# Towards Designing Environmentally Stable Conjugated Polymers with very Small Band-Gaps

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We have investigated substituent effect on the stabilization energies, and nucleus-independent chemical shifts of pentafulvalenes and on the electronic structures of the corresponding polypentafulvalenes to design environmentally stable semiconductive or conductive polymers. Geometrical optimizations of the molecules were carried out at the density functional level of theory with B3LYP hybrid functional and 6-311+G(d) basis set. Stabilization energies were estimated using isodesmic and homodesmotic reactions. As a criterion of aromaticity nucleus-independent chemical shifts of the molecules were computed using GIAO approach. For the polymers the geometrical parameters were optimized through AM1 band calculations and the electronic structures were obtained through modified extended Hückel band calculations. It is found that strong electron-withdrawing substituents increase isodesmic and homodesmotic stabilization energies of pentafulvalene, though it does not increase the aromaticity. Nitro-substituted pentafulvalene is estimated to have stabilization energy as much as azulene. However, substitution either with electron-donating groups or with electron-withdrawing groups does not significantly affect the electronic structures of polypentafulvalene and poly (vinylenedioxypentafulvalene).

**Key Words :** Quantum-chemical investigation, Aromaticity, Stabilization energy, Nucleus-independent chemical shifts, Small band-gap polymers

## Introduction

Recently, we have proposed that polypentafulvalenes possess small band gaps[1] or nearly zero band gaps.[2] These polymers are, however, expected to be very unstable against oxidative environments because their highest occupied molecular orbital (HOMO) energy levels are high. In fact, the monomer, pentafulvalene, is extremely reactive.[3] Such a high instability of pentafulvene and pentafulvalene is ascribed to high anti-aromatic character of the molecules.[4-9]

According to the Hückel [4n+2] $\pi$ rule, conjugated cyclic molecules with [4n+2] $\pi$ electrons are highly aromatic and very stable due to their delocalized $\pi$ electrons. However, very reactive cross-conjugated compounds such as pentafulvene and pentafulvalene also have [4n+2] $\pi$ electrons. Therefore, aromaticity and stability of conjugated cyclic molecules have been a great issue to chemists.[10] Also, the question of the aromatic/anti-aromatic character of fulvenes and fulvalenes have played dominant role in the studies of these systems.[11,12]

Though the definition of 'aromaticity' cannot be exactly described, there have been great efforts to estimate aromaticity of a variety of conjugated cyclic molecules. In 1965, Dewar and his coworkers defined the Dewar resonance energy as a stabilization energy due solely to cyclic conjugation[4] and used the resonance energy as a criterion of aromaticity.[5] In 1971, Hess and Schaad reported that the Dewar-type resonance energy can be defined within the framework of Hückel molecule orbital (HMO) theory.[6,7]

Aihara then found that the (topological) Dewar-type resonance energy can be defined by graph theory using HMO theory.[8] Several other criteria have been also established based on structural information of conjugated cyclic compounds. Julg and Francois,[13] and later Kruszewski and Krygowski[14] used bon-length equalization as a criterion of aromaticity in their harmonic oscillator measure of aromaticity (HOMA) model. Cyclic delocalization of mobile electrons, $\sigma$ or $\pi$, results in ring currents, which are responsible for abnormal magnetic properties: exalted magnetic susceptibilities, anisotropies, and displaced nuclear magnetic resonance chemical shifts. Therefore, these magnetic properties have been used as a measure of aromaticity.[15-21]

Substitution with halogens[22-25] or bulky groups[26] has been reported to considerably increase stability of pentafulvalene. In this respect, many attempts have been made to increase the stability of non-aromatic compounds by increasing their aromaticity using a variety of substituents.[27-31] However, the substituent effects on the aromaticity are controversial. Hess and Schaad have reported that halogens affect resonance energy of nonbenzenoid compounds through donating electrons,[32] while other researchers have suggested that halogens do not affect the aromaticity.[28-30]

