PHYSICAL REVIEW B VOLUME 44, NUMBER 11 15 SEPTEMBER 1991-I

Optical and structural effects of aniline intercalation in PbI_2

Vivek Mehrotra, S. Lombardo,* Michael O. Thompson, and Emmanuel P. Giannelis
Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

(Received 1 April 1991)

Aniline has been intercalated in lead iodide thin films by exposure to aniline vapors in an evacuated chamber. X-ray diffraction and Raman spectroscopy have confirmed the presence of aniline in the interlayer space of PbI_2. Intercalation leads to an increase of 0.5 eV in the optical band gap. The large increase in the band gap can be modeled by computing changes in the band structure resulting from the electrostatic interaction of the —NH_2 dipole of aniline with the iodine $5p_z$ electron. This interaction lowers and flattens the valence band along the ΓA direction. The band-gap increase, calculated for various possible configurations of the aniline molecule, is in the range 0.35–0.57 eV.

I. INTRODUCTION

Intercalation of graphite, transition-metal dichalcogenides, and layered silicates has been investigated quite extensively over the past two decades.[1-7] These layered systems are characterized by a spatial repetition of a single plane, three planes, and as many as seven planes of atoms, respectively. By carefully selecting host and guest species, and by exploiting the interactions between them, the properties of intercalated materials can be dramatically altered.

Heavy-metal iodides are composed of three planes of atoms and are structurally similar to transition-metal dichalcogenides. Lead iodide, one of the heavy-metal iodides, is a direct-band-gap semiconductor with a hexagonal layered structure. Each plane consists of strongly bonded atoms of the same element. The sequence of planes I-Pb-I defines a molecular layer. The bonding between the adjacent molecular layers is weak, van der Waals type. As a result, guest species can be introduced (intercalated) in the galleries between the molecular layers thus modifying many physical properties of the host.

In this paper we report on the optical and structural effects of aniline ($C_6H_5NH_2$) intercalation in lead iodide thin films. Intercalation leads to an increase of 0.5 eV in the optical band gap and an expansion of 3 Å in the c-axis. As discussed below, the increase in band gap cannot be explained simply by considering the lattice expansion.

Similar effects were observed by Al-Jishi *et al.* in lead iodide intercalated with hydrazine and methylated hydrazine.[8] These researchers have shown that the interaction between the dipole of the guest molecule and the outermost iodine electron has a strong effect on the PbI_2 band structure. This interaction increases appreciably the binding energy of the iodine electron. In addition, the electron is displaced towards the dipole. This reduces the coupling between the lead and iodine orbitals leading to a large increase in the band gap. In this paper, we show that the increase in band gap upon aniline intercalation can be explained by taking into account the electrostatic interaction of the iodine outermost electron with the $-NH_2$ dipole. However, we have found that the displacement of the iodine electron towards the dipole is very small. Consequently, the coupling between the lead and iodine orbitals is unaffected by the presence of aniline molecules in the interlayer space of PbI_2.

II. EXPERIMENT

Thin films of lead iodide were deposited on sapphire, quartz, or silicon substrates by electron-beam evaporation. Base pressure in the chamber was 10^{-7} Torr and rose to 10^{-5} Torr during deposition. The deposition rate, as monitored by a quartz crystal oscillator, was 15 Å/sec. Films were stoichiometric with thicknesses of $\approx$500–800 Å as determined by Rutherford backscattering spectrometry (RBS) using 2.4-MeV ^{4}He ions.[9]

Intercalation was achieved by exposing the films to aniline vapors in a container evacuated to 5×10^{-2} Torr at room temperature. Upon exposure to aniline vapors, the yellowish lead iodide film becomes transparent within a few minutes. X-ray diffraction patterns performed with a Scintag diffractometer (Cu $K\alpha$ radiation) indicated lattice expansion in the intercalated material. To confirm the presence of aniline, Raman spectroscopy was performed using the 514.5-nm line of an argon-ion laser with a typical power of 5 mW. The beam was focused to a spot size of about 300 μm. The use of low power density was necessary to prevent damage to the sample. Optical-absorption spectra were recorded in the range 190–900 nm at room temperature using a Perkin-Elmer Lambda 4A spectrophotometer.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of as-deposited and aniline intercalated films are shown in Figs. 1(a) and 1(b). As-deposited films were polycrystalline and textured with the c axis of the platelets oriented perpendicular to the substrate, in agreement with previous observations.[10] The unintercalated film shows four (001) harmonics corresponding to the repeat unit of 6.98±0.03 Å, the magnitude of the PbI_2 primitive translation vector $|\mathbf{c}|$. After intercalation, $|\mathbf{c}|$ expands to 10.0±0.05 Å, suggesting the presence of aniline molecules in the host galleries. A large difference in the full width at half maximum of the

