** are 0.0, 23.0 and 23.9 kJ/mol, respectively, and their band gaps are 2.35, 1.97 and 1.94 eV, respectively. Unlike the case of polyacetylene, both *cis* configurations **16** and **17** have a smaller band gap than the *trans* configuration **15**.

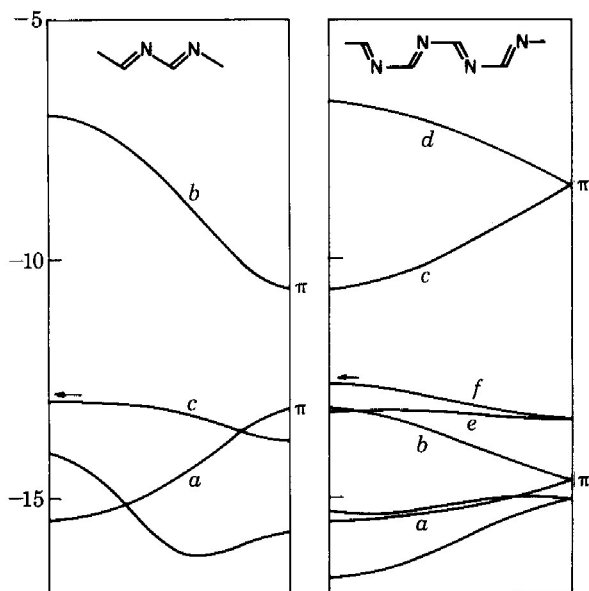
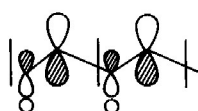
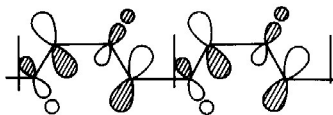


FIGURE 9. The band structures of polynitrile.



15c



16f

Polypyridinopyridine (Vohler *et al.* 1970, Brennan *et al.* 1962). Probable configurations of polypyridinopyridine are **18** and **19**. The band structure of **19** is given in figure 10. As in polynitrile, the top of the valence band is largely composed of nitrogen lone pair orbitals, as shown below. The stabilities of **18** and **19** are calculated to be nearly the same, the former being more stable by 1.7 kJ/mol per unit cell.

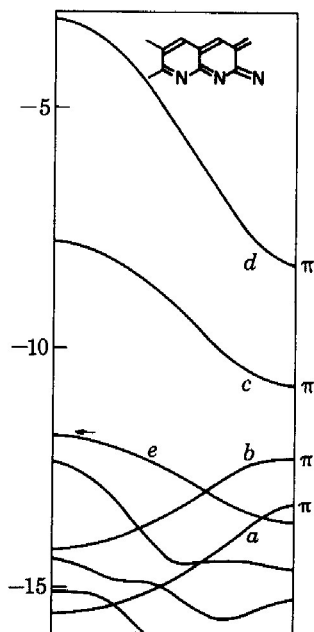
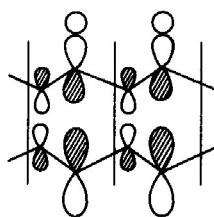


FIGURE 10. The band structure of polypyridinopyridine.



19_e

The band gaps of **18** and **19** are nearly the same, i.e. 1.03 eV, which is smaller than that of polynitrile. This trend is analogous to the band gap change in polyacetylene and polyacene.

Paracyanogen (Bircumshaw *et al.* 1954, Peska *et al.* 1966). As probable configurations of paracyanogen, the following three structures **20**, **21**, and **22** were considered by us. Figure 11a shows the band structure of **20**. The band structure of **21** or **22** is very similar to that of **20**. It is noticed from figure 11a that the π band *c* and the lone pair band *e* overlap, and consequently both of these bands are partially filled.

