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Electronic Structure of Polyazulene

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ABSTRACT: Electronic structure of polyazulene (PAz) has been studied based on its optimized structure of the neutral state using the one-dimensional tight-binding SCF-CO (self consistent field-crystal orbital) method. The oxidized states of polaron and bipolaron natures were also examined. It is found that the positive net charges of the oxidized states are mainly localized in the seven-membered ring and that in the polaron state the charge and the spin parts are separated in an azulene ring. It has been conjectured that confinement of the π hole in the seven-membered ring inherent in PAz is unfavourable for the intrachain electrical conduction.

KEY WORDS Polyazulene /Electrically Conductive Polymer / Electronic Structure /Polaron / Bipolaron /

Polyazulene (PAz) is one of the conducting polymers consisting of condensed aromatic rings and can be prepared from azulene monomer as a free standing film by the electrochemical polymerization[1,2] or as power by the chemical polymerization.[3] The electrical conductivity of PAz in its oxidized state has been reported in the order of 10^{-2} to 10^{0} $\mathrm{S\,cm^{-1}}$.[1,2] Measurement of temperature dependence of the bulk electrical conductivity of doped PAz has been elucidated by the three-dimensional variable range hopping mechanism.[4] The magnetic and optical properties observed[5] have suggested that bipolaron state prevails over the polaron state in the heavily oxidized PAz. Another interesting aspect of PAz is that it shows a large spin density of $\sim 10^{20}$ spins $\mathrm{g^{-1}}$ in its neutral state.[5]

On the other hand, there have been no reports of theoretical analysis about the electronic structure of PAz both in its neutral and oxidized states. Hence, in this work, we like to study the electronic structure of PAz in these states by theoretical calculations and discuss the experimentally observed properties based on the results calculated.

METHOD OF CALCULATION

Calculations were performed based on the one-dimensional tight-binding self consistent field-crystal orbital (SCF-CO) method under the CNDO/2 (complete neglect of differential overlap, version 2) level including all the valence electrons.[6] All of the bond distances and bond angles in the neutral PAz are energetically optimized employing the energy gradient method, the principle of which has been described elsewhere.[7] The density of states (DOS) and the π-DOS were evaluated in the conventional manner.[8] For the geometries of polaron and bipolaron states of PAz, that of the neutral state was employed for simplicity. Details concerning the selection of this

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geometry will be discussed later. The hole concentration, [Hole]/[Azulene ring], of the both polaron and bipolaron states was set to be unity representing an extremely heavily oxidized state to check their tendencies.

For the calculation of the closed-shell system, such as neutral and bipolaron states of PAz, the restricted Hartree–Fock (RHF) framework was employed. The unrestricted Hartree–Fock (UHF) concept (different orbitals for different spins) was applied to the calculation of the open-shell system (polaron state). This signifies that, in the polaron state, there was assumed a ferromagnetic alignment of spins. We have already applied this UHF SCF-CO method in a successful manner to estimate the electronic and the spin structures of a ferromagnetic polymer[9] and heavily oxidized state of polyaniline.[10]

RESULTS AND DISCUSSION

Neutral State

The linkage mode of PAz at the 1 and 3 positions (see Figure 1) is plausible from the substituent effect to the polymerization[11] and the result of ^{13}C NMR spectroscopy of PAz.[2] Therefore, in this work, the skeleton of poly(1,3-azulene) was employed in principle. It has been found by the energetical optimization that PAz favours the structure with the unit-cell symmetry of C_{2v} more than that of the asymmetric bond-alternant structure (unit-cell symmetry of C_s; see Figure 1). The C_s as well as non C_s structure even does not have a local minimum point on the energy hypersurface. The geometrical parameters of the optimized structure is shown in Figure 2. It is interesting to note that all the bond distances in the seven-membered ring are nearly the same each other, and shorter than those in the five-membered ring.

