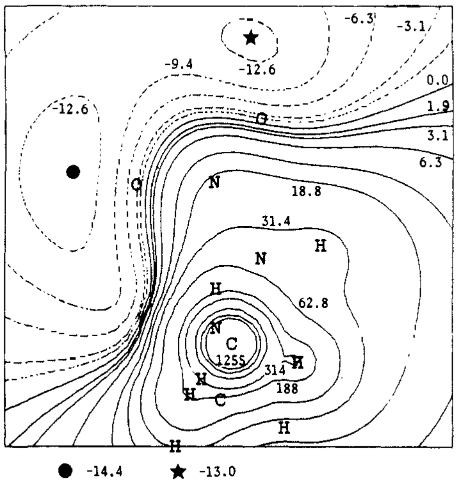

Figure 8. Calculated electrostatic potential of molecule VIII, 1.75 Å above the plane of the NNO_2 portion. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

nitrogen in VII has a strongly negative lone pair potential; it is centered in the molecular plane, but is still clearly apparent at 1.75 Å above this plane, where it extends above the nitrogen.

In VIII, the nonplanarity of the amino-type nitrogens indicates the absence of any strong contribution from structure X. The strongly negative lone pair potentials associated with these nitrogens have already been mentioned earlier in this discussion.

Summary

An important factor in determining the properties of the nitramines that we have studied is the planarity of the key portion of each molecule except VIII. In most instances, this planarity can be regarded as being due to the strong electron-withdrawing power of the NO_2 group, to which the molecule responds by the rearrangement depicted in structures IX and X. This introduces some degree of double-bond character into the $N-NO_2$ bond, its calculated bond order varying between 1.53 and 1.63 for the more typical nitramines, III–VI; it is 1.43 for the nitrimine VII and 1.36 for VIII, in which the amino-type nitrogens do not have planar configurations. Thus the $N-NO_2$ bond is weakest in these two latter molecules.

The planarity of the amino-type nitrogens in III–VII, in conjunction with the electron-withdrawing effect of NO_2, also result in the near elimination of the strong negative electrostatic potentials normally associated with the lone pairs of amino nitrogens. However, the imine nitrogen in VII and the pyramidal amino-type nitrogens in VIII do retain strong negative lone pair potentials.

An interesting feature of the nitramines III–VI is the indication of a significant hyperconjugative effect. This is revealed by the calculated electrostatic potentials in the regions above the molecular planes. The implication of enhanced acidic character is in accord with the experimentally observed properties of nitramines.

Acknowledgment. We greatly appreciate very helpful discussions with Dr. Ieva Ruks Politzer and Dr. Jack W. Timerlake. We are also grateful to the Office of Naval Research for its support of this work through Contract N00014-85-K-0217.

Band Structures of Polyfulvene and Related Polymers. A Model for the Effects of Benzannelation on the Band Structures of Polythiophene, Polypyrrole, and Polyfulvene

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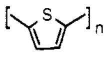
Abstract: At the level of Hückel theory, polyfulvene (PF) has a valence band/conduction band degeneracy much like that seen in polyacetylene. Higher levels of theory remove the degeneracy, but the band gap (E_g) is predicted to be significantly smaller than analogous structures such as polythiophene and polypyrrole at a fulvenoid geometry. An alternative geometry, which we have termed quinoid, is also conceivable for PF, and it is predicted to have a much larger E_g. The effects of benzannelation to produce analogues of polyisothianaphthene (3) have been evaluated. We propose a new model for such structures based on conventional orbital-mixing arguments. Several of the proposed structures have quite interesting properties, which suggest that they are excellent candidates for conducting polymers.

Since the discovery that polyacetylene can be doped to yield highly conducting materials, the number of conducting organic polymers has been increasing steadily.[1] Among the most studied of these compounds are those based on five-membered aromatic rings, such as polythiophene (1), polypyrrole (2), and related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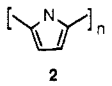
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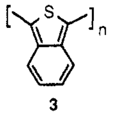
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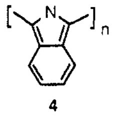
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structures. Recently, the benzannelated derivative polyisothianaphthene (3) has been prepared and found to have quite intriguing and potentially useful properties,[2] including the fact that it appears to be a transparent conductor. These findings prompted further theoretical work on such ring systems.[3,4,20]

Polyfulvene (PF) is a nonaromatic, hydrocarbon analogue of polypyrrole and polythiophene. It may also be viewed as a nonalternant isomer of poly-*p*-phenylene. In this paper we present

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(3) Brédas, J. L.; Themans, B.; André, J. M.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *11*, 343–352.