The nodal properties of the bands c and e of **20** at the zone centre and edge are shown below. In a unit cell of **20e** and **20e'** the orbital is largely an out-of-phase combination of σ_{CC} and n_+ (the in-phase combination of two nitrogen lone pair orbitals), reflecting a through-bond interaction (Gleiter 1974). That the overlap of the bands c and e in **20** is primarily due to this through-bond coupling can be seen from the

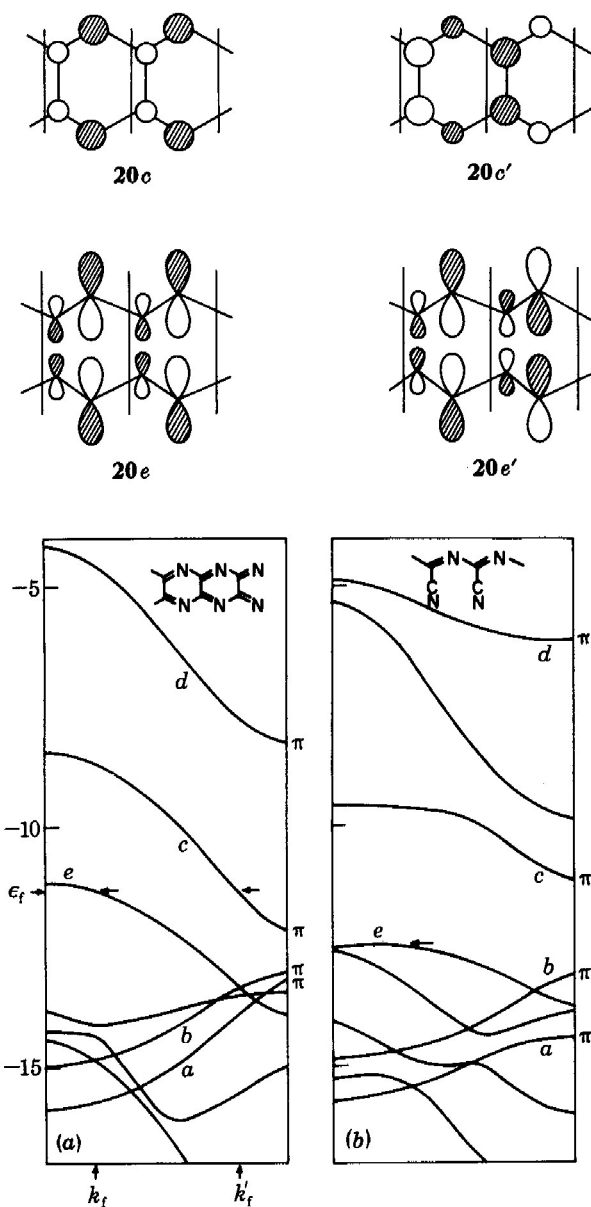


FIGURE 11. (a) The band structure of paracyanogen. (b) The band structure of polycyanonitrile.

band structure of **23**, polycyanonitrile (figure 11*b*), which shows a band gap of 1.41 eV.

The relative stabilities of **20**, **21**, and **22** are 0.0, 13.4, and 85.0 kJ/mol, respectively. As in the case of polyacene, the aromatic configuration **22** is less stable than the nonaromatic configuration **20** or **21**. The more stable one of the two nonaromatic ladder structures is the *cis* configuration **20**, which is calculated to be less stable than the linear structure **23** by 39.3 kJ/mol.

The electrical conductivity of the polymer material presumed to be made up of paracyanogen is in the semiconducting range (Paushkin *et al.* 1974). However, our calculations indicated that all of the ladder configurations **20**, **21**, and **22** have partially filled bands, so that their electrical conductivity is more likely to be metallic. If the electrical conductivity of the aforementioned polymer material is due to the electronic structure of individual polymer chains, it appears that each of these chains should adopt a structure different from **20**, **21**, or **22**. Further studies along both experimental and theoretical lines are needed to resolve this problem.

C_3N net. As ideal structures of graphite-like layer type obtained by dehydration of polypyridinopyridine, we have considered the structure **24**. The unit cell of **24** is a rectangle, and so is its Brillouin zone. The band structure of **24** is given in figure 12.