The experimental structure of azulene monomer is yet unclear.[12,13] Some theoretical predictions for the azulene monomer have favoured an asymmetric bond-alternant struc-

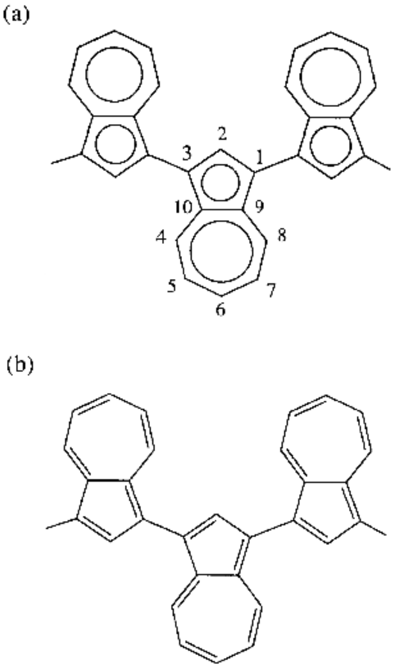

Figure 1. Structure and the numbering of PAz. (a) C_{2v}- and (b) C_s-type structures (see the text).

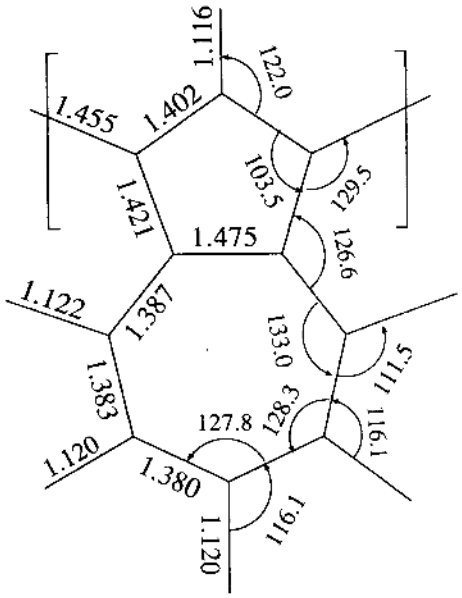

Figure 2. The optimized geometry of PAz. The bond lengths and the bond angles are designated in Å and degrees, respectively.

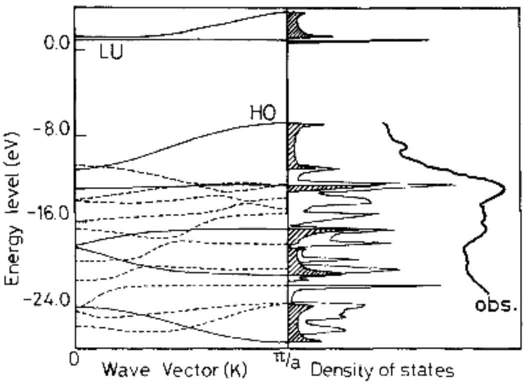

Figure 3. Band structure of neutral PAz. The solid and broken lines indicate the π- and σ-bands, respectively. The density of states (DOS) is also shown, where the hatched area indicates the π-DOS, along with the UPS data (obs.).[15]

Table I. The electronic properties of polyazulene (PAz) and polythiophene (PT) in their neutral states (in eV)

Polymer	Electron affinity	Ionization potential	Band gap[a]	Band width	
				HO	LU
PAz	−0.97	6.65	7.62[b] (2.8[c]) 7.79 (3.8[c])	4.45	0.17
PT[d]	0.73	8.30	7.57 (2.1[e])	4.04	6.59

[a] Values in parentheses are those obtained experimentally.
[b] Indirect gap.
[c] From ref 5.
[d] From ref 16.
[e] From ref 17.

ture with the C_s symmetry like the unit cell in Figure 1(b).[14] This signifies that azulene monomer has a tendency to be more olefinic than PAz. On the other hand, PAz favours rather an aromatic structure (C_{2v}) probably due to the energetical stabilization in terms of the delocalization throughout the polymer chain.

The calculated band structure and the density of states (DOS) of PAz are shown in Figure 3. Both the highest occupied (HO) and the lowest unoccupied (LU) bands are of π-nature. The shape of the DOS at the energy level of $-12 \sim -4$ eV is in good agreement with that observed by the UPS (UV photoelectron spectroscopy) measurement.[15] The electronic properties of PAz are shown in Table I, together with those of polythiophene (PT) for the sake of comparison.

