C. The angular motion of four ligands in a tetrahedral configuration, at a fixed distance R from the central metal and numbered as in Figure 1, can be decomposed into eight normal coordinates. The five JT-active bending coordinates follow e and t_2 representations and are denoted, respectively, Q_θ, Q_ϵ and Q_ξ, Q_η, Q_ζ. Furthermore there are three bodily rotations, denoted Q_x, Q_y, Q_z, which transform as a t_1 representation. Let $d\theta_i$ and $\sin \theta_i d\varphi_i$ represent infinitesimal angular displacement of ligand L_i in a Cartesian frame as in Figure 1. Equation 24 in the text can now be specified as in Table V. As an example Figure 2 represents the ligand motion associated with positive values of Q_θ and Q_ζ.

Effects of Chemical Substitution on Polymer Band Gaps: Transferability of Band-Edge Energies

John P. Lowe* and Sherif A. Kafafi

Contribution from the Department of Chemistry, Davey Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received December 5, 1983*

Abstract: Perturbation theory is used to clarify the effects of chemical substitution on π-band-edge energies in conjugated polymers. One can roughly estimate (without computation) the effect of chemical substitution on computed (extended Hückel) π band-edge energies, hence upon π band gaps. Furthermore, once an edge energy is actually computed for one polymer, it is, in many cases, quantitatively transferable to substitutionally related polymers. This allows π-band-gap energies to be predicted quite accurately for systems not yet studied theoretically. The transferability phenomenon does not appear to be nullified by bond-length alternation or to be dependent upon choice of theoretical method.

I. Introduction

During the past decade, conjugated polymers have become the subject of great research activity.[1-3] This interest is due to the discovery that the electrical conductivity of a large number of organic polymers, such as poly(acetylene),[4,5] poly(*p*-phenylene),[6] and poly (*p*-phenylene sulfide),[7] can be increased by 12–18 orders of magnitude up to the metallic level. This increase in conductivity is achieved by doping.

The increased experimental activity in conjugated polymers[8-10] has led to intensified efforts to achieve theoretical understanding using quantum chemical calculations. Whangbo and Hoffmann[11] have examined a variety of conjugated one- and two-dimensional polymers using the extended Hückel (EH) method. They have explored how 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. Duke et al.,[12-15] using the spectroscopically parameterized CNDO-S3 model, have studied the relationships between macromolecular architecture and characteristic features in the photoemission spectra of polymers. Recently, Brēdas et al.,[16-19] using a valence effective Hamiltonian (VEH) technique, have examined a number of organic polymers in order to define the variations in molecular, crystallographic, and defect structures that are compatible with high conductivity.

In this paper, we consider the effects of chemical substitution on π-band-edge energies in conjugated polymers. We find that it is possible to predict these effects semiquantitatively and hence to estimate, without calculation, the size of the π-band gaps in substitutionally related polymers. Furthermore, we show that calculated π-band-edge energies are transferable among related systems.

Throughout this paper, we will use the extended Hückel crystal orbital (EHCO)[11,20] method to illustrate our conclusions concerning the trans polymers shown in Figure 1.

The paper is structured as follows. In section II, we consider the effects of chemical substitution on the π-band-edge energies of regular *trans*-poly(acetylene). The effect of subsequent bond-length alternation is examined in section III. An illustration is given, in section IV, of the transferability of band-edge energies from known polymers to a new one, and the applicability of these ideas to SCF calculations is considered in section V.