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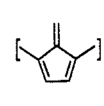
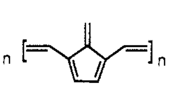
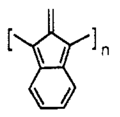


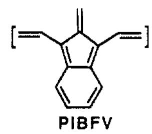
PF



PFV



PIBF



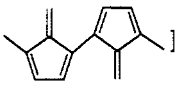
PIBFV

the results of theoretical studies on some polymers based on the fulvene system, in order to assess their viability as conducting polymers. In the course of this work we have developed a new model for the effects of benzannelation, and we have applied this model to polyisothianaphthene and the nitrogen analogue polyisobenzopyrrole (**4**).

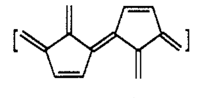
Along with the parent polyfulvene, we have studied polyfulvylenevinylene (PFV), polyisobenzofulvene (PIBF), and polyisobenzofulvylenevinylene (PIBFV), the latter two being analogues of polyisothianaphthene. It may at first seem that polyfulvene is a trivial analogue of polypyrrole and polythiophene, but there are in fact several unique features of the PF system.

Band structure calculations were performed with conventional Hückel molecular orbital (HMO) theory,[5] extended Hückel crystal orbital (EHCO) theory,[6] and the valence effective Hamiltonian (VEH) method.[7,8] In the context of conducting polymers, VEH has been shown to give accurate predictions of such parameters as the ionization potential (IP), band gaps (E_g), and bandwidths (BW) of conjugated polymers. All the band calculations assumed a planar structure. In PF and PIBF, steric interactions will almost certainly lead to a nonplanar structure.[9] In fact an MNDO calculation on fulvene dimer predicts essentially orthogonal rings. Thus, we do not expect the band structures we obtain for these materials to be accurate representations of the true polymers. We have included them primarily for the purpose of analysis. However, these steric interactions are greatly diminished when vinylene groups are used to space out the rings, as in PFV and PIBFV. For example, CPK models, which if anything, tend to overestimate steric repulsions, clearly show that a planar structure is quite feasible for PIBFV. We therefore expect these vinylene analogues to be essentially planar, and they are thus quite promising candidates for organic conductors. In addition, one can envision efficient synthetic routes to the vinylogues using the ring-opening olefin metathesis polymerization (ROMP) chemistry recently developed by Grubbs.[10,11]

For each polymer, two geometries were considered. One corresponds to a fulvenoid geometry, with single bonds external to the rings, while the other corresponds to a "quinoid" geometry,



fulvenoid



quinoid

with double bonds external to the rings. These are shown above for polyfulvene; analogous structures for the other polymers are easily visualized. For polypyrrole and polythiophene, of course, the analogue to the fulvenoid geometry is strongly preferred because it is aromatic. Doping leads to distortion toward the quinoid form, and this distortion has been a major feature of discussions of the properties of these materials.[12] Fulvene, however, is *not* aromatic. It is generally considered to be "nonaromatic", meaning its π delocalization energy is the same as that for an analogous acyclic polyene.[13] As such, the fulvenoid and quinoid forms of PF have, to first order, the *same* π energies. This suggests the possibility of two nearly degenerate structures for PF and related polymers, which is reminiscent of the situation in polyacetylene.[1] The same analysis holds for the vinylogue, PFV. For the benzannelated compounds PIBF and PIBFV, one might expect the quinoid forms to be favored, since this allows a classically aromatic six-membered ring. This is precisely opposite to the situation for **3** and **4**.

The geometries used for the VEH and EHCO calculations are shown in Figure 1. They are based on MNDO-optimized geometries on the corresponding monomers (fulvene and trimethylenecyclopentene). The MNDO structure for fulvene agrees reasonably well with the experimental structure obtained from microwave spectra;[14] no experimental data are available for comparison to the other structures.

Results and Discussion

What initially intrigued us about PF was its HMO band structure, shown in Figure 2. Surprisingly, there is an exact degeneracy between the valence band (VB) and the conduction band (CB) at the Fermi level (E_F). This is, of course, what is seen when polyacetylene is treated at a similar level,[5] and it suggested that PF could be quite an interesting material.

The origin of this effect can be understood after an examination of the HOMO and LUMO of fulvene (Figure 3). The HOMO is just the out-of-phase combination of the two π bonds of the ring. The LUMO is the in-phase combination of the π^* orbitals of these double bonds, plus a contribution from the exocyclic CH_2 and a small contribution from the ring carbon bonded to it. These two orbitals are, respectively, antisymmetric (A) and symmetric (S) with regard to a mirror plane that is perpendicular to the molecular plane and contains the exocyclic C–C bond. Inspection of the VB and CB of PF at the zone edge ($k = \pi/a$, where the degeneracy occurs) reveals their origin (Figure 4). The top of the VB (the highest occupied crystal orbital, HOCO[15]) derives from the HOMO and is precisely analogous to the HOCO in polyacetylene. There are exactly as many in-phase nearest-neighbor interactions as there are out-of-phase interactions and so the orbital is net nonbonding ($E = \alpha$ in HMO). Similarly, the bottom of the CB (the LUCO), derived from the LUMO, has equal numbers of in-phase and out-of-phase overlaps, plus a contribution from the exocyclic CH_2. However, unlike the monomer LUMO, the polymer LUCO at the HMO level has no contribution from the carbon bonded to the exocyclic CH_2. The CH_2 experiences no nearest-neighbor interactions in this orbital and so cannot make

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(6) Whangbo, M. H.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093–6098. Whangbo, M. H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, A* **1979**, *366*, 23–46.