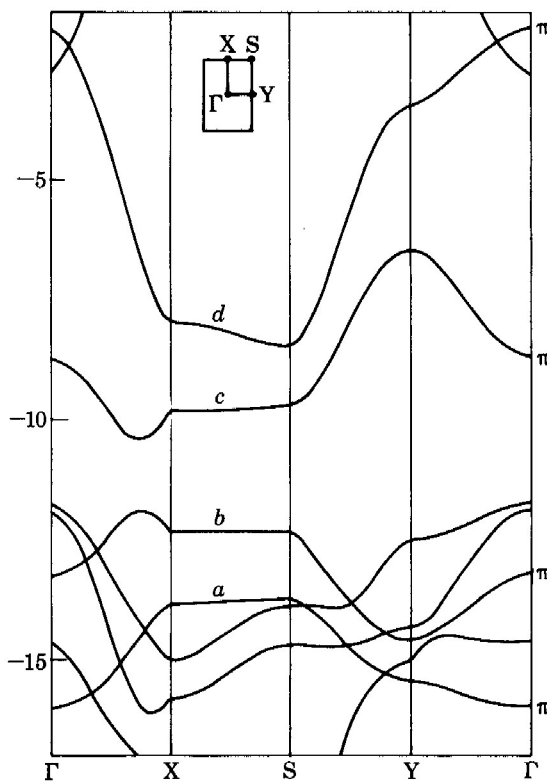


FIGURE 12. The band structure of **24**.

In **24** a unit cell contains five π electrons, which may be viewed as if one of the two lone pair electrons of **19** is used in making the σ framework of a two dimensional net, and the other electron is left over to its π framework. Thus in figure 12 the π band *c* is partially filled. It is also observed that the π bands *c* and *d* overlap along the line $S \rightarrow Y$. Actually two modifications of the C_3N net were examined, corresponding to different bond localization assumptions. No essential difference was found.

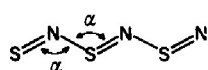
The band structure of polyeneamine, **25**, was examined. It is not shown here but contains, as expected, a substantial band gap.

(c) *Polymers with a nitrogen, sulphur, and carbon skeleton*

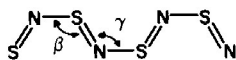
Among the conjugated systems described so far, partially filled bands occur in graphite, paracyanogen, and the C_3N net. In the conjugated polymers with a carbon skeleton both the conduction and valence bands are composed of π orbitals. These two bands merge into one in graphite leading to a partially filled band. In the conjugated polymers made up of carbon and nitrogen atoms the valence band is made of σ -orbitals, i.e. nitrogen lone pairs, while the conduction band is composed of π orbitals. Owing to through-bond conjugation these two bands overlap in paracyanogen, providing the partial occupancy. An odd number of electrons in a unit cell leads to the partially filled band of π orbitals in **24**.

The following discussion is concerned with some conjugated polymers of sulphur and nitrogen, and some with carbon as well, that have partially filled bands. The origins of the partial occupancy of these systems are similar to those described above. Chart III lists the systems examined below, which include polysulphur nitride (**26, 27, 28**), $(SN)_x$, and carbazyl sulphide (**29, 30, 31**), $(HCNSN)_x$, as examples of a linear chain and carbazidyl sesquisulphide (**32**), $C_2S_3N_6$, as an example of a two dimensional net. The latter two are hypothetical systems.

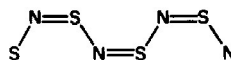
$(SN)_x$. Owing to its metallic properties and superconducting nature at low temperatures, $(SN)_x$ has been a subject of extensive experimental (Cohen *et al.* 1976) and theoretical (Salahub & Messmer 1976, Bright & Soven 1976, Kertesz



