Charge-Transfer Induced Large Nonlinear Optical Properties of Small Al Clusters: Al_4M_4 (M = Li, Na, and K)

Ayan Datta and Swapan K. Pati*

Theoretical Sciences Unit and Chemistry and Physics of Materials Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India

Received: June 28, 2004; In Final Form: August 2, 2004

We investigate the linear and nonlinear electric polarizabilities of small Al_4M_4 (M = Li, Na, and K) clusters. Quantum chemical calculations reveal that these compounds exhibit an exceptionally high magnitude of linear and nonlinear optical (NLO) coefficients which are orders of magnitude higher than the conventional π-conjugated systems of similar sizes. We attribute such phenomenal increase to noncentrosymmetricity incorporated in the systems by the alkali atoms surrounding the ring leading to charge transfer with small optical gap and low bond length alternation (BLA). Such a low magnitude of the BLA from a different origin suggests the possibility that these clusters are aromatic in character, and along with the large NLO coefficients, they appear to be better candidates for next generation NLO fabrication devices.

The development of materials with large nonlinear optical (NLO) properties is a key to controlling the propagation of light by optical means. In particular, the response of the materials to the application of the electric field has found tremendous applications in designing materials for NLO devices.[1] These devices are being used in numerous applications, from lasers to optical switches and optoelectronics. The NLO properties of organic π-conjugated materials have been studied in great details in the last few decades.[2,3] The second- and third-order nonlinear optical properties, β and γ, for the π-conjugated polymers increase with the conjugation length (L) roughly as L^3 and L^5, respectively.[4] Therefore, the general strategy to model NLO materials has been to increase the conjugation length. However, there exists an upper limit for every off-resonant susceptibilities.[5] Alternatives to these π-conjugated compounds are yet to be explored theoretically in a detailed fashion. But, with the gaining popularity of various ab initio level methods,[6] there has been a tremendous impetus in investigating the structure and electronic properties of both homogeneous and heterogeneous small clusters in recent years.[7,8] Small Al_4 rings such as Al_4M_4 and their anions $Al_4M_3^-$, M = alkali metals, have been a subject of current interest[9,10] because of their unique characteristics and close structural resemblance to C_4H_4. However, although C_4H_4 is an antiaromatic species, these Al_4-clusters are recently reported to be σ aromatic.[11] Thus, it would be interesting to ask whether these rings are better polarized than their organic counterpart, whether the structural characteristics have any role in their polarization response functions. Organic π-conjugated systems are stabilized due to π-electron delocalizations, while the inorganic metal complexes reduce their energy through strong charge transfer. There have been no previous efforts to study in detail the NLO properties of these all-metal clusters. We describe in the following that these metal clusters offer a unique polarization response due to their ionic character, contrary to conventional π-conjugated systems, leading to large optical coefficients.

We begin our calculations by optimizing the ground state geometries of the Al_4-clusters (Al_4Li_4, Al_4Na_4, and Al_4K_4). All the optimizations have been done using the 6-31G(d,p) basis set. Electron correlation has been included according to the DFT method using Becke's three parameter hybrid formalism and the Lee−Yang−Parr functionals (B3LYP)[12] available in the GAMESS[13] electronic structure set of codes. Since we want to compare the optical properties of these small four-membered rings with their organic analogue C_4H_4, we start with a planar initial geometry for the optimizations. We have varied the level of basis set from 6-31G(d,p) to 6-311G+(d) to ensure that these geometries correspond to the minima in the potential energy surface. The final geometries indeed remain independent of the selection of the basis set. Contrary to that of C_4H_4 having a rectangular ring, these Al_4-clusters are found to have a rhomboidal structure with four Al atoms forming a rhombus and the four alkali atoms around the four Al−Al bonds forming four Al−M (Li, Na, K)−Al triangles. One of the diagonals of the Al_4 ring is also connected by an Al−Al bond. The equilibrium geometries are shown in Figure 1 [**1(a)**, **1(b)**, and **1(c)**].