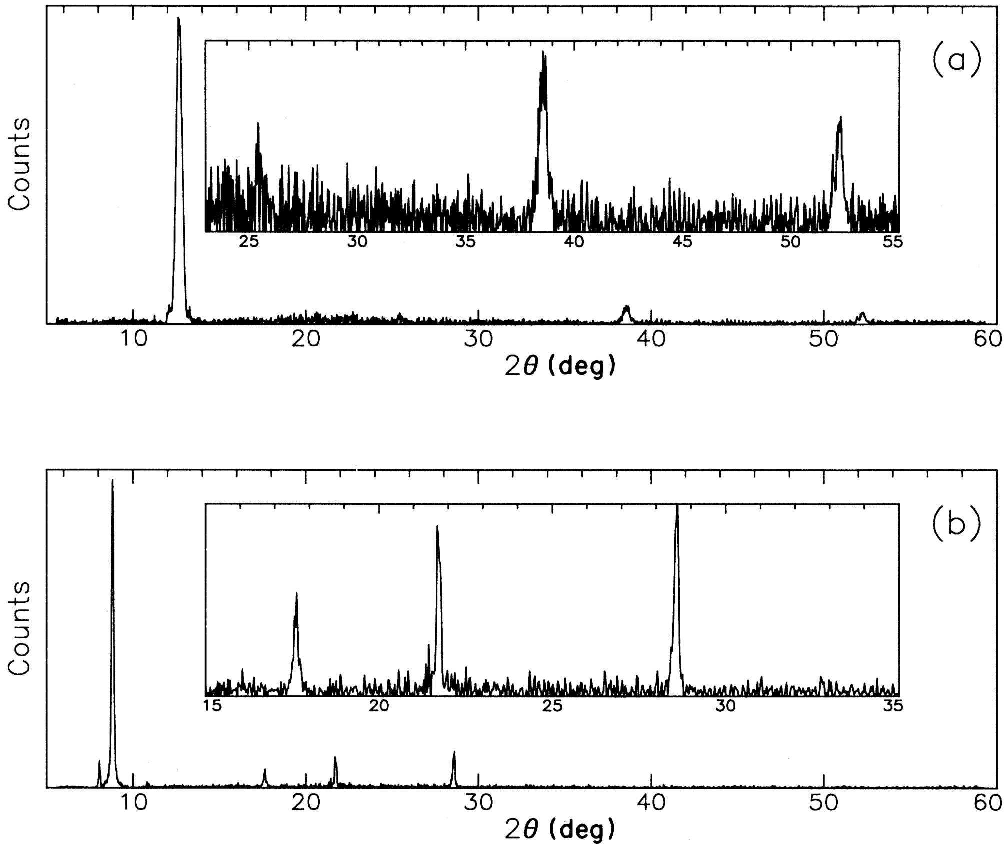

FIG. 1. X-ray diffraction pattern of (a) as-deposited PbI_2 and (b) aniline intercalated PbI_2. Upon intercalation, a large shift in (001) reflections, corresponding to an increase of 3 Å in $|\mathbf{c}|$, is evident.

(001) peaks can be seen by comparing Fig. 1(a) with Fig. 1(b). This indicates an increase in the effective domain size or crystalline quality of the platelets upon intercalation. With x-ray intensity plotted against the wave vector q, an out-of-plane correlation length $\xi = 2/\Delta q$ can be obtained, where Δq is the full width at half maximum of the Bragg peak.[6] We obtain $\xi \approx 70$ Å for the as-deposited film and $\xi \approx 170$ Å for the intercalated film. These values correspond to about 10 and 17 unit cells, respectively. Raman spectroscopy showed vibrations typical of the aniline molecule, confirming its presence in the intercalated film. The strongest peaks were observed at 996 (995), 1028 (1027), and 1600 (1601) cm^{-1}, where the values in parentheses have been reported for pure aniline.[11] The expansion of $|\mathbf{c}|$ to about 10 Å generates a free volume of about 93 Å^3 per unit cell between the molecular layers, a volume large enough to accommodate two aniline molecules in the interlayer space.