In this study, we investigated the stabilization energies, aromaticities, and nuclear magnetic properties of a variety of substituted pentafulvalenes in order to understand the effect of substituents on the stability of the molecules and, in the end, to design stable conductive polymers. In the first part of this report, two types of stabilization energies, aromaticity, and nuclear magnetic property of pentafulvalene are compared with those of other conjugated cyclic molecules shown in Figure

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1. In the second part, the substituent effects are discussed on the stability and aromaticity of pentafulvalene. In the last part, we present the electronic properties of the corresponding polypentafulvalenes and poly(vinylenedioxypentafulvalene)s.

## Methodology

To estimate properties of pentafulvalene and the other conjugated cyclic molecules in the neutral and cationic radical states, we employed the density functional theory (DFT)[33] with the B3LYP hybrid functional[34] and 6-311+ G(D) basis set implemented by the Gaussian 98 package.[35] The DFT method provides accuracy over Hartree-Fock (HF) theory for many molecular systems by including some of the effects of electron correlation in the way that individual electron instantaneously offset one another. Within a given symmetry each molecular structure was optimized with keywords of *Opt=Tight, SCF=Tight* and *Int(Grid=UltraFine)* for numerical integrations. Frequency calculations were also performed to ensure if the optimized structures represent minima in the potential energy surfaces and to obtain zero-point energies and thermodynamic properties of the molecules with corrections for hindered rotations.

Stabilization energies of the conjugated cyclic molecules were evaluated through isodesmic bond separation reactions[36] and homodesmotic reactions.[37-39] Isodesmic reaction equations can be set up by retaining the number of bonds or a given formal type (C-H, C-C, C=C etc.), but changing the formal relation to one another. On the other hand, homodesmotic reactions involve no change in hybridization of carbon atoms and minimal changes in the nature of the C-H bond. To eliminate the effect of the ring size normalization was

done by dividing the total stabilization energies by the number of $\pi$ electrons in a conjugated cyclic molecule.

Nucleus-independent chemical shift (NICS) values were computed at the center of a conjugated cyclic ring as a criterion of aromaticity as proposed by Schleyer.[21] Local paramagnetic contributions of the $\sigma$ bonds, however, counteract the diamagnetic $\pi$ ring current effect, thereby influencing NICS values estimated at the center. One can separate these two contributions by calculating NICS values above the center of a conjugated ring since the $\sigma$ contribution will fall off rapidly than the $\pi$ contribution.[17,40,41] The height at which the $\pi$ system has its maximum extent above the ring is dependent on the molecular system under consideration. Therefore, we calculated NICS values not only at the ring center but also every 0.1 Å above the center of a conjugated cyclic ring until locating a height where a maximum aromaticity is provided.

We employed the solid-state version of the MNDO method (MOSOL)[42] with the AM1 hamiltonian to optimize geometrical parameters of polymers. This version adopts the Born-von Kármán periodic boundary condition and Bloch functions for crystal calculations. The AM1 method has been successfully used to investigate geometrical structures and conformations of large molecules in particular.[43] For the geometrical optimizations, we chose 6 wave vectors with a regular interval from 0 to $\pi/a$ (where $a$ is a translation vector). The cutoff value used for interactions between atoms was set to 35 Å. All the calculations were performed for isolated single polymer chains without consideration of any intermolecular effects.

Electronic properties were calculated by applying the AM1 optimized structures to the modified extended Hückel (MEH) method.[44] This method expresses the off-diagonal elements of the EH method in a modified form, which has an additional distance-dependent empirical factor. This was parameterized to reproduce experimental $\lambda_{max}$ values for the $\pi-\pi^*$ transitions of some conjugated polymers such as *trans*-polyacetylene and PPP, not onset values that have been usually related to band gaps. This approach has predicted $\lambda_{max}$ values of a variety of conjugated polymers with fairly good accuracy, compared to experimental values.[45] Atomic parameters used in the MEH calculations are presented in Table 1.