II. Effect of Substitution on π-Band-Edge Energies

Backbone Substitution: Regular Poly(acetylene), Poly(methine imine), and Poly(sulfur nitride). First, we consider poly(acetylene)

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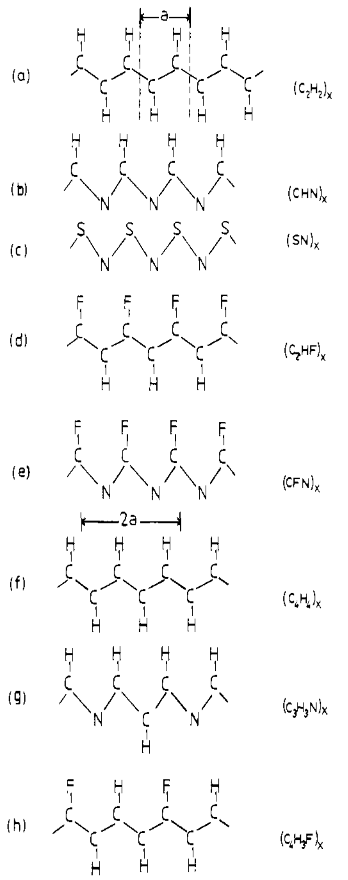

Figure 1. Trans polymers discussed in this paper: (a) poly(acetylene), (b) poly(methyine imine), (c) poly(sulfur nitride), (d) poly(fluoroacetylene), (e) fluorinated poly(methine imine), (f) poly(acetylene) with four-carbon unit cell, (g) poly(acetylene) with every fourth CH group replaced with nitrogen, (h) poly(acetylene) with every fourth H atom replaced with fluorine.

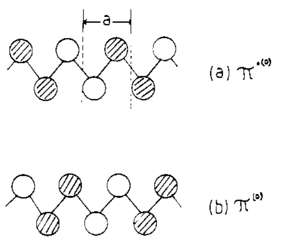

Figure 2. "Bonds" pair of crystal orbitals at $k = \pi/a$.

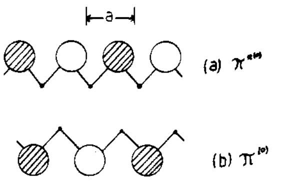

Figure 3. "Atoms" pair of crystal orbitals at $k = \pi/a$.

with uniform bond length. If the unit cell is taken to be a dimer, as shown in Figure 1, one finds two π bands. The occupied, lower, π band is comprised of crystal orbitals that are bonding, and the empty, upper, π^* band is made of crystal orbitals built from antibonding dimer π orbitals. At the Brillouin zone edge (BZE), where $k = \pi/a$, the π and π^* bands are degenerate. The degeneracy occurring at the BZE can be explained in terms of Figure 2. The crystal orbital (CO) at the top of the π band is bonding within a dimer and antibonding between dimers (Figure 2b), while the CO at the bottom of the π^* band is antibonding within the dimer and bonding between dimers (Figure 2a). For this case, with all bond lengths equal, there is no distinction between inter- and intradimer bonds, so these two COs are isoenergetic.[21] For this degenerate case, an infinite number of crystal orbital pair representations is possible.[22] Two of special interest are the "bonds" pair (Figure 2) and the "atoms" pair (Figure 3) (referred to by physicists as charge density waves), obtained by taking the sum and the difference of the "bonds" pair. These two pairs of COs are equally valid descriptions for the perfectly regular, unperturbed, polymer. But any perturbation, however slight, induces a *unique* proper zeroth-order description. Once this proper description is recognized, the effects of the perturbation are easily predicted to first order. Degenerate level perturbation theory[22] prescribes the requirement which the proper zeroth-order COs must meet for the perturbation V

$$(\pi^{(0)}|V|\pi^{*(0)}) = 0 \qquad (1)$$

where $\pi^{(0)}$ and $\pi^{*(0)}$ are the proper zeroth-order wave functions obtained from π and π^* COs. If V is a bond deformation (symmetric about any one of the bond centers), the proper zeroth-order wave functions are the "bonds" pair (Figure 2). If the perturbation occurs at an atom (symmetric about any single carbon), then the proper functions are the "atoms" pair (Figure 3). The proper zeroth-order pair of wave functions is, in effect, that pair which shows the *greatest difference* in first-order energy due to the perturbation.