Optical-absorption spectra of the PbI_2 thin films before and after intercalation with aniline are shown in Fig. 2. A complex exciton structure due to strong anisotropy can be seen in the optical absorption of the pure host material. The band edge, corresponding to the first exciton peak in the unintercalated film, appears at about 2.5 eV and agrees well with the value quoted in literature.[12] Upon aniline intercalation, the optical band gap increases to about 3 eV (Fig. 2).

Al-Jishi *et at.*[8] have shown that the interaction between the iodine $5p_z$ electron and the dipole moment of the guest molecules can produce large shifts in the optical band gap. This interaction also explains the results of our optical measurements. We analyze the modifications in the energy bands produced by the intercalation of ani-

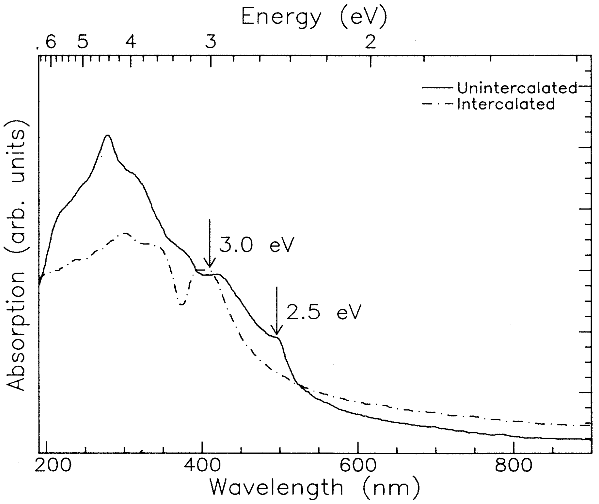

FIG. 2. Optical-absorption spectra for as-deposited and aniline intercalated PbI_2. Upon intercalation, the optical band gap increases by 0.5 eV.

line in the van der Waals gap. Since the molecule is confined between the iodine atomic planes, we expect that the main changes in the band structure are related to the perturbed iodine orbitals. The lowest conduction band is composed mainly of 6p lead atomic orbitals. This band is extremely flat[13,14] so that it will not be affected by the c-axis expansion after intercalation. However, the upper valence band has contributions from both the iodine $5p_z$ and the lead 6s orbitals. In the first Brillouin zone, this band lies between the A point ($|\mathbf{k}|=\pi/c$) and the Γ point ($k=0$). The valence band has been calculated using tight-binding method between the A and Γ points. The system is approximated as one dimensional. The interaction between the various atomic planes can be described by the following Hamiltonian matrix:

$$H=\begin{bmatrix} E_{\rm I} & V_1 & V_2+V_3e^{-ikc} \\ V_1 & E_{\rm Pb} & V_1 \\ V_2+V_3e^{ikc} & V_1 & E_{\rm I} \end{bmatrix} \tag{1}$$

where k is the wave vector, and $E_{\rm I}$ and $E_{\rm Pb}$ represent the energies of iodine and lead planes, respectively. V_1 is the interaction between neighboring lead and iodine planes (due to the coupling of atoms like A and B in Fig. 3). V_2 represents the interaction between iodine planes within the *same* I-Pb-I molecular layer (e.g., atoms B and C) and V_3 is the interaction between the iodine planes belonging to the *adjacent* molecular layers, across the van der Waals gap (e.g., atoms B and D). In the unintercalated system V_2 is approximately equal to V_3 because the I-I distances are approximately equal in the two cases. Diagonalizing H at each point in the Brillouin zone from $k=-\pi/c$ to $k=\pi/c$ yields three eigenvalues corresponding to three valence bands. When the parameters are set to the values given in Table I (unintercalated), the two uppermost valence bands (Fig. 4) coincide, within 0.02 eV, with those obtained by an elaborate band-structure calculation of Schlüter and Schlüter.[13] In the calculations, the maximum energy of the highest valence band is set to zero. The lowermost band calculated with this simple approximation is shifted by about 1.2 eV. However, we can ignore this shift because the band gap increase is determined by the lowering of the uppermost valence band.