## Stability of Pentafulvalene

In this section, we discussed the geometry, stabilization energies, and NICS values of pentafulvalene in comparison with other cyclic conjugated molecules to estimate relative stability of the molecule.
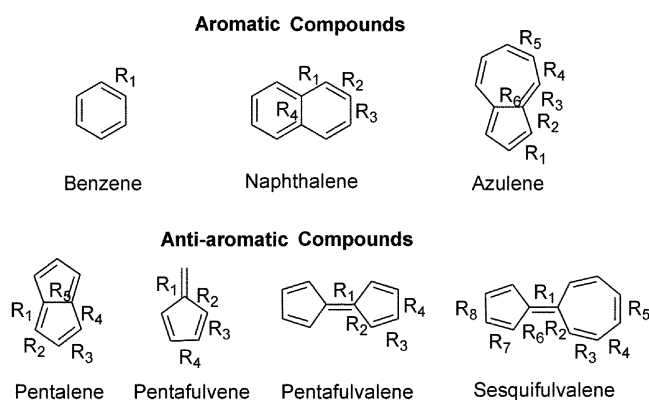


**Figure 1**. Aromatic and anti-aromatic compounds under investigation.

**Table 1**. Valence Shell Atomic Parameters Used in the Modified Extended Hückel Band Calculations

| atom | $n$ | $l$ | $H_{ii}$ (eV) | $\zeta$ (a.u.) | $n$ | $l$ | $H_{ii}$ (eV) | $\zeta$ (a.u.) |
|------|-----|-----|---------------|----------------|-----|-----|---------------|----------------|
| H | 1 | 0 | −13.60 | 1.300 | | | | |
| B | 2 | 0 | −15.20 | 1.300 | 2 | 1 | −8.500 | 1.300 |
| C | 2 | 0 | −21.40 | 1.625 | 2 | 1 | −11.40 | 1.625 |
| N | 2 | 0 | −26.00 | 1.950 | 2 | 1 | −13.40 | 1.950 |
| O | 2 | 0 | −32.30 | 1.975 | 2 | 1 | −14.80 | 1.975 |
| F | 2 | 0 | −40.00 | 2.425 | 2 | 1 | −18.10 | 2.425 |

**Geometries.** In Table 2 we presented optimized geometrical parameters for the molecules shown in Figure 1. Benzene belongs to the $D_{6h}$ point group where complete bond-equalization is accomplished with all the six C-C bonds equal in length. The calculated C-C bond length is 1.395 Å, which is intermediate between C-C single and double bonds. Naphthalene shows a rather large bond-length alternation. Bond lengths of the C-C bonds are in the range of 1.375-1.432 Å. Azulene, a structural isomer of naphthalene $C_{10}H_8$, is 139.4 kJ/mol higher in energy than naphthalene. This value is in excellent agreement with the experimental result (139 kJ/mol).[46] In azulene, the geometry optimization essentially converges the $C_s$ structures into the $C_{2v}$ structures. All the C-C bonds of azulene are quite similar (1.396-1.405 Å) in length except the bond (1.499 Å) shared with the pentagon and the heptagon. It seems that azulene does not consist of two rings, but is made up of one delocalized 10-membered ring. Structural information[47] on naphthalene and azulene is available for comparison in literature.
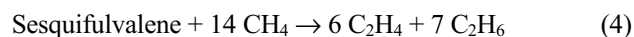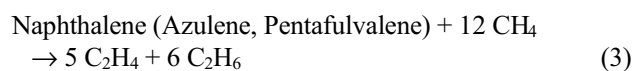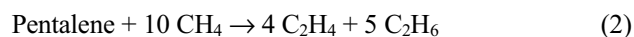
Pentalene is known to be highly reactive due to its anti-aromaticity. Unsubstituted pentalene has been recently prepared in argon matrics by photocleavage of the corresponding dimer,[48] though there have been isolations of some substituted pentalene[49] such as hexaphenylpentalene early in 1960s. In the neutral state pentalene is optimized to a $C_{2h}$ structure with localized carbon-carbon single and double bonds. The bond-length difference between the longest and the shortest C-C bonds is quite large, 0.14 Å, compared to other conjugated molecules. This large difference reflects the large degree of anti-aromaticity of pentalene. The $D_{2h}$ structure ($^1A_g$) with delocalized C-C bonds is 28.3 kJ/mol less stable than the $C_{2h}$ structure. Frequency calculations indicate the $D_{2h}$ structure does not represent a minimum but a first-order saddle point. B3LYP/6-31G(D) calculations have shown that a triplet $D_{2h}$ structure of pentalene corresponds to an energy minimum and 32.3 kJ/mol higher in energy than the singlet $C_{2h}$ state.[50]