It is convenient to imagine any perturbation of regular $(C_2H_2)_x$ as occurring in steps. Imagine for example that one CH group in the infinite uniform polymer has been replaced by a nitrogen atom. In this case, the proper zeroth-order wave functions are the "atoms" pair. To first order, the CO which is nonzero at the substitution site drops in energy while the other is unaffected since it has a node at that point. This energy shift is infinitesimal since we have substituted only one site from an infinite number. [An accurate calculation of the COs and their energies for this monosubstituted polymer would require going to higher levels of perturbation theory to allow for electronic charge redistribution induced by the substituent. However, since we are ultimately interested in periodic substitutions of high density, we need not go beyond the zeroth-order wave functions.] If we now make a second substitution, we have two choices. Putting the nitrogen atom at a site such that the energy of the previously lowered CO is further lowered will again not affect the energy of the other CO, to first order. In this case the second substitution reinforces the first, and we have a *cooperative substitution*. The other choice would be *anticooperative*, leading back to a degenerate situation (to first order) and loss of unique proper zeroth-order functions. It is apparent that uniform poly(acetylene) with every second CH group replaced by a nitrogen atom (i.e., poly(methineimine)) is the limiting case reached by *cooperative substitution*. In this limit, the zeroth-order wave functions shown in Figure 3 become correct to infinite order. The finite band gap for $(CHN)_x$ is the sum of the infinite number of infinitesimal cooperative contributions in our imagined stepwise process.

The higher energy band-edge CO consists of a carbon atom π AO on every second carbon atom, with nodes at the intervening nitrogen atoms. Thus, it is a "nonbonding" carbon π CO. If it were truly nonbonding in the simple Hückel sense of no interactions between AOs, the CO energy would occur at the valence-state ionization potential (VSIP) for a carbon 2pπ AO: −11.4 eV. In fact, our EHCO calculations yield an energy of −10.7794 eV for this CO energy. This is a reflection of the antibonding interaction between second-nearest-neighbor atoms (see Figure 3), which is not neglected in extended Hückel calculations. We see this again when we compare our lower band-edge energy, due to a "nonbonding" nitrogen π CO (−13.1578 eV), with the nitrogen π VSIP (−13.4 eV). In general, we find that the second-nearest-neighbor antibonding effect raises band-edge energies above the VSIP level by a few tenths of an electron volt to 1.6 eV, depending on atomic orbital size.

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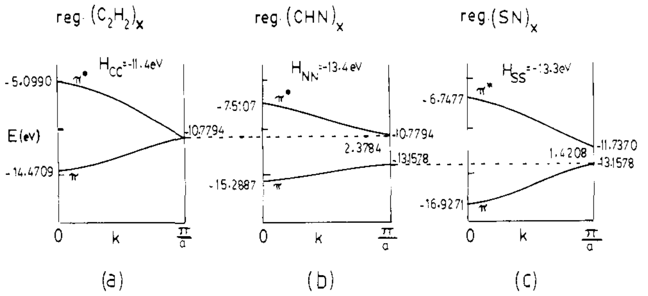

Figure 4. EHCO π and π* bands in regular *trans*-$(C_2H_2)_x$, $(CHN)_x$, and $(SN)_x$. In these model calculations, all bond lengths have been fixed at 1.40 Å. In this and all other band structures presented here, only energy values at $k = 0$ and $k = \pi/a$ (or $\pi/2a$) have been computed. Connecting lines are merely sketched.

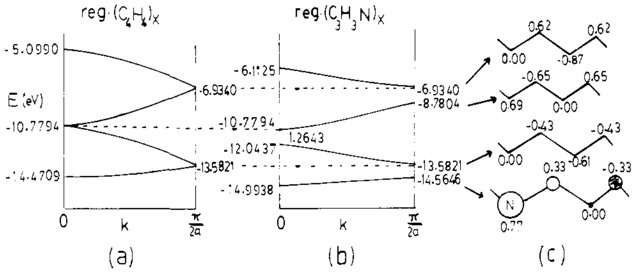

Figure 5. Folded π-band structure for regular *trans*-$(C_4H_4)_x$ and $(C_3H_3N)_x$, with all bond lengths equal to 1.40 Å.