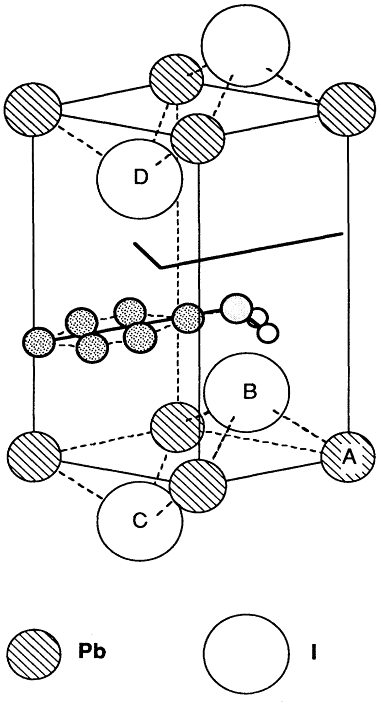

FIG. 3. Schematic showing a possible orientation of the aniline molecules within the interlayer space of PbI_2. This configuration corresponds to a dipole-iodine distance of ≈ 2.5 Å with the dipole tilted by $\approx 40°$ with respect to the c axis. For simplicity, only one of the aniline molecules is fully drawn.

TABLE I. Tight-binding parameters for unintercalated and intercalated PbI_2. For the intercalated case, V_1 and V_3 are calculated from Eq. (2) and $E_{\rm I}$ from Eq. (4).

	Unintercalated	Intercalated
$E_{\rm Pb}$ (eV)	-2.15	-2.15
$E_{\rm I}$ (eV)	-3.30	-3.61–-4.40
V_1 (eV)	-1.90	-1.90
V_2 (eV)	-0.75	-0.75
V_3 (eV)	-0.75	0
c (Å)	6.98	10.0

When aniline molecules are intercalated in the galleries of PbI_2, the interaction between the iodine planes belonging to different layers is appreciably reduced. This results in a change in the value of V_3 which, in turn, causes a significant reduction in the bandwidth. In order to estimate the variation of V_3 upon intercalation, we have evaluated the matrix element:[15]

$$\langle \Psi_{{\rm I}(B)}(\mathbf{r}) | \frac{1}{r} | \Psi_{{\rm I}(D)}(\mathbf{r}-\mathbf{d}) \rangle \tag{2}$$

where $\Psi_{{\rm I}(B)}(\mathbf{r})$ is the wave function of the outermost elec-

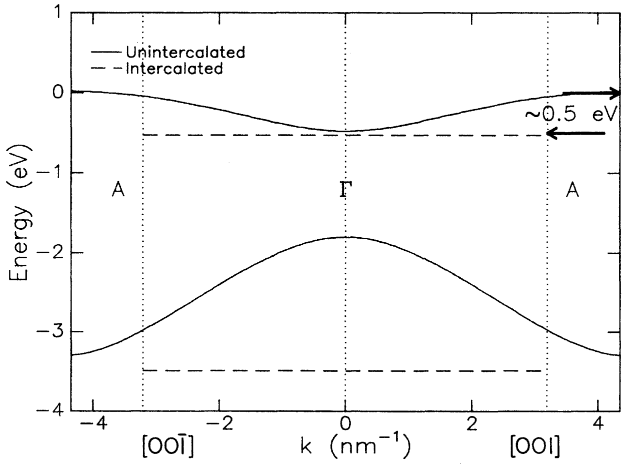

FIG. 4. Band diagram for pristine and aniline intercalated PbI_2. The aniline intercalated PbI_2 bands are calculated for an iodine-dipole distance of 2.5 Å with the dipole tilted by 40° with respect to the c axis.

tron of the iodine atom located at the position B (Fig. 3) and $r=|\mathbf{r}|$. $\Psi_{\mathrm{I}(D)}(\mathbf{r}-\mathbf{d})$ is the same wave function displaced by $\mathbf{d}$, relative to the atom at position D. Hydrogenlike wave functions have been used in the calculations. The radial part of these wave functions is expressed in terms of the dimensionless variable r/a_0. The parameter a_0 has been calculated by equating $\langle\Psi(\mathbf{r})|r|\Psi(\mathbf{r})\rangle$ to the atomic radius. The matrix element $\langle\Psi_{\mathrm{I}(B)}(\mathbf{r})|(1/r)|\Psi_{\mathrm{I}(D)}(\mathbf{r}-\mathbf{d})\rangle$ is evaluated with $5p_z$ states for which $a_0 \approx 0.11$ Å. On increasing $|\mathbf{d}|$ from 4.21 to 6.91 Å, the matrix element decreases by several orders of magnitude and essentially becomes zero. This behavior is characteristic of one-dimensional atomic chains.[16] Based on the above calculations, we set $V_3=0$ for the intercalated $\mathrm{PbI_2}$. However, considering only this reduced interaction between the iodine orbitals across the van der Waals gap, the band gap increases by only 0.25 eV as opposed to the experimental value of 0.5 eV.