Similarly, pentafulvene, pentafulvalene, and sesquifulvalene are computed to possess quite localized long and short bonds with large bond-length alternations, indicating that these molecules are highly anti-aromatic. Pentafulvene is 143.1 kJ/mol less stable than its structural isomer, benzene, and pentafulvalene 241.2 kJ/mol less stable than naphthalene. The differences between the long and short bonds of the molecules are not as large as that found in pentalene. On
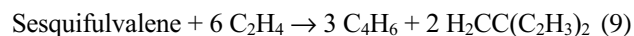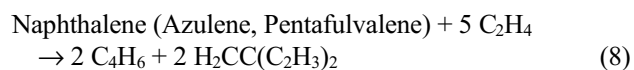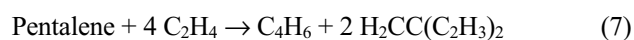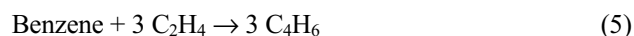
going from pentafulvene to sesquifulvalene via pentafulvalene the exo-double bond increases from 1.342 Å to 1.392 Å. The increase in the exo-bond lengths is due to repulsion between the two connected rings.

**Stabilization energies.** Stabilization energies (SE) of conjugated cyclic compounds can be estimated from the enthalpy changes for hypothetical reactions where products are usually short open chains, which are arbitrarily chosen as reference molecules. Therefore, SE strongly depends on the choice of reference molecules.

We set up isodesmic reactions for estimating isodesmic stabilization energies (ISE) of benzene, naphthalene, azulene, pentalene, pentafulvene, pentafulvalene, and sesquifulvalene, respectively, as follows:

$$\text{Benzene (Pentafulvene)} + 6\,CH_4 \rightarrow 3\,C_2H_4 + 3\,C_2H_6 \quad (1)$$

$$\text{Pentalene} + 10\,CH_4 \rightarrow 4\,C_2H_4 + 5\,C_2H_6 \quad (2)$$

$$\text{Naphthalene (Azulene, Pentafulvalene)} + 12\,CH_4 \\ \rightarrow 5\,C_2H_4 + 6\,C_2H_6 \quad (3)$$

$$\text{Sesquifulvalene} + 14\,CH_4 \rightarrow 6\,C_2H_4 + 7\,C_2H_6 \quad (4)$$

Homodesmotic stabilization energies (HSE) of the molecules were estimated using the following equations.

$$\text{Benzene} + 3\,C_2H_4 \rightarrow 3\,C_4H_6 \quad (5)$$

$$\text{Pentafulvene} + 2\,C_2H_4 \rightarrow C_4H_6 + H_2CC(C_2H_3)_2 \quad (6)$$

$$\text{Pentalene} + 4\,C_2H_4 \rightarrow C_4H_6 + 2\,H_2CC(C_2H_3)_2 \quad (7)$$

$$\text{Naphthalene (Azulene, Pentafulvalene)} + 5\,C_2H_4 \\ \rightarrow 2\,C_4H_6 + 2\,H_2CC(C_2H_3)_2 \quad (8)$$

$$\text{Sesquifulvalene} + 6\,C_2H_4 \rightarrow 3\,C_4H_6 + 2\,H_2CC(C_2H_3)_2 \quad (9)$$