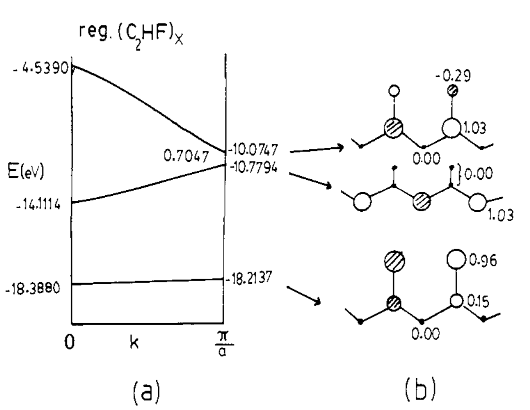

Figure 6. (a) π band structure for regular *trans*-(C_2HF). C–C and C–F bond lengths are fixed at 1.40 and 1.33 Å, respectively. (b) COs at the BZE.

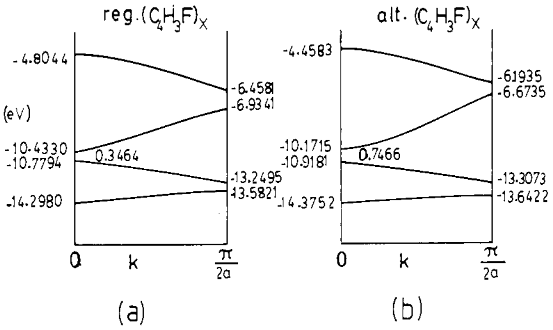

Figure 7. Folded π band structure of (a) regular and (b) alternating *trans*-$(C_4H_3F)_x$. In the alternating structure, the C=C and C—C bond lengths are 1.34 and 1.42 Å, respectively. Remaining data are given in Figure 6.

Even though we cannot exactly equate band-edge energies with VSIPs, *we can transfer certain band-edge energies from one polymer to another.* Thus, the higher energy π* carbon "nonbonding" CO in uniform $(CHN)_x$ is essentially the same as one of the "atoms" COs in uniform poly(acetylene), and so they should have very nearly the same energy, slight differences arising from the difference between C–C and C–N bond lengths. Another way of seeing this is to recall that cooperative substitution affects the energy of one CO but not the other, so the energy of the unaffected CO must be the same in two polymers related by cooperative substitution. Comparison of EH π band plots for $(C_2H_2)x$ and $(CHN)_x$ in Figure 4a,b (using for now the same bond length in each case) makes this point clear. Extending the idea, we now substitute S for CH in $(CHN)_x$, to obtain $(SN)_x$. These cooperative substitutions affect only the CO which has antinodes at the substitution positions—the π*-band edge. The π-band edge (N nonbonding) is unaffected. Therefore, we expect the π-band edge in $(SN)_x$ to be very close in energy to that in $(CHN)_x$, which Figure 4c shows to be the case.

If we substitute every fourth CH group of regular poly(acetylene) by nitrogen, instead of every second, our first-order energy prediction is that the resulting π–π* gap will be half as great. (The zeroth-order "atoms" wave functions of Figure 3 are not exact for this situation, but they are so nearly correct as to give negligible error.) The folded band structures for unit cells having four backbone atoms are compared for uniform poly(acetylene) and uniform $(C_3H_3N)_x$ in Figure 5. The EHCO computed gap energy of 1.2643 eV in the latter system is to be compared with 2.3784 eV in uniform $(CHN)_x$ (Figure 4b). The slight deviation from 1:2 results from the slight difference in long-range antibonding between C and N compared to N and N. At the BZE (now found at $k = \pi/2a$) the energies are degenerate in the unperturbed molecule (Figure 5a). At $k = \pi/2a$, the CO wavelength is twice as long as at π/a, so our "nonbonding atoms" COs of Figure 3 are replaced by "nonbonding triatomic molecules" COs like those shown in Figure 5c. Substituting at every fourth position produces two types of triatomic molecule—C_3 and CNC. The C_3 edge energies are identical with the corresponding energies in poly(acetylene), while those for CNC are lowered. (See Figure 5b). As we shall see, the same C_3 edge energies (−13.5821 and −6.9340 eV) are found in regular $(C_4H_3F)_x$ (Figure 7a). Clearly, edge energies at $k = \pi/2a$ can be understood and transferred in a manner similar to those at π/a.