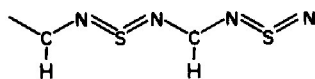
26



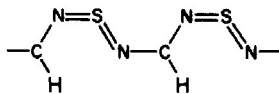
27



28

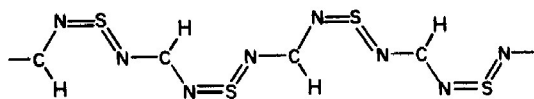


29

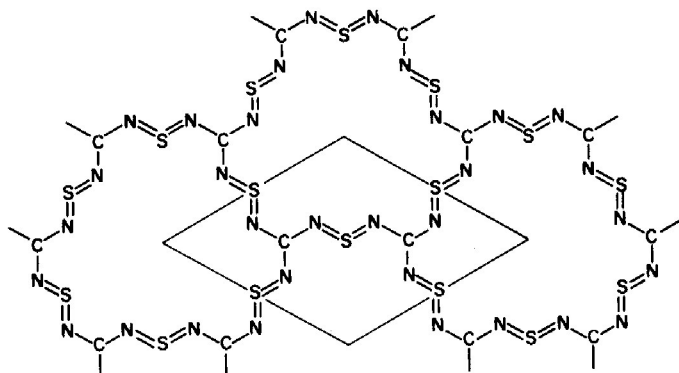


30

CHART III (continued on p. 42)



31



32

CHART III (continued)

et al. 1976, Baughman *et al.* 1976, Kamimura *et al.* 1976, Parry & Thomas 1975, Tanaka *et al.* 1978) studies. Structures for $(\text{SN})_x$ examined in the following are the *trans* configuration **26** and two *cis* configurations **27** and **28**. Figures 13a and 13b show the band structures of **26** and **27**, respectively. The π band *b* of **26** is half filled, since its unit cell contains three π electrons. Owing to the twofold screw axis in **27**,

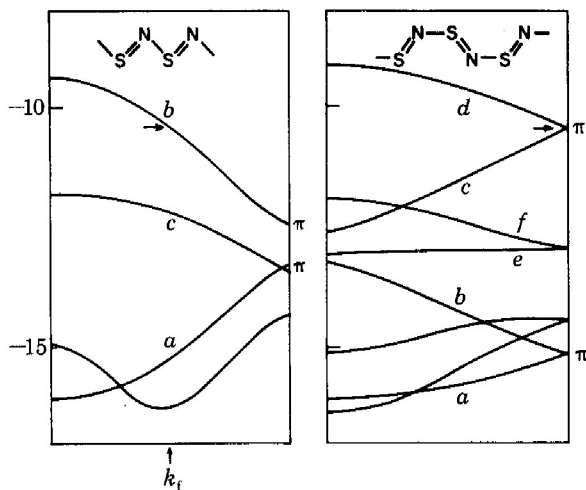


FIGURE 13. The band structures of polysulphurnitride.

the π bands of **27** exhibit degeneracies at the zone edge. Thus the π bands *c* and *d* together provide a partially filled band. Interchain overlap in the three dimensional structure appears to provide the conditions necessary for metallic behaviour.

The total energies per unit cell for **26**, **27**, and **28** were studied as a function of the valence angles α , β , and γ . The results are summarized in figure 14. The optimum value of α in **26** is about 120° . In **27** the optimum value of β is in good agreement with experiment, but that of γ is too large compared to experiment. A deficiency of extended Hückel calculations is that they often give too large angles at nitrogen. With the experimental bond lengths and bond angles the stabilities of the two *cis*