It has been found that the band gap of PAz is indirect, the value of which is a little larger than that of PT.[16] There is another band-gap value due to the direct interband transition at $K=\pi/a$ (see Figure 3) from the top of the HO band to the top of the LU band. This could be assigned to the second interband transition experimentally observed.[5] Thus the electrons at the HO crystal orbital (HOCO) would be rather difficult to be excited to the LU crystal orbital (LUCO) compared with PT. In fact, the electrical conductivities of the neutral PAz and PT are about 10^{-11} and $10^{-8}\,\mathrm{S\,cm^{-1}}$,[18] respectively. The smaller ionization potential and the larger HO band width compared with those of PT suggest that PAz can form high electrically-conducting material with a wider range of electron-accepting dopants than PT in principle. However, this will not actually take place as discussed below. On the other hand, the negative electron affinity and narrow LU band width suggest that increase of electric conductivity by *n*-type doping would be ineffective. This narrowness stems from the confinement of the LUCO in the seven-membered ring moiety as shown in Figure 4(b).

The open-shell structure of PAz with one unpaired electron in an azulene ring, that is, the ferromagnetic state of PAz has been calculated to be less stable than the optimized closed-shell structure by 1.19 eV for the unit cell. Hence it can be said that large spin density found in the neutral PAz[5] comes from accidental defects and so on incorporated into the polymer chain. For instance, our own measurement[19] of the spin densitly of chemically polymerized PAz with the catalyst $(NH_4)_2S_2O_8$ has indicated the value of this quantity to be 1.14×10^{19} spins g^{-1}, being one order smaller than that of electrochemically

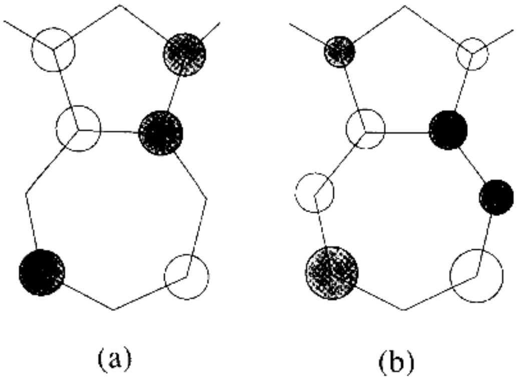
(a) (b)

Figure 4. (a) The HOCO and (b) the LUCO patterns of the neutral PAz. Round marks in the patterns indicate the phase and magnitude of π-atomic orbital coefficients.

Table II. Atomic net charges and spin densities of PAz in oxidized states[a]

Atom	Polaron state		Bipolaron state
	Net charge[b]	Spin density[c]	Net charge[b]
C_1, C_3	0.04 (0.03)	0.21 (0.20)	0.07 (0.07)
C_2H	0.08 (0.06)	0.17 (0.14)	0.03 (0.02)
C_4H, C_8H	0.11 (0.12)	0.00 (−0.03)	0.08 (0.09)
C_5H, C_7H	0.16 (0.13)	0.12 (0.12)	0.17 (0.16)
C_6H	0.21 (0.17)	−0.04 (−0.05)	0.16 (0.13)
C_9, C_{10}	0.04 (0.03)	0.10 (0.09)	0.09 (0.10)
Total	1.00 (0.85[d])	1.00 (0.85[d])	1.00 (1.00)

[a] The numbering of atoms is designated in Figure 2.

[b] Values in parentheses stand for the contribution from the π-hole.

[c] Values in parentheses stand for the contribution from the π electron.

[d] The fractional value signifies that there is also the contribution from σ component.

polymerized PAz.[5] This suggests that the spin density of PAz depends on the preparation method and hence that the observed large spin density does not come from the intrinsic nature of PAz.

Oxidized State

It was found that the positively charged bipolaron state is more stable by 1.60 eV per unit cell (one azulene ring) compared with two separated positive polaron states. This result is in agreement with the observed decrease of spin density in the heavily doped PAz.[5] Although the calculation of the oxidized states utilized the optimized geometry of the netural state, this energy difference is remarkable and hence it is expected that the privilege of the bipolaron state would not change for the optimized geometries of the oxidized stages.