While Al_4Li_4 and Al_4K_4 have a planar structure (D_{2h}), Al_4Na_4 has a distorted structure, with the four Na atoms arranged in a nonplanar geometry around the planar ring (the Na atoms are distorted by 13° from the plane of Al_4 ring). This can be understood by considering the increase in size of the alkali ions and the distances of the ions from the Al_4-ring. With the progressive increase in the ionic radii of counterion, Li to K (Li = 0.68 Å, Na = 0.97 Å, and K = 1.33 Å), the structures are expected to be distorted, and the four alkali atoms should arrange in a noncentrosymmetric geometry around the Al_4 ring to minimize steric repulsion. However, the average Al−M distance increases while going from Al_4Li_4 (2.65 Å) to Al_4Na_4 (3.00 Å) to Al_4K_4 (3.35 Å). Although the ionic radius of K ion is more than that of Li and Na, in Al_4K_4, the four K ions are far separated from the Al_4 ring, allowing a planar structure. For Al_4Na_4, both the ionic radius of Na and the average Al−M distance fall between Al_4Li_4 and Al_4K_4, and thereby these minimize the steric repulsion through distortion. Also, very close

---

* To whom correspondence should be addressed. E-mail: pati@jncasr.ac.in.

10.1021/jp047204c CCC: $27.50

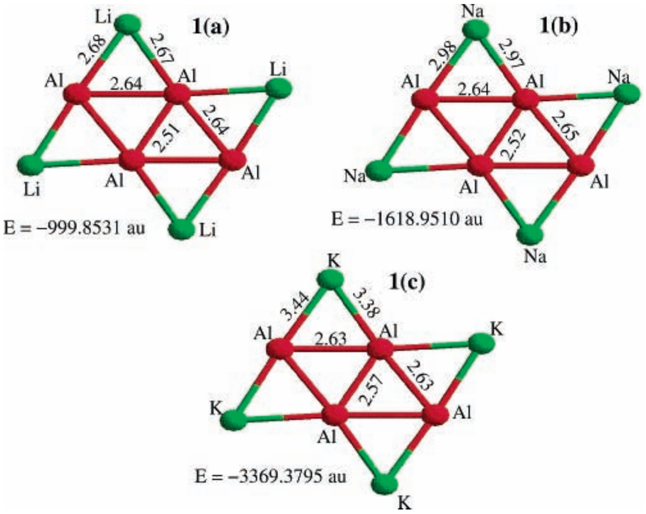

Figure 1. Equilibrium ground state geometries for Al_4Li_4, Al_4Na_4, and Al_4K_4. The footnote of each structure contains the ground state energies in au.

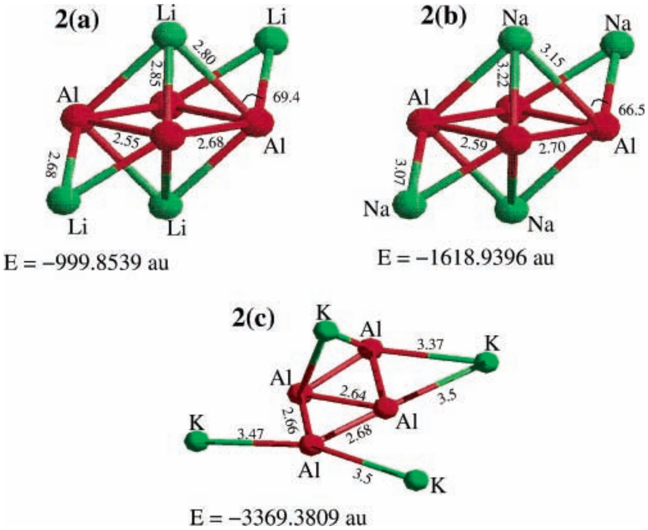

Figure 2. Equilibrium ground state geometries for the other set of Al_4Li_4, Al_4Na_4, and Al_4K_4, very close in energy to those in Figure 1. The footnote of each structure contains the ground state energies in au.

in energy to these planar rhomboidal structures for these Al_4-clusters are the capped octahedron structures for the Al_4Li_4 [**2(a)**] and Al_4Na_4 [**2(b)**] (with C_{2h} symmetry) and a distorted tricycle-like structure for Al_4K_4 [**2(c)**]. These geometries are shown in Figure 2. At the footnote of each structure, the corresponding ground state energies are given. It has, however, not escaped our attention that previous work on alkali derivatives of Al_4-clusters has predicted more than one unique structure for these systems.[14] This calls for a study to elucidate whether the optical properties for these Al_4-clusters for different geometries are substantially different or are very similar. Hence, both the geometries for each cluster were considered for computing the optical response functions.