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(8) In our version of the VEH program, all interactions up to the fourth neighboring unit cell are considered. The band energies are calculated at 11 equidistant points in half of the first Brillouin zone of the polymer, and the band structure is obtained by fitting a cubic spline function to the calculated points. In order to preserve translational symmetry, the VEH calculations employed a unit cell consisting of two ring units, with the rings oriented alternately up and down. The band structures so obtained were then unfolded to obtain the band structure corresponding to monomeric unit cells. Thus the band structures shown in Figures 2 and 5 correspond to polymers that do *not* possess full translational symmetry; instead, they have a twofold screw-symmetry axis along the polymer chain. This necessitates an additional phase factor of π in formulating the Bloch orbitals, causing the Brillouin zone to be "shifted" by π/a. Thus, the band orbitals consist of fully in-phase combinations of monomers orbitals at the zone *edge* ($k = \pi/a$) and fully out-of-phase combinations at the zone *center* ($k = 0$). See also ref 15.

(9) For example, see: Pranata, J.; Dougherty, D. A. *Synth. Met.* **1987**, *22*, 171–178.

(10) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894–896.

(11) In fact, preliminary synthetic efforts have been encouraging. Thus, the ROMP of the adduct between benzyne and 6,6-dimethylfulvene has been achieved with a tungsten-based catalyst. Oxidation of this material with DDQ produces an insoluble brick red material, which, on the basis of CP-MAS ^{13}C NMR, appears to be the dimethyl analogue of PIBFV: Swager, T. M.; Grubbs, R. H., unpublished results. Further studies of this synthesis and the results of doping are in progress and will be reported elsewhere.

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(14) Baron, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* **1972**, *43*, 401–410. Suenram, R. D.; Harmony, M. D. *J. Chem. Phys.* **1973**, *58*, 5842–5843.

(15) Lowe, J. P.; Kafafi, S. A.; LaFemina, J. P. *J. Phys. Chem.* **1986**, *90*, 6602–6610.