We normalized stabilization energies by dividing the total stabilization energy by the number of $\pi$ electrons in a conjugated cyclic molecule to eliminate the effect of the ring size. In Table 3 are shown the normalized ISE and HSE of the molecules together with the NICS values. B3LYP/6-311+G(d) predictions are in excellent agreement with the experimental values and are consistent with the MP2 calculations,[52] which predict that naphthalene is more stable than azulene and pentalene by 15.1 and 26.0 kJ/mol per $\pi$ electron, respectively.

The ISEPE decreases in the following order: naphthalene > benzene > azulene > sesquifulvalene > pentafulvalene > pentafulvene > pentalene. The order of decreasing HSEPE is

**Table 2**. Optimized C-C Bond Lengths (in Å) for the Molecules Shown in Figure 1 Through B3LYP/6-311+G(D) Calculations

|  | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | $R_7$ | $R_8$ |
|---|---|---|---|---|---|---|---|---|
| Benzene | 1.395 | | | | | | | |
| Naphthalene | 1.412 | 1.404 | 1.390 | 1.431 | | | | |
| Azulene | 1.403 | 1.405 | 1.390 | 1.396 | 1.396 | 1.499 | | |
| Pentalene | 1.354 | 1.496 | 1.354 | 1.474 | 1.458 | | | |
| Pentafulvene | 1.342 | 1.474 | 1.352 | 1.474 | | | | |
| Pentafulvalene | 1.362 | 1.472 | 1.352 | 1.476 | | | | |
| Sesquifulvalene | 1.392 | 1.452 | 1.361 | 1.436 | 1.358 | 1.462 | 1.364 | 1.455 |

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**Table 3**. Isodesmic and Homodesmotic Stabilization Energies Per $\pi$ Electrons (ISEPE and HSEPE, respectively, in kJ/mol) at 298 K and Nucleus-Independent Chemical Shifts at the Center of the Ring and above the Center (NICS(0) and NICS(h), respectively)

| | ISEPE[a] | HSEPE[a] | NICS (0) | NICS (h)[b] |
|---|---|---|---|---|
| Benzene | 45.36 (44.98) | 15.90 (15.13) | −7.9 | −10.5 (0.8) |
| Naphthalene | 50.06 (50.26) | 19.64 | −8.4 | −11.0 (0.8) |
| Azulene[c] | 36.24 (35.41) | 5.82 | −16.7 | −19.8 (0.6) |
| | | | −5.5 | −7.8 (0.9) |
| Pentalene | 17.86 | −12.81 | 25.0 | 9.0 (1.6) |
| Pentafulvene | 21.50 | −3.85 | 1.1 | −2.5 (1.2) |
| Pentafulvalene | 25.94 | −4.48 | 3.2 | −1.5 (1.6) |
| Sesquifulvalene[c] | 28.83 | −1.44 | 2.4 | −1.3 (1.6) |
| | | | 9.2 | 0.6 (3.0) |

[a]The SEPE values in the parentheses were estimated from the experimental values for enthalpies of formation tabulated in Ref. 51. [b]The numbers in the parentheses indicate the height in Å where the corresponding NICS values were evaluated. [c]Upper NICS values are for the 5-membered ring and lower values for the 7-membered ring.

consistent with that of the ISEPE except that the order of pentafulvalene and pentafulvene is reversed. Negative HSEPE values of the cross-conjugated cyclic compounds indicate that these molecules are anti-aromatic and certainly unstable compared to the corresponding open conjugated chains. Therefore, it is quite straightforward to tell from the sign of a HSEPE value whether the molecule is aromatic or anti-aromatic. This is the advantage of HSEPE over ISEPE.