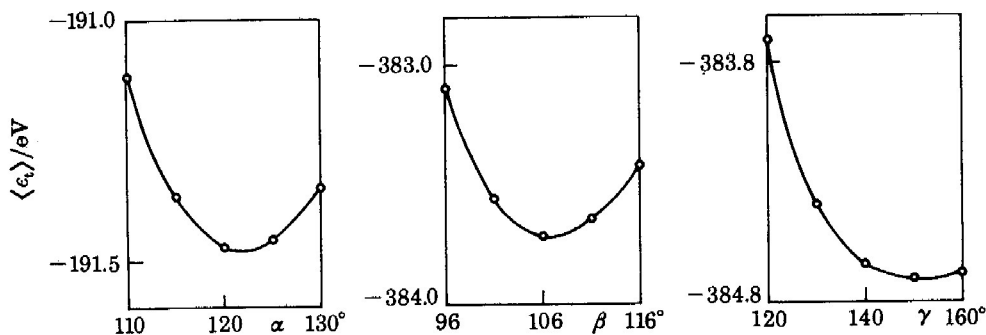


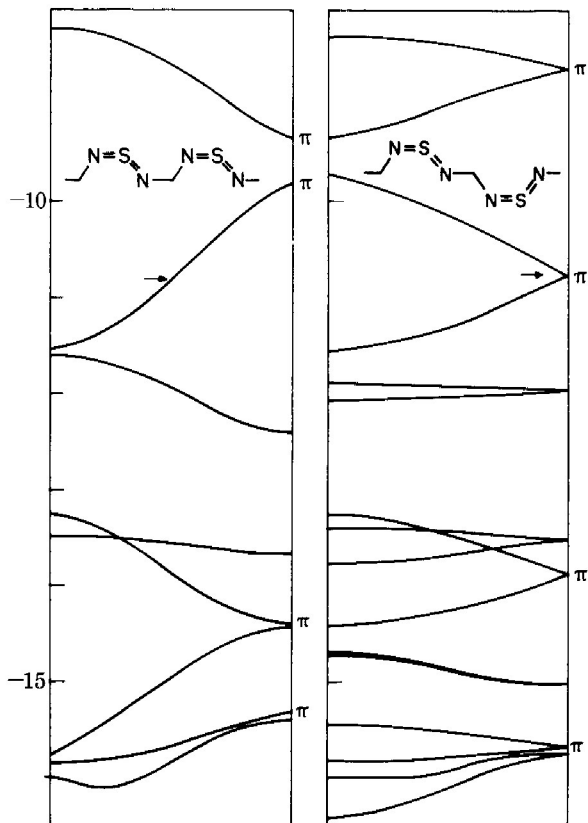
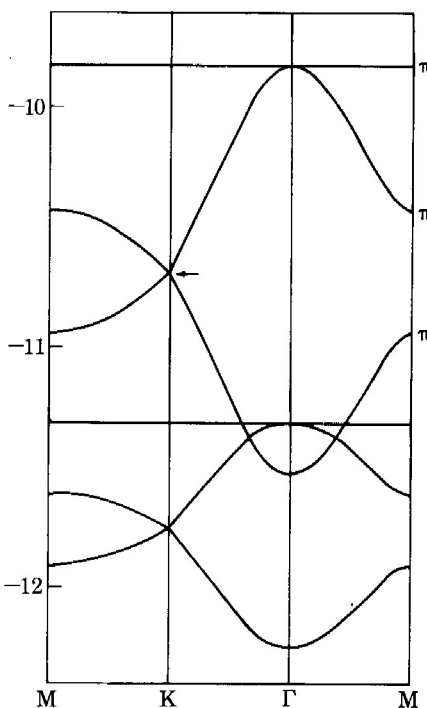
FIGURE 14. The total energy per unit cell $\langle \epsilon_i \rangle$ in polysulphurnitride as a function of α , β , and γ .

configurations of **27** and **28** are nearly the same, the latter being 0.4 kJ/mol less stable. The optimized *trans* configuration **26** is less stable than the *cis* configuration **27** of the experimental (optimized) geometry by 76.6 (172.4) kJ/mol, in agreement with the fact that only the *cis* structure has been observed.

Carbazyl sulphide $(\text{HCNSN})_x$ and *carbazidyl sesquisulphide* $\text{C}_2\text{S}_3\text{N}_6$. As a simple extension of $(\text{SN})_x$, we might speculate upon a possible conducting polymer based upon the sulphurdiimide ($-\text{N}=\text{S}=\text{N}-$) linkage. Structure **29** or **30** has five π electrons and four π orbitals in a unit cell, and thus it has a half filled π band as shown in figure 15*a*. A unit cell of **31** is twice as large as that of **30**, and **31** has the additional symmetry of twofold screw rotation. Therefore **31** leads to a half filled π band as well (figure 15*b*), in a manner similar to the *cis* configuration of $(\text{SN})_x$.