Side Atom Substitution: **Regular Poly(fluoroacetylene).** Consider the case where every second hydrogen atom of regular *trans*-$(C_2H_2)_x$ is replaced by a fluorine atom. The fluorine atom supplies each unit cell with an additional 2pπ AO, so a total of three π bands results. As before, our proper zeroth-order wave functions are analogues of the atoms pairs. The CO which has a node at the substitution site remains unaffected. The carbon π CO which is nonzero at the substitution site combines with the fluorine π AO in phase and out of phase to produce the other two π-band-edge energies. These COs are shown in Figure 6b. The band-edge energies due to C–F π interactions are slightly higher (due to antibonding interactions between neighboring unit cells) than the energies we calculate for truly isolated C–F π bonds (−18.3099 eV) or antibonds (−10.6666 eV).

If we make the substitution at every fourth H atom, the gap due to substitution decreases by 50%: The energy gap of regular $(C_4H_3F)_x$ is 0.3464 eV compared with 0.7047 eV in regular $(C_2HF)_x$. (Compare Figures 6a and 7a.)

In both of these fluorinated derivatives of poly(acetylene), the band edge corresponding to "nonbonding carbon atoms" has a computed energy of −10.7794 eV, which is identical with the value for the corresponding CO in uniform poly(acetylene); cooperative substitution has not affected the energy of the CO which has nodes at the substitution sites.

III. Effect of Bond-Length Alternation on π-Band-Edge Energies

Again we begin with unsubstituted, regular poly(acetylene) ($(C_2H_2)_x$) and consider the effect of a bond compression in one of the unit cells. Our proper zeroth-order wave functions for the band-edge COs are now the "bonds" pair of Figure 2. CO 2b is (infinitesimally) stabilized, to first order, since the bonding interaction increases. CO 2a is destabilized because the antibonding interaction increases. Performing similar bond compressions in every second C–C bond gives a cooperative effect and opens up

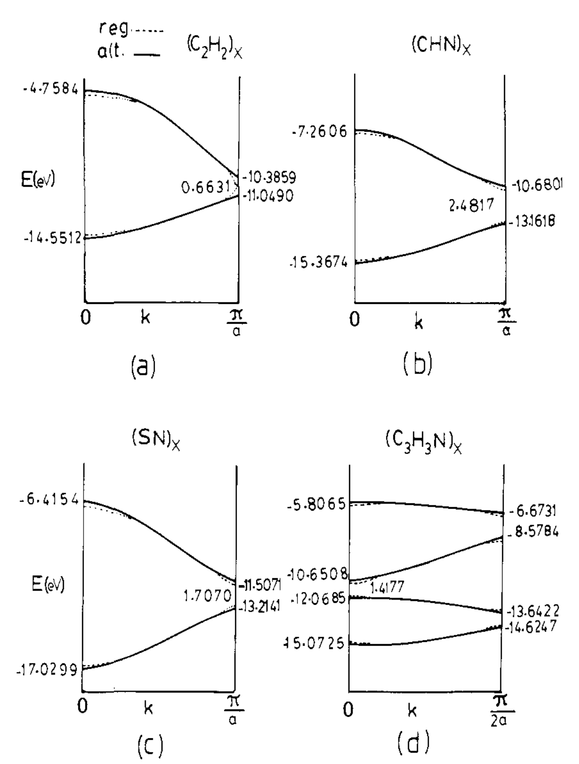

Figure 8. EHCO band structures for alternating *trans*-$(C_2H_2)_x$, $(SN)_x$, and $(C_3H_3N)_x$. (Dashed lines show results for regular polymers.) All short bonds are taken to be 1.34 Å long, all long bonds are 1.42 Å.