Atomic net charges and spin densities of these oxidized states are listed in Table II. It was found in the polaron state that spin part and positive-charge part are separated into the five-membered and the seven-membered rings, respectively, of an azulene ring unit. This situation is similar to the π-spin component and the π-hole distribution also listed in Table II. This separation mode is illustrated in Figure 5(a). It is also clear that most of the net charges in the bipolaron state are confined in the seven-membered ring as shown in Figure 5(b) similar to the situation in the polaron state.

It is interesting to note that the HOCO pattern of the neutural PAz shown in Figure 4(a) has large components in the five-membered ring, but that the π-hole is eventually injected into the seven-membered ring as described above. This signifies that the seven-membered ring has a strong tendency to form a stable 6π-electron system like a tropylium cation. This peculiar situation would explain the relatively small electrical conductivity of the doped PAz compared with that of the doped PT,[16] since the injected hole is rather localized or, even more, confined in the seven-membered ring.

The calculated π-bond orders in the bipolaron state are shown in Figure 5(c) along with the predicted bonding mode of the main chain part of PAz. The energetical stabilization in the bipolaron state is, as a matter of course, caused by the single-spin formation or, in other words, a sort of the spin-Peierls transition of coupled polarons. It is hence understood that there would appear a bond-alternative tendency in the main chain in the bipolanic state. It is noted that, on the contrary, the negative

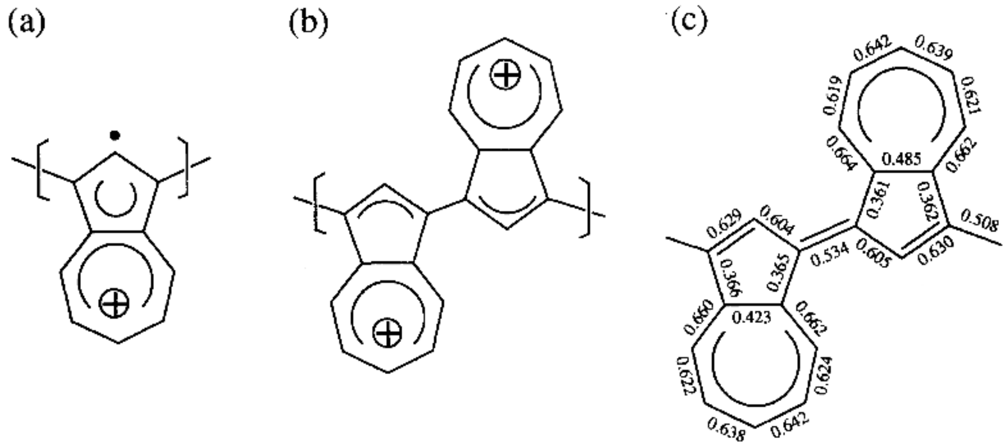

Figure 5. Illustration of the proposed models of (a) the polaron and (b) the bipolaron states. The π-bond orders and the predicted C=C bonds in the bipolaron state are shown in (c).

polaron state would be rather stable in PAz due to the narrowness of the LU band width as described in the above.

CONCLUSION

We have studied the electronic structure of PAz in the neutral and the oxidized states. Six major features have been found as follows:

(1) The optimized structure of neutral PAz favours the unit-cell symmetry of C_{2v} probably due to the delocalization stabilization throughout the polymer chain.

(2) In the polaron state of PAz, the π hole and the spin are separated into the seven-membered and the five-membered rings, respectively, of an azulene ring.

(3) The formation of bipolaron lattice is expected to be energetically more favourable than the spatially isolated polaron states, which agrees with the experimental observation in the heavily doped PAz.

(4) The positive charges of PAz in the bipolaron state are rather confined into the seven-membered ring, which could decrease the mobility for the intrachain electrical conduction.

(5) Judging from the LUCO pattern and the LU band width of the neutral PAz, the efficiency of the *n*-type doping of PAz would not be so promising.

(6) The ferromagnetic state in the neutral PAz does not seem to be of intrinsic nature of this polymer.

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