These geometries were used to compute the SCF MO energies and then the spectroscopic properties using the Zerner's INDO method.[15] We have varied the levels of CI calculations, with singles (SCI) and multireference doubles(MRDCI) CI , to obtain a reliable estimate of the second-order optical response. The latter method is particularly important since it includes substantial correlation effects. The MRDCI approach adopted here has been extensively used in earlier works and was found to provide excitation energies and dipole matrix elements in good agreement with experiment.[16,17] As reference determinants, we have chosen those determinants which are dominant in the description of the ground state and the lowest one-photon excited states.[18] We report the MRDCI results with 4 reference determinants including the Hartree−Fock (HF) ground state. For each reference determinant, we use 5 occupied and 5 unoccupied molecular orbitals to construct a CI space with configuration dimension 800−900. To calculate NLO properties, we use the correction vector method, which implicitly assumes all the excitations to be approximated by a correction vector.[19] Given the Hamiltonian matrix, the ground state wave function, and the dipole matrix, all in CI basis, it is straightforward to compute the dynamic nonlinear optic coefficients using either the first-order or the second-order correction vectors. Details of this method have been published in a number of papers.[20−22]

TABLE 1: Bond Length Alternation, Δ*r* (in Å), Optical Gap (in au), and Average Mulliken Charge (Δ*q*) on the Ring for the Clusters from ZINDO Calculations

molecule	Δr	gap	Δq
Al_4Li_4 **1(a)**	0.1283	0.0819	−0.592
Al_4Li_4 **2(a)**	0.1276	0.024	−0.506
Al_4Na_4 **1(b)**	0.1302	0.0909	−0.174
Al_4Na_4 **2(b)**	0.1103	0.0607	−0.127
Al_4K_4 **1(c)**	0.0656	0.0663	−0.634
Al_4K_4 **2(c)**	0.0649	0.0867	−0.618
C_4H_4	0.245	0.2410	−0.030
C_6H_6	0.000	0.2588	−0.009

Table 1 shows the bond-length alternation (BLA), Δr, the optical gap, and the average Mulliken charge on the Al_4 ring for all the geometries. The Δr is defined as the average difference between the bond lengths of two consecutive bonds in the Al_4-ring, and the optical gap is calculated as the energy difference between the geometry relaxed ground state and the lowest optically allowed state with substantial oscillator strength. This corresponds to the vertical absorption gap. To directly compare the efficiency of these Al_4-clusters with the conventional π conjugated systems, we calculate the optical properties of the 1,3-cyclobutadiene (C_4H_4) and benzene (C_6H_6) at the same level of theory. For the Al_4-clusters, there is a substantial amount of charge transfer from the alkali atoms to the Al atoms (negative charge), making them act as donor and acceptor, respectively. Such a charge transfer induces polarization in the ground state structure and reduces the optical gap. On the other hand, with the C−H bond being perfectly covalent, there is almost no charge transfer in the cases of C_4H_4 and C_6H_6, and thus, they have a large optical gap due to finite size molecular architecture.

Charge transfer stabilizes the system with very small changes in the bond lengths. The chemical hardness, η, defined as $^1/_2$(ionization potential − electron affinity), decreases as one moves from Li to K. More specifically, the η values for Li, Na, and K are 2.39, 2.30, and 1.92 eV, respectively.[23] So, the extent of charge transfer from the alkali atom to the Al_4-ring should increase with the decrease in the chemical hardness of the alkali atoms which is evident from Table 1. From Al_4Li_4 to Al_4Na_4 to Al_4K_4, the Mulliken charge on the Al_4-ring increases leading to a decrease in the BLA along the series with the exception of Al_4Na_4 [**1(b)** and **2(b)**] which has much lower Mulliken charge on the Al_4-ring. For the Al_4Na_4 [**1(b)**] as mentioned above, there is a substantial distortion of the Na atoms from the Al_4-ring. For the Al_4Na_4, with C_{2h} symmetry [**2(b)**] even though there is no distortion, the large Al−Na distance reduces the ionicity of the bond. As a result, the extent of charge transfer is less for Al_4Na_4.