Table I. Effect of Bond-Length Alternation on π-Band Gaps in Poly(acetylene) and Substitutionally Related Polymers[a]

system	π–π^* band gap with const bond length, eV	additional gap opening with bond-length alternation, eV
$(C_2H_2)_x$	0	0.6631
$(C_4H_3F)_x$	0.3464	0.4002
$(C_2HF)_x$	0.7047	0.2630
$(C_3H_3N)_x$	1.2643	0.1534
$(SN)_x$	1.4208	0.2862
$(CHN)_x$	2.3784	0.1033

[a] All data are from EHCO calculations with structural parameters described in Figures 4–8.

a band gap. Bond *extensions* in the intervening positions augment these energy shifts. It is clear that the "bond" COs are precisely the ones which will differ most in their first-order energy changes due to such a perturbation. Figure 8a shows that EHCO calculations on alternating poly(acetylene) give a π-band-gap value of 0.6631 eV, the entire gap resulting from bond-length alternation.[21]

In the cases of $(CHN)_x$, $(SN)_x$, etc., chemical substitution has removed the degeneracy at the BZE even before we consider the effects of bond-length alternation, giving band-edge COs which are of the "atoms" type—nearly nonbonding in nature. Hence, the effects of bond-length changes on the energies of these COs should be smaller than in the case of $(C_2H_2)_x$. We find this to be the case. Comparison of Figures 4 and 8, for example, indicates that the additional gap opening due to bond-length alternation is only 0.1033 eV in $(CHN)_x$ and 0.2862 eV in $(SN)_x$. (These and subsequent calculations on effects of bond-length alternation are carried out by using the same alternating bond lengths, 1.34 and 1.42 Å in all cases, in order to facilitate comparisons. The effects of using experimentally observed bond distances are described later.)

The effect of bond alternation on the edge energies tends to be larger when the size of the gap due to substitution is smaller, although, as Table I indicates, there are exceptions to this trend. The tendency for these perturbations to compete results from the fact that the "atoms" COs, which *maximize* the energy differences due to substitution, also *minimize* the energy effects due to bond-length changes. Thus, the presence of a powerful substitutional perturbation (which gives a large gap) can maintain the COs primarlily in the "nonbonding atoms" form when bond alternation is present, thereby decreasing the effect of this second perturbation on the CO energies.

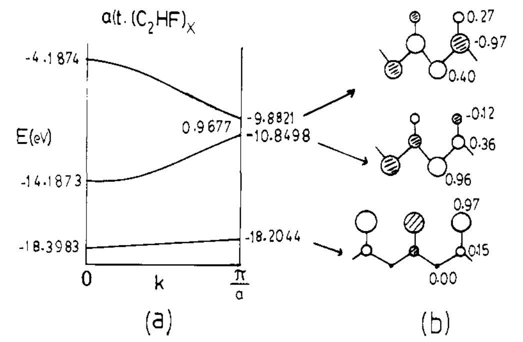

Figure 9. (a) EHCO π-band structure for alternating *trans*-$(C_2HF)_x$. (Bond lengths as in Figures 6 and 7.) (b) COs at the BZE.