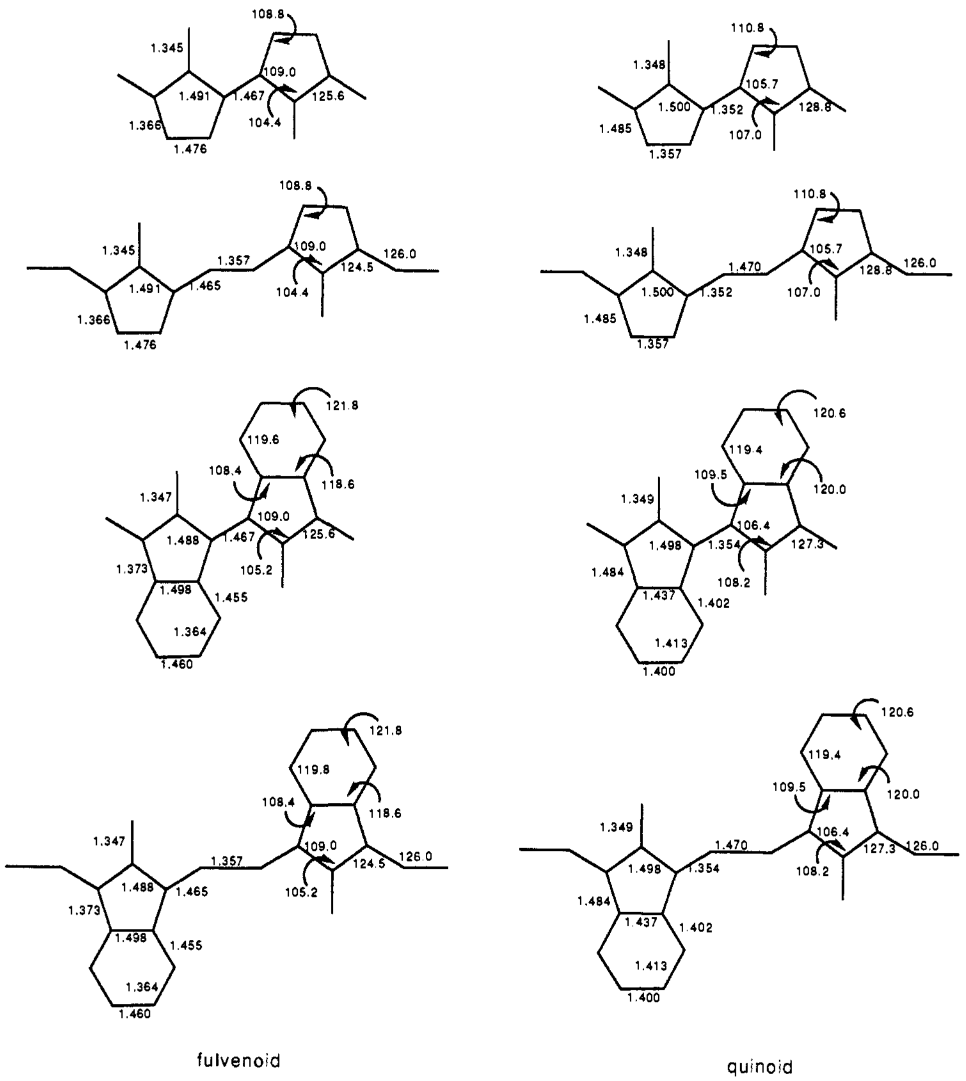

Figure 1. Geometries of PF, PFV, PIBF, and PIBFV used in the band structure calculations.

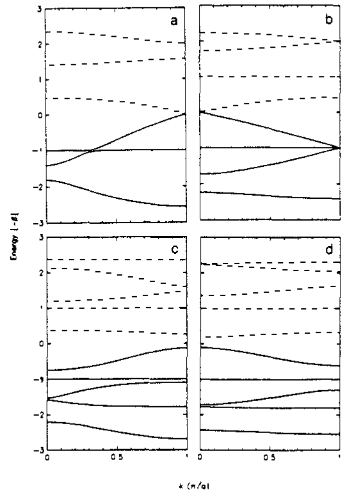

Figure 2. HMO band structures of (a) PF, (b) PFV, (c) PIBF, and (d) PIBFV. The zero of energy corresponds to the energy of an isolated p orbital (α). Solid lines indicate occupied bands; dashed lines indicate empty bands. In (d) the bands at $E = \beta$ and $E = -\beta$ are doubly degenerate.

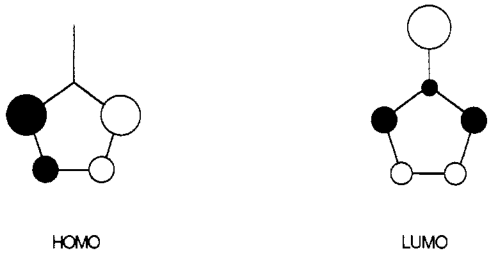

Figure 3. HOMO and LUMO of fulvene at the HMO level.

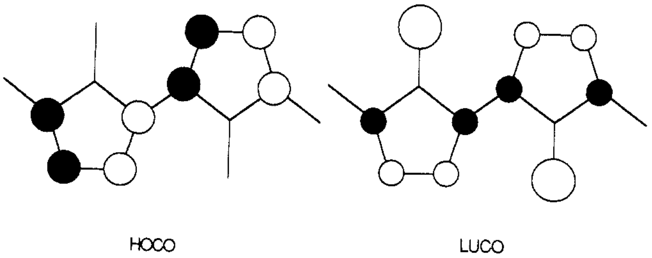

Figure 4. HOCO and LUCO of polyfulvene at the HMO level.

the orbital any more or less stable than an isolated p orbital ($E = \alpha$).

In actual PF, two factors would operate to remove the VB/CB degeneracy. The first is a Peierls distortion exactly analogous to that seen in polyacetylene.[5] Bond alternation (in standard HMO all bonds are the same length) could be introduced in one of two ways, producing either the fulvenoid or quinoid structures. As suggested above, these two distortion modes could have very similar energies, much as the two distortion modes in *trans*-polyacetylene have identical energies. Consideration of non-nearest-neighbor interactions should also split the degeneracy. The

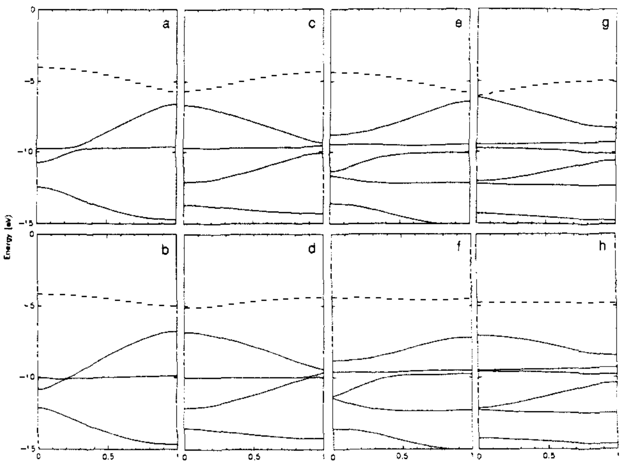

Figure 5. VEH band structures of (a) fulvenoid PF, (b) quinoid PF, (c) fulvenoid PFV, (d) quinoid PFV, (e) fulvenoid PIBF, (f) quinoid PIBF, (g) fulvenoid PIBFV, and (h) quinoid PIBFV. Only the π bands are shown. Dashed lines indicate the lowest unoccupied π band.