TABLE 2: Ground State Dipole Moment, μ_G, Linear Polarizability, α, First Hyperpolarizability, *β*, and Second Hyperpolarizability, *γ*, (Tumbling Average) for the Clusters and the for *trans*-Polyacetylene Chain from ZINDO-MRDCI Calculations[a]

molecule	μ_G	$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$
Al_4Li_4 **1(a)**	0.000	4.9×10^3	542.5	1.91×10^7
Al_4Li_4 **2(a)**	0.000	5.5×10^3	244.9	5.33×10^8
Al_4Na_4 **1(b)**	0.076	5.9×10^3	8465.2	1.09×10^7
Al_4Na_4 **2(b)**	8.6×10^{-4}	8.7×10^3	1098.5	2.00×10^8
Al_4K_4 **1(c)**	0.004	5.4×10^3	79.3	2.60×10^7
Al_4K_4 **2(c)**	5.720	4.7×10^3	1.2×10^5	1.90×10^7
C_4H_4	0.000	2.9×10^2	0.000	4.76×10^3
C_6H_6	0.000	5.4×10^2	0.000	8.44×10^3
$(CH{=}CH)_n$, $n = 1$	0.000	136.3	0.000	2.78×10^4
$(CH{=}CH)_n$, $n = 2$	0.000	421.0	0.000	4.15×10^4
$(CH{=}CH)_n$, $n = 3$	0.000	852.4	0.000	6.17×10^5
$(CH{=}CH)_n$, $n = 4$	0.000	1455.2	0.000	2.82×10^6
$(CH{=}CH)_n$, $n = 5$	0.000	2203.2	0.000	8.41×10^6
$(CH{=}CH)_n$, $n = 6$	0.000	3074.9	0.000	2.07×10^7

[a] The units are in au. *n* is the number of $-CH{=}CH-$ units.

Benzene is aromatic with $\Delta r = 0$. Although BLA cannot be regarded as the sole measuring index of aromatic character, the small BLA found for the Al_4-clusters (together with large BLA for the antiaromatic C_4H_4) tends to suggest that the Al_4-clusters are more like aromatic but most certainly not antiaromatic species, as has been proposed recently.[10] The distorted Al_4K_4 structure [**2(c)**] is very interesting. The Al_4-ring is distorted from planarity by 9.5°. Such a distortion arises to minimize the steric repulsion in accommodating four bulky K atoms on a plane, very similar to that of cyclooctatetraene, which undergoes a distortion from planar to tub-shaped geometry to minimize the ring-strain.[24] Thus, this structure of Al_4K_4 is neither aromatic nor antiaromatic but can be considered to be nonaromatic just like cyclooctatetraene. This is supported by the energies for the structures for Al_4K_4 [**1(c)** and **2(c)**]. The distorted structure is more stable than the planar structure. Thus, the steric repulsion for the four large K atoms overwhelms the stability of the planar undistorted aromatic Al_4K_4 making the Al_4K_4 cluster nonaromatic.

In Table 2, the magnitudes of the ground state dipole moment, μ_G, and the linear (α) and nonlinear (β and γ) polarizabilities for the clusters are reported from the ZINDO calculations. Note that we report the magnitudes for the tumbling averaged $\bar{\alpha}$, $\bar{\beta}$, and $\bar{\gamma}$, defined as[25]

$$\bar{\alpha} = \frac{1}{3}\sum_i (\alpha_{ii})$$

$$\bar{\beta} = \sqrt{\sum_i \beta_i \beta_i^*}; \quad \beta_i = \frac{1}{3}\sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

$$\bar{\gamma} = \frac{1}{15}\sum_{ij} (2\gamma_{iijj} + \gamma_{ijji}) \qquad (1)$$