The substituent is not 100% effective in locking in "atoms"-type COs. (That is, the charge–density waves are not firmly "pinned" by the substitutents.) As figure 9 illustrates, bond alternation results in COs which are of mixed "bond–atoms" nature. This causes the upper energy CO to rise in energy and the lower one to drop because of the changes in bonding and antibonding interactions discussed earlier. However, another new energy contribution enters too. Taking $(CHN)_x$ as our example, the upper energy CO, originally pure "carbon nonbonding", now resides partly on the intervening nitrogen atoms. These will tend to lower the energy of this CO somewhat because of nitrogen's lower VSIP. The lower CO, originally "nitrogen nonbonding" is similarly delocalized onto the carbons and experiences an energy raising influence. Thus, these second-order effects tend to counteract the splitting due to bond–antibond interactions. As a result, certain band-edge energies remain transferable, to a reasonable degree, even in the presence of bond alternation, provided that chemical substitution exists to dampen the bond alternation effects. Thus, the "nonbonding carbon" π^* CO energies in alternating $(CHN)_x$ and $(C_3H_3N)_x$ are almost identical (−10.6801 and −10.6508 eV, respectively), as are the "nonbonding nitrogen" π CO's of alternating $(CHN)_x$ and $(SN)_x$ (−13.1618 and −13.2141 eV, respectively). Observe, however, that the "carbon nonbonding" COs in $(C_2HF)_x$ and $(C_4H_3F)_x$, at −10.8498 and −10.9181 eV, respectively, are in less good agreement with their analogues in $(CHN)_x$ and $(C_3H_3N)_x$. This arises from the fact that these COs are the *upper* energy members of the π gap in the latter polymers (Figure 8b,d) and hence are raised in energy by bond-length alternation but are the *lower* energy members in the fluorinated polymers (Figures 7b, and 9), hence are lowered by alternation. We are therefore alerted to the desirability, when transferring band-edge energies from polymer to polymer, of transferring lower edge to lower edge, upper to upper, whenever possible.

Finally, we examine what happens to the band-edge energies as the bond lengths in alternating $(CHN)_x$ and $(SN)_x$ are allowed to relax to the values actually observed; i.e., $r(C{=}N) = 1.33$ Å, $r(C{-}N) = 1.46$ Å, $r(S{=}N) = 1.593$ Å, and $r(S{-}N) = 1.628$ Å.[11] We find that the π- and π^*-band-edge energies in alternating $(CHN)_x$ change from −13.1618 to −13.2257 eV and from −10.6801 to −10.6463 eV, respectively. For $(SN)_x$, the corresponding changes are from −13.2141 to −13.2088 eV and from −11.5071 to −11.9537 eV. Except for the last case, these changes are small. On the basis of our discussion in the preceding paragraphs, this is what we would expect. The larger change for the π^* edge of $(SN)_x$ results from the fact that this is primarily a "sulfur atoms" CO. The sulfur π AOs are large and have relatively large antibonding interactions with each other in this CO. These are noticeably reduced when we use the significantly longer observed S═N and S—N bond lengths. The band-edge energies related by cooperative substitution, π of $(CHN)_x$ and π of $(SN)_x$, continue

Table II. Comparison of Computed π-Band-Edge Energies in Regular and Alternating $(CFN)_x$ with Analogous Energies in the Substitutionally Related Polymers $(CHN)_x$ and $(C_2HF)_x$[a]

polymer	nature of CO at BZE	energy, eV	corresponding computed band-edge energy in $(CFN)_x$, eV
Regular Polymers			
reg $(CHN)_x$	N nonbonding	−13.1578	−13.1576
reg $(C_2HF)_x$	$\pi_{C\text{-}F}$ nonbonding	−18.2140	−18.2136
	$\pi_{C\text{-}F}{}^*$ nonbonding	−10.0747	−10.0725
Alternating Polymers			
alt $(CHN)_x$	mostly N nonbonding	−13.1618	−13.1553
alt $(C_2HF)_x$	$\pi_{C\text{-}F}$ nonbonding[b]	−18.2044	−18.2045
	mostly $\pi_{C-F}{}^*$ nonbonding[b]	−9.8821	−9.9852

[a] C–N and C–F bond lengths in regular polymers are taken to be 1.40 and 1.33 Å, respectively. In the alternating polymers, C=N = 1.34 Å, C–N = 1.42 Å, C—F = 1.33 Å. [b] See Figure 9 for the coefficients of this CO.

to be almost identical in these actual alternating-bond-length polymer calculations.