Table I. VEH Calculation Results (eV)

polymer	IP[a]	E_g	BW
PF (fulvenoid)	4.68	0.87	3.21
PF (quinoid)	4.90	1.80	3.26
PFV (fulvenoid)	4.74	0.98	2.72
PFV (quinoid)	4.93	1.74	2.61
PIBF (fulvenoid)	4.49	0.65	2.37
PIBF (quinoid)	5.34	2.69	1.58
PIBFV (fulvenoid)	4.20	0.05	2.15
PIBFV (quinoid)	5.17	2.26	1.41
1	5.39	1.77	2.26
3	4.60	0.54	2.61
2	4.14	3.45	3.67
4	3.27	1.06	3.70
trans-polyacetylene[b]	4.7	1.4	6.5
poly-*p*-phenylene (planar)[b]	5.5	3.2	3.9

[a] 1.9 eV subtracted from calculated values.[7] [b] Brédas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. *J. Chem. Phys.* **1982**, *76*, 3673–3678. All other results are from the present work.

VEH and EHCO calculations described below include both these effects. The results from HMO, however, are usually qualitatively correct. Interestingly, polypyrrole and polythiophene do not possess a comparable VB/CB degeneracy in HMO. This suggested that PF could have a smaller E_g than these known conducting polymers.

The VB/CB degeneracy persists in PFV, at the HMO level (Figure 2), and arguments exactly analogous to those for PF explain this result (remembering that the degeneracy for PFV occurs at the zone center, $k = 0$). Fusion of a benzene ring to produce PIBF or PIBFV removes the degeneracy (Figure 2).

The VEH band structures for PF, PFV, and PIBFV in both the fulvenoid and quinoid geometries are shown in Figure 5. Table I presents the IP, E_g, and BW data obtained from the band structures. The EHCO results are consistent in every way with the VEH data, and so we will emphasize the presumably more accurate VEH results in our discussion. For comparison, the VEH data for polyacetylene, poly-*p*-phenylene, polypyrrole, polythiophene, polyisothianaphthene, and polyisobenzopyrrole are also included in Table I. As predicted by HMO, E_g for PF *at the fulvenoid geometry* is much smaller than for polypyrrole and even polythiophene. We consider this a manifestation of the Hückel degeneracy.

Brédas, Heeger, and Wudl have investigated the effect of bond length alternation on the electronic structures of poly-*p*-phenylene, polypyrrole, and polythiophene.[4,16] They concluded that the substantial reduction in E_g observed on going from polythiophene (**1**) to polyisothianaphthene (**3**) was a consequence of increased quinoid character in the benzologue.[4] Given this, our results for the fulvene-based polymers are at first sight surprising. In all four cases the fulvenoid and quinoid structures have qualitatively similar band structures, but the quinoid forms have the greater band gaps. An explanation can be found in a more detailed consideration of the HOCO and LUCO of these structures.

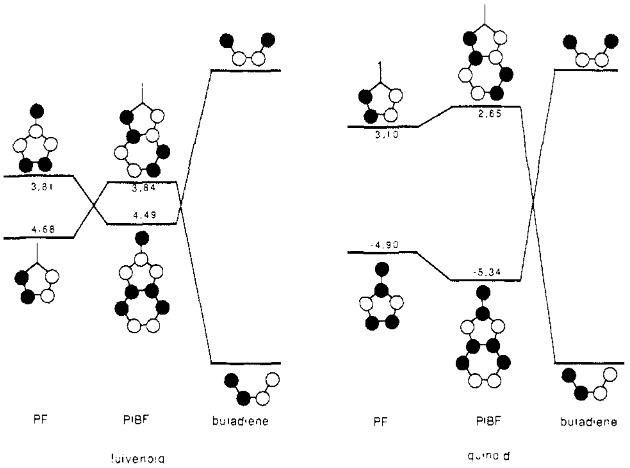

Figure 6. Orbital-mixing diagram for the benzannelation of polyfulvene.