where the sums are over the coordinates x, y, z (i, $j = x, y, z$) and β_i^* refers to the conjugate of the β_i vector. The ground state dipole moment μ_G and $\bar{\beta}$ are zero for the C_4H_4 and C_6H_6 due to its perfect centrosymmetric geometry, although $\bar{\alpha}$ and $\bar{\gamma}$ have finite values. For the Al_4-clusters with the progressive increase in the ionic radii of counterion, the ground state dipole moment increases. Thus, while Al_4Li_4 has no ground state dipole moment, Al_4Na_4 and Al_4K_4 have substantial ground state dipole moments (particularly **1(b)** and **2(c)** due to their noncentrosymmetric structures discussed above). For Al_4K_4, although the rhomboidal geometry has a very low ground state dipole moment, the distorted tricycle-like structure has a very high dipole moment. Thus, due to the out-of-plane charge transfer, the dipole matrix elements are also larger, resulting in a particularly large value for $\bar{\beta}$. For Al_4Li_4 and Al_4Na_4 [**2(b)**], the polarization is in the excited state as the ground state dipole moment is zero. However, it is not the case for the insulating C_4H_4 and C_6H_6 which have zero polarization both in the ground and the optical excited states. Thus, $\bar{\beta}$ is zero for C_4H_4 and C_6H_6.

The optically active states are the low-energy states of these metallic clusters, and the lowest optical gap is about 0.07 au for Al_4-clusters compared to 0.25 au for the C_4H_4 and C_6H_6. Since the optical coefficients are inversely proportional to the optical gaps and proportional to the dipolar matrices, a large optical gap implies low magnitudes for the optical coefficients. C_4H_4 has the highest magnitude of BLA and optical gap and the least charge transfer on the ring structure, and therefore the smallest magnitude of $\bar{\gamma}$. On the other hand, although BLA is zero for C_6H_6 due to complete π-electron delocalization, there is no charge transfer in the finite molecular structure leading to large optical gap and weak polarization. Consequently, $\bar{\gamma}$ is much smaller also for C_6H_6.

In contrast, the optical coefficients in general are quite large for the Al_4-clusters. For example, the $\bar{\gamma}$ values for the Al_4-clusters are roughly 10^4 times more than that for C_4H_4 and C_6H_6. This is because the $\bar{\gamma}$ is a third-order property with 4 dipolar matrices in the numerator and 3 optical gaps in the denominator.[26] The $\bar{\gamma}$ for the Al_4-clusters increases with an increase in the polarization of the Al−M bonds and follows the following trend: $\bar{\gamma}$ of Al_4Li_4 < $\bar{\gamma}$ of Al_4Na_4 < $\bar{\gamma}$ of Al_4K_4 (same trend as η). However, the distorted structures for Al_4Na_4 and Al_4K_4 [**1(b)** and **2(c)**] have smaller $\bar{\gamma}$ values due to less polarization of the Al−M bonds. For C_4H_4 ($\Delta r = 0.245$ Å), C_6H_6 ($\Delta r = 0.00$ Å), and the linear chain, $(-CH{=}CH-)_n$, $n = 3$ ($\Delta r = 0.1$ Å), the $\bar{\gamma}$ values are 2.21, 2.63, and 192.85 (all in au) per CH bond, respectively. This is in agreement with previous findings that the magnitude of γ varies nonlinearly with Δr and its maxima occurs at an optimal $\Delta r \neq 0$.[27] However, for the Al_4-clusters, because of strong charge transfer, the $\bar{\gamma}$ values are less sensitive to variation in Δr, and even for $\Delta r = 0.0$ Å (perfect square Al_4 ring) and $\Delta r = 0.245$ Å (rectangular Al_4 ring like C_4H_4) the $\bar{\gamma}$ values are similarly high, as found for the optimized structures. Such charge transfer induced large NLO coefficients have also been observed for bulk materials such as $CsLiB_6O_{10}$ (CLBO).[29]

The maximum possible value for the off-resonance $\gamma(Al_4M_4)$ calculated using the Kuzyk's simple two-state model[5] is about 2825 times more than that for $\gamma(C_4H_4)$. This is in very good agreement with our MRDCI calculations at a low frequency (0.001 au), which predict $\gamma(Al_4M_4)/\gamma(C_4H_4) \approx 10^4$.