Recently, Schaad and Hess reviewed resonance energies of conjugated cyclic molecules with a variety of reference structures.[10] Most of the reference structures produce the resonance energy of benzene greater than that of naphthalene except Hückel reference structure. Also, the resonance energy of pentalene has been predicted to be larger than that of pentafulvalene except Dewar and de Llano reference structure. Tewari and Srivastava[53] estimated resonance energy of pentafulvalene larger than that of pentalene using a new version of IOC-$\omega$-technique, being consistent with our result.
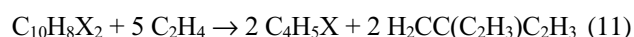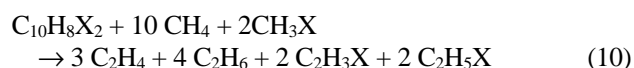
**NICS values**. Benzene, naphthalene and azulene possess negative NICS values whose absolute values are large, indicating that they are highly aromatic (see Table 3). The NICS values of naphthalene are more negative than those of benzene, suggesting that the former molecule is the more aromatic than the latter one. This is quite parallel with the order of stabilization energies of these molecules. The small ring of azulene is predicted to be more aromatic than the larger one, and than benzene and naphthalene.

The cross-conjugated cyclic molecules are predicted to have small positive NICS(0) values and slightly negative NICS(h) values, implying that these compounds own much less aromaticity than benzene. Investigation of $^3J$(H,H) coupling constants of pentafulvenes and pentafulvalenes suggests that $\pi$ delocalization is very small in these molecules.[16] From the NICS values we expect that the aromaticities of the cross-conjugated cyclic molecules are not quite different from each other. As found in the azulene case, the 5-membered ring of sesquifulvalene is estimated to be more aromatic than the 7-membered ring where maximum aromaticity could not

found up to 3 Å above the center of the ring. Pentalene has the largest positive NICS values, indicating that the molecule has the greatest degree of anti-aromaticity.
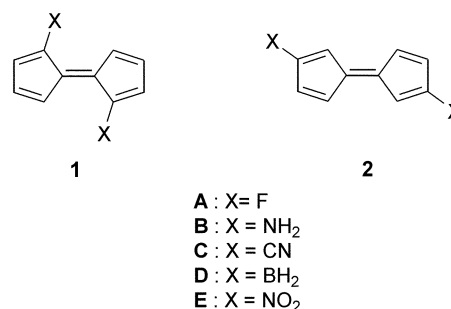
## Stability of Substituted Pentafulvalenes

A variety of substituents (fluorine, amino, cyano, boryl, and nitro groups) are placed at two different substitutional sites (see Figure 2) to assess effects of the substituents and the substitutional sites on the stabilization energy and aromaticity of pentafulvalene. Isodesmic and homodesmotic reactions for the substituted pentafulvalenes were set up, respectively, as follows.

$$C_{10}H_8X_2 + 10\,CH_4 + 2CH_3X$$
$$\rightarrow 3\,C_2H_4 + 4\,C_2H_6 + 2\,C_2H_3X + 2\,C_2H_5X \qquad (10)$$

$$C_{10}H_8X_2 + 5\,C_2H_4 \rightarrow 2\,C_4H_5X + 2\,H_2CC(C_2H_3)C_2H_3 \quad (11)$$

In Table 4 are summarized the calculated stabilization energies and NICS values of the substituted pentafulvalenes.