In order to account for the additional 0.25 eV, the electrostatic interaction between the iodine $5p_z$ electron and the $-\mathrm{NH_2}$ dipole of the aniline molecule must be considered. The orientation of aniline molecules within the gallery space is governed primarily by three factors. For minimization of the c-axis expansion, the aniline molecules will tend to orient with the benzene rings inclined towards the $\mathrm{PbI_2}$ basal plane. In addition, the π electrons of the aniline aromatic ring will be repelled by the nitrogen lone pair of the neighboring molecule. These two factors contribute to a *keying in* of aniline into the $\mathrm{PbI_2}$ molecular layer. However, because of the electrostatic interaction with the iodine $5p_z$ electron, the $-\mathrm{NH_2}$ dipole will tend to be perpendicular to the basal plane. This orientation will cause lattice expansion along the c axis. Based on the above considerations and the observed lattice expansion, we consider only configurations of the aniline in which the $-\mathrm{NH_2}$ dipole is oriented between 20° and 60° with respect to the c axis. These two limiting cases correspond to the aromatic ring lying flat or keyed in, respectively. Moreover, the dipole will be at a distance of $\approx 2.5-3$ Å from the iodine nucleus. Figure 3 shows a sketch of the molecules for an iodine-dipole distance of ≈ 2.5 Å and a tilt of $\approx 40°$ in the $\mathrm{PbI_2}$ structure.

The potential from the dipole at the position (x,y,z) affecting the $5p_z$ electron is

$$V(x,y,z) = -\frac{ep}{4\pi\epsilon_0}\frac{y\sin\phi+(z+b)\cos\phi}{[x^2+y^2+(z+b)^2]^{3/2}} \tag{3}$$

where p is the dipole moment. The dipole is approximated as a point dipole at $(0,0,-b)$ and tilted by an angle ϕ with respect to the z axis. The electrostatic attraction on the iodine $5p_z$ electron in the vicinity of the $-\mathrm{NH_2}$ dipole will increase its binding energy with the first-order correction to E_{I} given by

$$\Delta E_{\mathrm{I}} = \langle 5p_z|V|5p_z\rangle \; . \tag{4}$$

The origin is taken at the iodine nucleus, and b is the distance between the iodine nucleus and the point dipole. With $b=2.5-3$ Å, $\phi=20°-60°$ and $p=5.14\times10^{-30}$ C m,[17] ΔE_{I} is in the range -0.31 to -1.1 eV (Table II).

TABLE II. Correction to the tight-binding parameter E_{I} for various possible configurations of the aniline molecule. The corresponding increase in band-gap (ΔE_g) is also tabulated.

Angle	b (Å)	ΔE_{I} (eV)	ΔE_g (eV)
20°	2.5	−1.10	0.57
20°	3.0	−0.58	0.43
40°	2.5	−0.94	0.53
40°	3.0	−0.47	0.40
60°	2.5	−0.67	0.46
60°	3.0	−0.31	0.35

Moreover, the outermost iodine electron will be attracted towards the $-\mathrm{NH_2}$ dipole. Considering the first-order correction to the electron state, mainly due to the $6s$ orbital, the electron displacement is given by

$$\langle z\rangle = 2\frac{\langle 6s|V|5p_z\rangle\langle 5p_z|z|6s\rangle}{E_{5p_z}-E_{6s}} \tag{5}$$

where $E_{5p_z}-E_{6s}$ is the energy difference between the two orbitals and is approximately 5 eV.[13] Evaluating Eq. (5) numerically, we get $\langle z\rangle$ in the range 0.02–0.05 Å. Although such displacements could reduce the overlap between the lead and iodine orbitals (V_1), the variations in V_1 calculated using the same procedure as for V_3 are negligible. The modified tight-binding parameters for the intercalated $\mathrm{PbI_2}$ are given in Table I. The bands calculated for $\Delta E_{\mathrm{I}}=-0.94$ eV ($b=2.5$ Å and $\phi=40°$) are shown in Fig. 4. This leads to an increase in band gap of about 0.5 eV at the A point of the Brillouin zone. The lowering and flattening of the upper valence band can be clearly seen in Fig. 4. The band-gap shifts (ΔE_g) for various possible aniline configurations are in the range 0.35–0.57 eV and are tabulated in Table II.