IV. Transferability of Extended Hückel π-Band-Edge Energies: Predicting the Gap in Fluorinated Poly(methine imine)

To demonstrate the transferability of π-band-edge energies we now compare these transferred energies with directly computed values for regular and alternating trans-fluorinated poly(methine imine) (Figure 1e). We expect this system to have three π bands. For regular $(CFN)_x$ at the BZE, one of these should be built from C–F π-bonding functions, separated by nodes at intervening nitrogen atoms, another should be similar, except built from C–F antibonding functions, and the third should be built from nitrogen π AOs, with nodes at the C–F positions. The energies of these bands should be essentially the same as in related polymers: the C–F cases can be taken from regular $(C_2HF)_x$, the N case from regular $(CHN)_x$. Table II is a collection of some of the data obtained from the previously discussed regular and alternating polymers. Comparing the computed π-edge energies of regular $(CFN)_x$ with those obtained from related polymers in Table II, we find excellent agreement. Also, if we compare the computed edge energies of alternating $(CFN)_x$ with those obtained from related polymers (Table II) we find only small changes except for the last edge energy. That is, the edge energy of the CO dominated by C–F π antibonding functions, occurring −9.8821 eV in alternating $(C_2HF)_x$, occurs at −9.9852 eV in alternating $(CFN)_x$. This CO, sketched in Figure 9b, is mainly "nonbonding C–F*" in character but has significant magnitude on the intervening atoms (due to the bond alternation perturbation). These intervening atoms are carbon in $(C_2HF)_x$, nitrogen in $(CFN)_x$. Therefore, the energy of this CO is noticeably lowered in $(CFN)_x$.

V. Transferability of SCF π-Band-Edge Energies

Are band-edge energies transferable at the SCF level as well? There are few data available for comparison. Virtual level energies are not appropriate for consideration since they are not optimized in the manner of filled orbital energies.[23] Inspection of the π-band structures resulting from ab initio calculations on alternating *trans*-$(SN)_x$[24] and $(CHN)_x$[25] suggests that band-edge energy transferability persists at this level. In each of these systems, the π-band-edge CO (which is predominantly on the nitrogen atoms) has an energy of about 0.41 au (−11 eV). Further comparisons must await more SCF computations. However, there is no obvious reason to think transferability will not hold at this level.

VI. Conclusions

We have shown that perturbation theory can be useful in understanding the effects of chemical substitution on π-band-edge energies. The size of the EHCO π-band gap can be roughly predicted in substituted polymers using VSIPs, and calculated π-band-edge energies are transferable with good accuracy in substitutionally related polymers. Bond alternation has a relatively small effect on gaps already widely opened by substitution, and so edge-energy transferability persists in the presence of bond alternation, with slight loss of accuracy in certain recognizable circumstances.

We find that the perturbational analysis presented here is appropriate for other substitutionally related polymer systems, such as *cis*-poly(acetylene) and related systems, polyacene and its nitrogen-substituted derivatives, and poly(*p*-phenylene) PPP) and its derivatives. Details on such systems will be published separately. We also intend to apply this approach to other aspects of periodic structures. For instance, when impurities enter a periodic structure and select residence sites, there may be cases where cooperative effects exert significant control on site selection. We are also examining the possibility that chemisorption patterns on periodic surfaces can be influenced by cooperativity of this sort.

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Registry No. *trans*-$(C_2H_2)_x$, 25768-71-2; *trans*-$(CHN)_x$, 91280-07-8; *trans*-$(SN)_x$, 91280-08-9; *trans*-$(C_2HF)_x$, 91280-09-0; *trans*-$(CFN)_x$, 91280-10-3; *trans*-$(C_3H_3N)_x$, 91239-41-7; *trans*-$(C_4H_3F)_x$, 91239-42-8.

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