In fulvene, the HOMO is A; the LUMO is S, as discussed above. Increasing quinoid contribution increases the energy of the A orbital and decreases the energy of the S orbital. The A orbital has bonding interactions between pairs of atoms that are connected by double bonds in the fulvenoid structure. Transformation to the quinoid structure shifts most of the double bonds to pairs of atoms having *antibonding* interactions. Thus, the quinoid contribution destabilizes this orbital. In contrast, the S orbital has double bonds between pairs of atoms having antibonding interactions in the fulvenoid structure. The shift to the quinoid structure places double bonds between pairs of atoms having bonding interactions. This orbital is therefore stabilized by quinoid contribution. This pattern has been noted previously.[4]

In this context, the VEH band structures of these materials are easily understood. In the fulvenoid geometry, the VB and CB of PF can be directly related to the HOMO and LUMO of fulvene along the lines discussed above. In the quinoid structure, the intercell interactions are much stronger because they correspond to double bonds, and this perturbs the band structure. At the zone center ($k = 0$), disregarding the weakly avoided crossing between the VB and the very narrow second filled band, the composition of the VB and CB is the same as in the fulvenoid geometry. That is, the VB and CB correlate to the fulvene HOMO and LUMO, respectively. Because of the increased intercell overlap, these bands rise and fall much more steeply as one progresses back toward the zone edge, and this gives rise to an intended, but avoided, VB/CB crossing in the quinoid structures. Thus, at the zone edge, the VB and CB have changed character and now correspond to the LUMO and HOMO of fulvene, respectively. Inspection of the coefficients of the VEH crystal orbitals confirms this analysis. The crossing is apparently fairly strongly avoided, and a significant band gap is opened up.

From this starting point, the effect of benzannelation can be rationalized readily. One can think of the conversion of PF to PIBF as resulting from the fusion of fulvene with 1,3-butadiene (Figure 6).[17,20] The important orbitals of butadiene are the HOMO and LUMO, which are A and S, respectively, with regard to the previously mentioned symmetry plane. In Figure 6, we show the mixing of these orbitals with the PF HOCO, and LUCO at the zone edge. It can be seen that this mixing provides a mechanism for closing E_g. In fact, the mixing is strong enough to reverse the HOCO/LUCO ordering, and in PIBF at $k = \pi/2$, the VB is comprised of S orbitals, and the CB, A. Thus, ben-

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(16) Brédas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808–3811.

(17) The HOCO and LUCO energies of Figures 6 and 7 are derived from VEH calculations. More correctly, the orbitals to be mixed are those of "polybutadiene", i.e. an infinite row of butadienes nonbonded to each other.

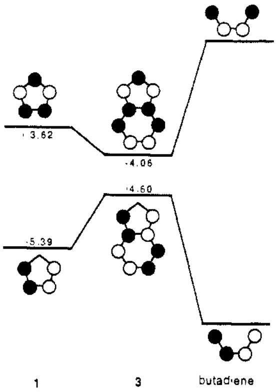

Figure 7. Orbital-mixing diagram for the benzannelation of polythiophene (**1**) to polyisothianaphthene (**3**).

zannelation onto PF in the fulvenoid geometry induces an avoided crossing exactly analogous to the one seen in the quinoid form of PF.

In the quinoid form of PF, the S/A crossing has already occurred at $k = \pi/a$. As shown in Figure 6, benzannelation can only increase E_g, and indeed this is the case. All the effects of benzannelation listed in Table I can be fully rationalized with the simple model of Figure 6. Exactly analogous arguments apply to the conversion of PFV to PIBFV. Apparently, the balance of effects in PIBFV is such that the S and A orbitals become almost degenerate at $k = 0$, producing a *very* small band gap.

We note that these arguments are somewhat different from those of Bredâs, Heeger, and Wudl concerning the conversion of thiophene to polyisothianaphthene.[4] As mentioned above, in thiophene there is a strong intrinsic preference for what we have termed the fulvenoid geometry, because thiophene enjoys an aromatic stabilization in this geometry. Thus, we would analyze the thiophene → isothianaphthene conversion in terms of the left-hand side of Figure 6. The only difference is that E_g in polythiophene is larger than for PF, as discussed above. The actual mixing is shown in Figure 7. Again, E_g is reduced by benzannelation (in a "fulvenoid" geometry), but no crossing occurs because of the larger initial E_g.

The earlier work[4] concluded that the substantial diminution in E_g that occurs on going from polythiophene (**1**) to polyisothianaphthene (**3**) (and a similar effect in the monomers) is a consequence of increased quinoid contributions to the electronic structure. Earlier work has shown that *geometrical* distortions toward a quinoid form provide a mechanism for closing E_g in **1**.[16] On the basis of this, the observation of a smaller E_g in **3** was interpreted as resulting from quinoid contributions to the *electronic* structure. We note, however, that typically when one considers a mixing in of an alternative electronic structure, the argument carries with it definite geometrical connotations. For example, in the benzyl cation the resonance structures that place the charge in the ring have an exocyclic C–C double bond. This implies a shortening of this bond compared to localized cations, as is observed. In the **1**/**3** system, the reported geometries[3] for the two monomers are not consistent with this reasoning. The calculated difference between C–C single and double bond lengths is 0.088 Å in thiophene. In isothianaphthene, this value increases to 0.102 Å. In a structure with quinoid character this number should be smaller, and so benzannelation does not produce a *geometrical* change indicative of increased quinoid character. Ultimately, of course, the current model for these effects and the previous one are equivalent. We believe, though, that the scheme of Figures 6 and 7 presents a clearer view of the electronic changes that occur upon benzannelation.