We also considered one of many possible two dimensional layer structures, **32**, based upon the sulphurdiimide linkage. A unit cell of **32** ($\text{C}_2\text{S}_3\text{N}_6$) has fourteen π electrons, and the Brillouin zone of **32** is a regular hexagon as in graphite. The two dimensional band structure of **32** is given in figure 16. At K the valence and conduction π bands of **32** overlap as in graphite.

The two dimensional network of $\text{C}_2\text{S}_3\text{N}_6$ is very open. Model building indicates that the framework holes can be effectively filled with planar guanidinium cations $\text{C}(\text{NH}_2)_3^+$, ideally held in place by six hydrogen bonds to their amine hydrogens. A hypothetical neutral solid of composition $\text{C}_2\text{S}_3\text{N}_6 \cdot \text{C}(\text{NH}_2)_3$ would effectively

FIGURE 15. The band structures of **30** and **31**.FIGURE 16. The band structure of **32**.

transfer one electron per unit cell into the lowest unfilled band of $C_2S_3N_6$. The use of properly designed ions, held by secondary forces, as means of titrating electrons in or out of open framework structures is a general strategy, which is the subject of further experimental and theoretical studies in our research groups.

CONCLUDING REMARKS

The band structures of various one and two dimensional conjugated polymers were surveyed in the present work with the main objective being to examine how the sizes of band gaps or the occurrence of partially filled bands are related to unit cell constitution or its geometrical disposition. The conclusions, at times speculative, of this work are based upon the one electron approximation of the extended Hückel method. They may require re-examination by theory beyond the one electron approximation. There is no doubt that the macroscopic properties of any real polymeric material are significantly affected by a number of important factors such as structural defects, chemical impurities, and interchain or interplane interactions. It may be difficult to secure a correlation between the microscopic and macroscopic

properties. This is not a deterrent for studies like ours, because a reference framework for understanding all materials is obtained by examining an ideal chain or net that is free from structural defects or chemical impurities. We hope the present work will stimulate further experimental and theoretical studies.

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APPENDIX

Atomic parameters of the extended Hückel method (i.e. exponents ξ_μ and valence state ionization potentials $H_{\mu\mu}$ for atomic orbitals χ_μ) employed in the present work are listed in table 1. For **1**, **4**, **13**, **BN**, **15**, and **26** the lattice sums were carried out to second nearest neighbours. In **10**, **11**, **18**, **19**, **20**, and **21** the single bonds connecting alternate unit cells were taken to be the standard bond lengths, so that the bond

TABLE 1. ATOMIC PARAMETERS

χ_μ	ξ_μ	$H_{\mu\mu}/\text{eV}$
H 1s	1.3	-13.6
C 2s	1.625	-21.4
C 2p	1.625	-11.4
N 2s	1.950	-26.0
N 2p	1.950	-13.4
O 2s	2.275	-32.3
O 2p	2.275	-14.8
S 3s	1.817	-20.0
S 2p	1.817	-13.3

angles associated with these bonds are not the standard bond angle, 120° ; in **14** $r_{\text{CC}} = 1.42 \text{ \AA}$; in **BN**, $r_{\text{BN}} = 1.446 \text{ \AA}$; in **18-21**, $r_{\text{C=C}} = r_{\text{C=N}} = 1.33 \text{ \AA}$; in **22** all the bond lengths and bond angles are the same as those of pyrazine (Wheatley 1957); in **26-28**, $r_{\text{S=N}} = 1.593 \text{ \AA}$ and $r_{\text{S-N}} = 1.628 \text{ \AA}$; in **29-31**, $r_{\text{C-N}} = 1.464 \text{ \AA}$, $r_{\text{N=S}} = 1.53 \text{ \AA}$ and angle $\text{NSN} = 120^\circ$.

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