It is quite apparent that nitro groups, a strong electron-withdrawing group, in **2E** greatly increase the stabilization energies of pentafulvalene and produce a large positive HSEPE value for **2E**. The ISEPE and HSEPE values of **2E** are as large as those of azulene, implying that pentafulvalene



**A** : X= F
**B** : X = NH$_2$
**C** : X = CN
**D** : X = BH$_2$
**E** : X = NO$_2$

**Figure 2**. Pentafulvalenes substituted at two different sites.

**Table 4**. Isodesmic and Homodesmotic Stabilization Energies Per $\pi$ Electron (ISEPE and HSEPE, respectively, in kJ/mol) at 298 K and NICS Values of Substituted Pentafulvalenes with a Variety of Substituents

| Molecules | ISEPE | HSEPE | NICS(0) | NICS(h)[a] |
|---|---|---|---|---|
| Pentafulvalene | 25.94 | −4.48 | 3.2 | −1.5 (1.55) |
| 1A | 13.97 | −12.18 | 3.8 | −0.3 (2.55) |
| 1B | 14.05 | −6.77 | 7.4 | 0.0 (3.0)[b] |
| 1C | 25.19 | −2.70 | 3.0 | −1.6 (1.55) |
| 1D | 28.47 | 0.45 | 3.3 | −2.6 (1.30) |
| 1E | 16.94 | −6.22 | 2.9 | −0.9 (1.80) |
| 2A | 17.00 | −7.46 | −0.8 | −1.8 (1.35) |
| 2B | 19.73 | −1.10 | −1.0 | −2.1 (1.50) |
| 2C | 25.34 | −3.19 | 2.0 | −1.7 (1.45) |
| 2D | 28.03 | 0.01 | 5.1 | −1.4 (1.65) |
| 2E | 36.24 | 13.08 | 1.8 | −1.5 (1.60) |

[a]The numbers in the parentheses indicate the heights above the centers of the rings. [b]Maximum aromaticity could not be found up to 3.0 Å above the center of the ring.

**Table 5**. Electronic Properties (in eV) of Polypentafulvalenes and Poly(vinylenedioxypentafulvalenes)

| Polymers | $E_{HOMO}$ | $\Delta E_{gap}{}^a$ | Polymers | $E_{HOMO}$ | $\Delta E_{gap}{}^a$ |
|---|---|---|---|---|---|
| polypentafulvalene | −12.07 | 1.13 | poly(vinylenedioxypentafulvalene) | −9.50 | 0.03 |
| 3A | −11.72 | 0.87 | 5A | −9.35 | 0.01 |
| 3B | −11.20 | 0.56 | 5B | −9.43 | 0.03 |
| 3C | −11.01 | 1.12 | 5C | −9.64 | 0.04 |
| 3D | −11.88 | 1.07 | 5D | −9.94 | 0.02 |
| 3E | −11.95 | 1.00 | 5E | −9.56 | 0.05 |
| 4A | −12.06 | 1.45 | 6A | −9.35 | 0.05 |
| 4B | −11.31 | 1.05 | 6B | −9.43 | 0.04 |
| 4C | −12.09 | 0.99 | 6C | −9.66 | 0.01 |
| 4D | −12.06 | 1.18 | 6D | −9.86 | 0.02 |
| 4E | −12.10 | 1.28 | 6E | −9.57 | 0.01 |

[a]HOMO-LUMO gap.

with nitro substituents might be as stable as azulene. In **1E**, where nitro groups are rotated by 34.3° from the molecular plane, nitro groups rather decrease stabilization energies of pentafulvalene. Therefore, it can be recognized that resonance effect is involved in the stabilization through the efficient π-overlap between the nitro group and pentafulvalene. Such a π-overlap results in the strong bonding interaction between the HOMO of pentafulvalene and the π* orbital of the nitro group, reflecting a C-N bond length of 1.451 Å much shorter than the bond length of 1.496 Å found in 2-nitrobutadiene. Boryl substitution slightly increases the stabilization energies of pentafulvalene, irrespective of substitutional sites. It is seen that cyano substituent, an electron-withdrawing group, hardly affects the stabilization energies of pentafulvalene.