In Table I we also show the consequences of converting polypyrrole (**2**) to polyisobenzopyrrole (**4**). Again, a substantial reduction in E_g occurs due to effects exactly analogous to the thiophene system.

Similar reasoning provides a straightforward explanation of another intriguing feature of PF. While we invoked the vanishing E_g at the HMO level to explain the smaller E_g in PF vs **1**, PF also has a significantly smaller E_g than polyacetylene, which shows the same HMO degeneracy. Inspection of Figure 4 provides the explanation of this effect. One can "prepare" fulvenoid PF by combining trans-cisoid polyacetylene with ethylene end on. The HOCOs of the two materials are exactly the same as the HOCO of Figure 4, and indeed their VEH IPs are identical if the polyacetylene geometry is constrained to be the same as the PF geometry. The diminished E_g in PF arises because of a lowering of the LUCO. The VEH LUCO of fulvenoid PF is as in Figure 4 except there is a small contribution from the central carbon, with the phase relationship of the LUMO of Figure 3. It can be seen that such an orbital is just the in-phase combination of the polyacetylene LUCO and the ethylene π^* orbital. This π^* orbital is higher in energy than the polyacetylene LUCO, so the mixing lowers the energy of the LUCO, thereby diminishing E_g.[18]

As discussed above, the feasible target molecules are PFV and PIBFV. The vinylene spacers do not produce any qualitative changes in the band structures of the materials. As summarized in Table I, these polymers should have quite intriguing properties, if they adopt the fulvenoid geometry. The quinoid geometry, on the other hand, produces much less promising materials. It is not a simple matter to determine the preferred form. Simple calculations using the EHCO method and the geometries discussed above suggest that the two forms are close in energy, as expected.[19] An accurate estimate of the relative energies would require extensive geometry optimization on a high oligomer, which is not currently feasible. This is especially true for the quinoid form, for which there is no simple dimer or trimer structure without severe end-group perturbations. Rather than attempt such optimizations, we have chosen to emphasize the limiting forms (fulvenoid and quinoid), which most clearly illustrate the fundamental bonding principles. It is perhaps safe to anticipate that in the benzologue (PIBFV) the quinoid form would be preferred, because it allows the six-membered ring to be aromatic.

While it is difficult to predict the structures of PFV and PIBFV in the undoped state, it seems certain that doping will favor the fulvenoid structures. That is, oxidative (reductive) doping always leads to distortions toward the structure with the higher (lower) energy VB (CB),[12] and that is the fulvenoid structure. We thus conclude that PFV and PIBFV could be quite promising materials, and efforts to prepare and characterize them are under way.[11]

Conclusions

At the HMO level, PF exhibits a VB/CB degeneracy exactly analogous to the degeneracy seen in polyacetylene. Also like polyacetylene, Peierls distortion can produce two structures that are, to first order, degenerate. When higher order effects are included, the two forms, which we have termed fulvenoid and quinoid, will not be degenerate, but our calculations indicate that they are close in energy. VEH calculations indicate that PFV should have properties that compare quite favorably with the known conducting polymers polypyrrole and polythiophene.

An analysis of the band structures of the benzo-fused compounds PIBF and PIBFV suggests a new model for the effects of benzannelation in these and related structures. Rather than consider possible geometrical distortions, we emphasize the intrinsic electronic structures of these materials using straightforward orbital-mixing arguments analogous to those used so frequently in molecular systems. All the consequences of benzannelation

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(18) We note that this analysis can be pursued further. In particular, the COs of quinoid PF can be obtained from mixing an ethylene fragment (end on) with the COs of cis-transoid polyacetylene, and **1** and **2** can be obtained by mixing S or N with cisoid polyacetylene. Full details will be published in: Pranata, J. Ph.D. Thesis, California Institute of Technology, 1989. See also ref 15 and 20.

(19) The energy difference for PF at the EHCO level is 0.21 eV/monomer, the quinoid form being lower in energy. For PFV, PIBF, and PIBFV, the energy differences are 0.21, −0.32, and 0.21 eV, respectively.