These calculations indicate that the electrostatic interaction between the $-\mathrm{NH_2}$ dipole and the iodine $5p_z$ electron is very effective in lowering the energy of the system. Under similar conditions, the benzene molecule, which does not possess a dipole moment, cannot be intercalated. So, this interaction appears to be the driving force for intercalation in $\mathrm{PbI_2}$. Moreover, an increase in the out-of-plane correlation length has been observed upon intercalation. The formation of the $-\mathrm{NH_2}\ldots\mathrm{I}$ bond results in the coverage of both sides of the $\mathrm{PbI_2}$ molecular layers with aniline molecules. We speculate that steric effects could tend to orient the aniline covered molecular layers, thus improving their stacking.

IV. CONCLUSIONS

Lead iodide thin films have been intercalated with aniline by exposure to aniline vapors in an evacuated chamber. Upon intercalation, an increase of 0.5 eV in the optical band gap has been observed. This effect cannot be explained simply by considering the lattice expansion along the c axis. The large increase in the band gap is modeled by computing changes in the band structure resulting from the electrostatic interaction of the iodine $5p_z$ electron with the dipole moment of the aniline molecule. The interaction of the dipole with the outermost iodine electron provides the driving force for intercalation in PbI_2.

Note added in proof. The 3-Å expansion in the c axis could also be accounted for by a single aniline molecule per unit cell of PbI_2 with the $-NH_2$ dipole approximately perpendicular to the iodine plane ($\phi \approx 0°$). In this configuration, the band-gap increase, calculated as described above, is ≈ 0.4 eV.

ACKNOWLEDGMENT

This work was sponsored by the National Science Foundation (Grant No. DMR-8818558) through the Materials Science Center at Cornell.

---

*On leave from Istituto di Metodologie e Tecnologie per la Microelettronica, Consiglio Nazionale delle Ricerche, Corso Italia 57, I-95129, Catania, Italy.

[1] *Intercalation Chemistry,* edited by M. S. Whittingham and A. J. Jacobson (Academic, New York, 1982).

[2] *Intercalated Layered Materials,* edited by F. Lévy (Reidel, Dordrecht, 1979).

[3] *Intercalation in Layered Materials,* edited by M. S. Dresselhaus (Plenum, New York, 1986).

[4] S. Lee, H. Miyazaki, S. D. Mahanti, and S. A. Solin, Phys. Rev. Lett. **62**, 3066 (1989).

[5] V. Mehrotra and E. P. Giannelis, Solid State Commun. **77** (2), 155 (1991).

[6] N. Wada, D. R. Hines, and S. P. Ahrenkiel, Phys. Rev. B **41**, 12 895 (1990).

[7] T. J. Pinnavaia, Science **220**, 365 (1983).

[8] R. Al-Jishi, C. C. Coleman, R. Treece, and H. Goldwhite, Phys. Rev. B **39**, 4862 (1989).

[9] L. C. Feldman and J. W. Mayer, *Fundamentals of Surface and Thin Film Analysis* (North-Holland, New York, 1986), p. 13.

[10] M. R. Tubbs, Phys. Status Solidi B **67**, 11 (1975).

[11] B. Schrader, *Raman/Infrared Atlas of Organic Compounds* (VCH, Weinheim, 1989), pp. F 1–52.

[12] M. R. Tubbs, Phys. Status Solidi B **49**, 19 (1972).

[13] I. C. Schlüter and M. Schlüter, Phys. Rev. B **9**, 1652 (1974).

[14] J. Robertson, Solid State Commun. **26**, 791 (1978).

[15] Roundoff and step-size errors in the evaluation of the integrals were negligible.

[16] R. Hoffman, Angew. Chem. Int. Ed. Engl. **26**, 849 (1987).

[17] *Aniline* (National Aniline Division, Allied Chemical Corporation, New York, 1964), p. 2.