To compare and contrast these clusters with their organic counterparts, we calculate the NLO properties of the well-known π-conjugated systems, the *trans*-polyacetylene chain, $(-CH{=}CH-)_n$, by varying the number of spacers, n, from $n = 1$ to 6, and thereby extending the length of conjugation from 2.65 to 29.11 au. The geometries were optimized by the same method as mentioned above. The linear and nonlinear polarizations are calculated at the same frequency (0.001 au). Our calculated values for the optical properties compare fairly well with trends with the experimental results that the linear (α) and nonlinear (γ) optical properties increase steadily with the increase in the conjugation length of the chain (see Table 2). For example, for ethylene, $\gamma_{expt} = 1504.9$ au, for butadiene ($n = 2$), $\gamma_{expt} = 4566.4$ au, and for hexatriene ($n = 3$), $\gamma_{expt} = 14950.1$ au.[28] Note that our calculations are done at a lower frequency compared to the laser frequency used in the experiment (0.066 au). However, the magnitudes of all the polarization quantities are much higher for the charge transfer complex (Al_4M_4 clusters) compared to the conventional π conjugated chains with comparable conjugation length. Only when there are very large numbers of spacers ($n = 5-6$), do the magnitudes become comparable to those of the much smaller Al_4-clusters. For example, $\gamma[(-CH{=}CH-)_6] \approx \gamma(Al_4M_4)$. $(-CH{=}CH-)_6$ has 12 atoms in conjugation while Al_4M_4 has only 4. So, as a rule of thumb, one can state that γ for the Al-atoms in the charge transfer ring scales three times that for π-conjugated organic materials.

As discussed, the large NLO properties for Al_4M_4 are due to the charge transfer from the alkali metals to the Al_4 ring. It will thus be of interest to compare these heteroatomic all-metal clusters with alkylated organic compounds such as lithiated benzene or organolithium and organosodium derivatives such as $C_8H_6Li_2$ and $C_8H_6Na_2$. These alkylated organic compounds also exhibit larger NLO coefficients. For example, $\gamma(C_6Li_6)/\gamma(C_6H_6) = 7.3 \times 10^2$.[30] Similarly, $\gamma(C_8H_6Li_2)/\gamma(C_8H_6) = 5.5$ and $\gamma(C_8H_6Na_2)/\gamma(C_8H_6) = 20$.[31] However, the NLO responses for the Al_4M_4 are much higher than the values for these alkylated organic compounds compared to pure organic materials. Also, there have been previous efforts to calculate the NLO coefficients in inorganic clusters such as GaN, GaP, and GaAs.[32] These systems have higher gaps than the Al_4M_4 clusters so the NLO coefficients are smaller.

To conclude, our theoretical study shows that the small four-membered Al_4-clusters functionalized with various metal cations provide an innovative route for selection of materials with very high nonlinear optical properties. Some of these compounds have already been well characterized from stable alloys,[10] but the laser evaporation technique is not the route to stabilize these materials for the NLO experiments. One way to stabilize these clusters is to form a sandwich-type geometry by incorporating a suitable transition metal ion.[33] Effective polarization through solvents can also stabilize such charge transfer complexes. We believe that our study will motivate further experiments on these small Al_4-clusters.

Acknowledgment. S.K.P. thanks CSIR and DST, Government of India, for the research grants.

References and Notes

(1) (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (b) *Nonlinear Optical Materials*; Karna, S. P., Yeates, A. T., Eds.; ACS Symposium Series 628; American Chemical Society: Washington, DC, 1996.

(2) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.

(3) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

(4) (a) Li, D.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem*. **1992**, *96*, 4325. (b) Ramasesha, S.; Soos, Z. G. *Chem. Phys. Lett*. **1988**, *158*, 171.

(5) Kuzyk, M. G. *Phys. Rev. Lett* **2000**, *85*, 1218.