(20) After submission of this work, we became aware of several papers by Kertesz that include a similar analysis of **1** and **3**. Kertesz, M.; Lee, Y. S. *J. Phys. Chem.* **1987**, *91*, 2690–2692. Lee, Y. S.; Kertesz, M. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1987**, *No. 21*, 163–170. Lee, Y. S.; Kertesz, M. *J. Chem. Phys.* **1988**, *88*, 2609–2617.

are rationalized by this model. The quantitative (VEH) calculations indicate that PIBFV could have a very small band gap, making it an interesting experimental target.

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Do Stable Isomers of N_3H_3 Exist?

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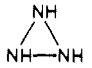
Abstract: The potential energy surface of the unknown N_3H_3 molecule is investigated by using ab initio coupled-cluster and many-body perturbation theory. Five stable isomers of N_3H_3 are identified. In decreasing order of stability, these are triazene, triimide, *cis*-triimide, triaziridine, and *cis*-triaziridine. The infrared spectra of the principal isomers are predicted at the MBPT(2) level by using newly developed analytical second-derivative techniques and are compared to SCF predictions. The thermochemical quantities of enthalpy, entropy, Gibbs free energy, and heat capacity at constant volume are also computed. The predicted IR spectra and these thermochemical properties should aid experimental attempts to synthesize and isolate these compounds, some of which should be observable in low-temperature matrices.

I. Introduction

For many years chemists have studied small ring compounds such as cyclopropane and cyclobutane. These systems are made thermodynamcially unstable and kinetically reactive by ring strain. Thus, their synthesis is particularly challenging. These compounds also interest kineticists, as shown by the fact that the rearrangement of cyclopropane to its open-chain isomer is one of the most studied unimolecular reactions.[1]

A compound similar to cyclopropane can be imagined, in which the methylene units ($-CH_2-$) are replaced by nitrenes ($-NH-$). This ring system of nitrogen is called triaziridine (**1**). It has never been synthesized and isolated. To predict the structure and properties of triaziridine and of other N_3H_3 isomers, we have performed theoretical investigations of the N_3H_3 hypersurface by using the modern computational procedures of ab initio coupled-cluster (CC) and many-body perturbation theory (MBPT), including analytical MBPT energy-derivative techniques.



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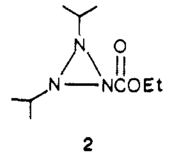
Triaziridine is a member of a class of inorganic compounds called homocycles, of which the sulfur S_8 is perhaps the best known. Homocycles in general have received little theoretical or experimental attention; however, triaziridine and its alkyl derivatives have been the subject of some investigations.

In 1977 Kim, Gilje, and Seff[2] reported the serendipitous synthesis of a minute amount of triaziridine on a zeolite crystal in a capillary. They used ammonia in an attempt to reduce the silver ions trapped in a silver-exchanged zeolite, but an X-ray crystal structure of the resulting zeolite indicated the presence of triaziridine facially complexed to the silver ions. The three nitrogen atoms formed an equilateral triangle, but the positions of the three hydrogen atoms could not be determined due to the proximity of the heavy silver atom. The N–N bond length in the ring was 1.49 Å, and the length of the Ag–N bond was 2.59 Å. Further evidence of the formation of triaziridine came from high resolution mass spectroscopy of the gases exiting the zeolite. Peaks representing both $N_3H_3^+$ and $N_3H_2^+$ were observed while the zeolite was between room temperature and 75 °C, suggesting that the N_3H_3 molecule possesses remarkable stability in the gas phase. Despite this observation, neither these investigators nor any other research team has repeated this synthesis of triaziridine.

In spite of this evidence for the formation of triaziridine, there are still many questions about the molecule and its synthesis that remain unanswered. If ammonia is converted to triaziridine, hydrogen gas should be a byproduct, but hydrogen was never observed. The silver ions presumably catalyze the conversion, but do they also stabilize the product through complexation? What is the arrangement of the hydrogens in triaziridine? In the zeolite one expects that the hydrogens are located on the side of the ring opposite the silver ion so that charge repulsion is minimized, but this may not be the structure of the molecule in the gas phase. The mass spectral data suggest that a molecule with empirical formula N_3H_3 is present, but is it triaziridine or one of its isomers?

More recently the synthesis of two alkyl derivatives of triaziridine has been reported by Leuenberger, Hoesch, and Dreiding.[3] They were able to make and isolate 1-(ethoxycarbonyl)-*trans*-2,3-diisopropyltriaziridine (**2**) and 2,3-(*cis*-1,3-cyclopentyl)-1-(methoxycarbonyl)triaziridine (**3**). On standing at room temperature compound **2** thermolyzed to the corresponding azimine (**4**). This reaction proceeded with a half-life of 3 days. Although one would expect triaziridine itself to be even less stable than an alkyl derivative, this observation is not inconsistent with the stability that Kim et al. observed.



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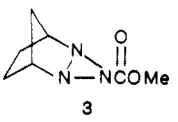

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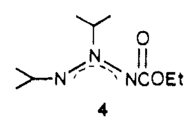

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