On the other hand, fluorine and amino substituents destabilize pentafulvalene. These substituents release electrons through the resonance effect and withdraw electrons through the inductive effect. Therefore, it is obvious that the interaction between the substituents and pentafulvalene occurs through resonance. Hess and Schaad[32] also suggested that fluorine might act as an electron donor in the fulvalene system. Other reports support that halogens do not significantly affect the delocalization energy of cyclopentapropenyl cation,[29] and aromaticity of 4-silartriafulvene,[28] and rather destabilize cyclopentadiene.[30]

It is seen that substitution either with electron-withdrawing groups or with electron-donating groups does not significantly

affect the NICS(0) and NICS(h) values of pentafulvalene. It seems that substituents barely increase aromaticity of pentafulvalene.
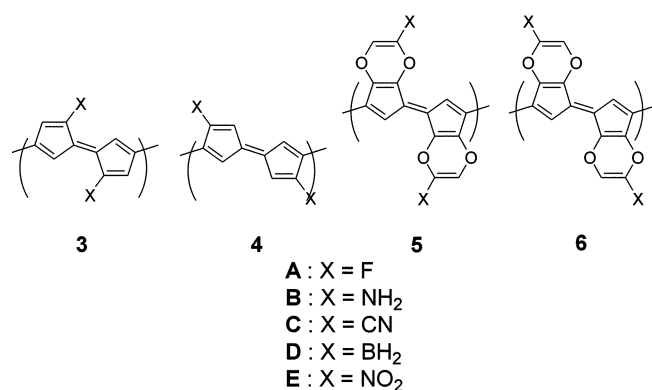
**Polypentafulvalenes**

Unsubstituted polypentafulvalene is predicted to be semi-conductive with the HOMO-LUMO gap of 1.13 eV.[1] Substitution with an electron-donating group or with an electron-withdrawing group further decreases the gap, depending on the substitutional site. Moreover, fusion with dioxabenzene is expected to close the gap.[2] In this section, we present the electronic structures of the substituted polypentafulvalenes in Figure 3.

As shown in Table 5 the substituents barely affect HOMO energy levels and HOMO-LUMO gaps of polypentafulvalene and poly(vinylenedioxypentafulvalene). Substitution with electron-donating groups such as F and NH$_2$ groups slightly elevates the HOMO energy levels and decreases the HOMO-LUMO gap of polypentafulvalene. It is found that boryl substitution lowers the HOMO energy levels of poly (vinylenedioxy-pentafulvalene) by 0.4 eV.

**Conclusion**

Comparison of bond-length alternation, stabilization energies (ISEPE and HSEPE) and NICS values of pentafulvalene was made with those of other aromatic and anti-aromatic compounds. Overall, it is estimated that pentafulvalene is as anti-aromatic as and as reactive as pentafulvene and sesquifulvalene.

It is found that substituents affect the stabilization of pentafulvalene through the efficient π-overlap. Such a resonance effect induces electron-withdrawing groups to increase the stability of pentafulvalene, but induces electron-donating substituents to decrease the stability. In 5,5'-disubstituted cyclopentadiene,[30] the same trend is observed. It is encouraging that nitro-substituted pentafulvalene can be as stable as azulene. We expect that multi-substitution with strong electron-withdrawing groups would induce considerable increase in the stability of pentafulvalene as observed in



**3**     **4**     **5**     **6**

**A** : X = F
**B** : X = NH$_2$
**C** : X = CN
**D** : X = BH$_2$
**E** : X = NO$_2$

**Figure 3**. Polypentafulvalenes and poly(vinylenedioxypentafulvalenes).

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the case of cyclobutadiene.[31] Judging from the NICS values, the substituents are, however, hard to significantly increase the aromaticity of pentafulvalene.

It is calculated that substituents hardly affect the electronic structures of polypentafulvalene and poly(vinylenedioxy-pentafulvalene), except a few cases. Amino group tends to slightly reduce the HOMO-LUMO gaps. The HOMO energy levels of poly(vinylenedioxypentafulvalene) can be depressed by 0.4 eV through boryl substitution, though the levels are still high.

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