(6) Helgaker, T.; Jorgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John Wiley & Sons: New York, 2000.

(7) Rao, B. K.; Jena, P. *J. Chem. Phys*. **2000**, *113*, 1508.

(8) (a) Wu, K.; Chen, X.; Snijders, J. G.; Sa, R.; Lin, C.; Zhuang, B. *J. Cryst. Growth* **2002**, *237*, 663. (b) Maroulis, G.; Pouchan, C. *J. Phys. Chem. B* **2003**, *107*, 10683.

(9) Shetty, S.; Kanhare, D. G.; Pal, S. *J. Phys. Chem. A* **2004**, *108*, 628.

(10) Kuznetsov, A.; Birch, K.; Boldyrev, A. I.; Li, X.; Zhai, H.; Wang, L. *Science* **2003**, *300*, 622.

(11) Chen, Z.; Corminboeuf, C.; Heine, T.; Bohmann, J.; Schleyer, P. V. R. *J. Am. Chem. Soc*. **2003**, *125*, 13930.

(12) (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 1372. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(14) Chacko, S.; Deshpande, M.; Kanhare, D. G. *Phys. Rev. B* **2001**, *64*, 155409.

(15) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111. Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21.

(16) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974**, *35*, 33.

(17) Shuai, Z.; Beljonne, D.; Bredas, J. L. *J. Chem. Phys*. **1992**, *97*, 1132.

(18) Beljonne, D.; Shuai, Z.; Cornil, J.; dos Santos, D.; Bredas, J. L. *J. Chem. Phys.* **1999**, *111*, 2829.

(19) Ramasesha, S.; Soos, Z. G. *Chem. Phys. Lett.* **1988**, *153*, 171. Soos, Z. G.; Ramasesha, S. *J. Chem. Phys*. **1989**, *90*, 1067.

(20) Ramasesha, S.; Shuai, Z.; Bredas, J. L. *Chem. Phys. Lett*. **1995**, *245*, 224. Albert, I. D. L.; Ramasesha, S. *J. Phys. Chem.* **1990**, *94*, 6540. Ramasesha, S.; Albert, I. D. L. *Phys. Rev. B* **1990**, *42*, 8587.

(21) (a) Datta, A.; Pati, S. K. *J. Chem. Phys*. **2003**, *118*, 8420. (b) Datta, A.; Pati, S. K. *J. Phys. Chem. A* **2004**, *108*, 320. (c). Beljonne, D.; Cornil, J.; Friend, R. H.; Janssen, R. A. J.; Bredas, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6453.

(22) (a) Pati, S. K.; Ramasesha, S.; Shuai, Z.; Bredas, J. L. *Phys. Rev. B* **1999**, *59*, 14827. (b). Pati, S. K.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc*. **2001**, *123*, 7287.

(23) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.

(24) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 4th ed.; John Wiley and Sons: New York, 1992.

(25) Ramasesha, S.; Shuai, Z.; Bredas, J. L. *Chem. Phys. Lett.* **1996**, *250*, 14.

(26) (a) Armstrong, J. A.; Bloembergen, N.; Ducuing, J.; Pershan, P. S. *Phys. Rev.* **1962**, *127*, 1918. (b) Ward, J. *Rev. Mod. Phys.* **1965**, *37*, 1. (c) Pati, S. K.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 7287.

(27) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science* **1993**, *261*, 186.

(28) Ward, J. F.; Elliot, D. S. *J. Chem. Phys.* **1978**, *69*, 5438.

(29) Li, J.; Duan, C.-g.; Gu, Z.-q.; Wang, D.-s. *Phys. Rev. B* **1998**, *57*, 6925.

(30) Theologitis, M.; Screttas, G. C.; Rapis, S. G.; Papadopoulos, M. G. *Int. J. Quantum Chem.* **1999**, *72*, 177.

(31) Papadopoulos, M. G.; Raptis, S. G.; Demetropoulos, I. N. *Mol. Phys.* **1997**, *92*, 547.

(32) Korambath, P. P.; Karna, S. P. *J. Phys. Chem. A.* **2000**, *104*, 4801.

(33) Mercero, J. M.; Ugalde, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 3380.