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Electronic Origin of the Thermochromic Effect in 2,2′,5,5′-Tetramethylbistibole

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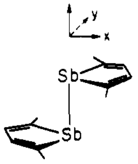
Abstract: The observed thermochromic effect in 2,2′,5,5′-tetramethylbistibole is explained by the one-dimensional electronic band structure for the material. The experimental spectral red shift is well accounted for by the calculations. An alternative "regular" structure for the material is discussed, and suggestions for stabilizing this alternative are given.

Recently Ashe et al. synthesized an air-stable distibine, 2,2′,5,5′-tetramethylbistibole (**1**), and found it to exhibit a remarkable thermochromic effect.[1] Crystals of **1** reflect iridescent purple-blue light and appear red to transmitted light, yet they melt reversibly to a pale yellow oil at 99 °C. Solutions of **1** in toluene or carbon tetrachloride are pale yellow with a shoulder in the UV at 346 nm, whereas thin film crystals have a broad absorption maximum in the visible region at 520 nm. Thus, crystallization leads to a red shift of about 1.2 eV in the absorption of **1**.



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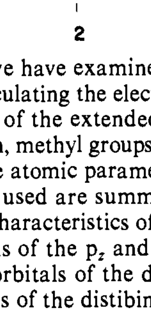
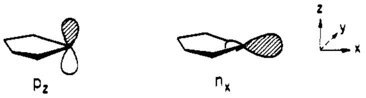
The crystal structure of **1** determined by Ashe et al. reveals that all the antimony atoms are aligned in a colinear chain with a short Sb···Sb intermolecular separation as shown in **2**. The solid-state structure indicates that the red shift is related to interactions between molecular units of **1** along the ···Sb–Sb···Sb–Sb chain.



2

In the present work we have examined the origin of the thermochromic effect by calculating the electronic structures of **1** and **2** within the framework of the extended Hückel method.[2] For simplicity of computation, methyl groups of **1** and **2** were replaced by hydrogen atoms. The atomic parameters of Sb(5s, 5p), C(2s, 2p), and H(1s) orbitals used are summarized in the Appendix. In describing the main characteristics of **1** and **2**, it is convenient to classify them in terms of the p_z and n_x orbitals of Sb shown in **3** and the π and π^* orbitals of the diene moiety shown in **4**.



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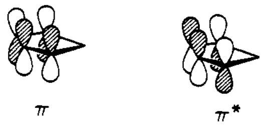

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The molecular orbitals of the distibine molecule are shown in Figure 1 and are labeled as gerade (g) or ungerade (u) combinations of the orbital types set forth in **3** and **4**. The σ_g orbital is a symmetric combination of primarily the p_z orbitals shown in **3**. The HOMO (n_{xg}) of **1** is mainly a symmetric combination of two n_x orbitals while the LUMO ($\pi^*{}_n$) is principally an antisymmetric combination of two π^* orbitals. Note that the $\pi_u{}^*$ orbital is below the $\pi_g{}^*$ orbital because the former is stabilized by mixing in of an Sb–Sb σ^* component and the latter is destabilized by mixing in of an Sb–Sb σ component. The HOMO–LUMO ($n_{xg} \rightarrow \pi_u{}^*$) electronic transition is allowed, with a calculated excitation energy of about 2.5 eV.

The electronic structure of **2**, calculated by using the tight binding (LCAO) method[3,4] is shown in Figure 2. For the purpose of comparison the MO's of **1** are also displayed. Because the "π-type" orbitals are strongly localized on the diene parts of the distibine, there is negligible perturbation of these levels upon crystallization. Thus, the conduction (lowest unoccupied) band of **2** is flat, and the character of the levels of this band retain the integrity of the $\pi_u{}^*$ MO for all k. On the other hand, the valence (highest occupied) band shows significant dispersion, composed as it is of orbitals localized mainly on the antimony atoms. At the zone center ($k = 0$) this band has primarily lone-pair character (n_{xg}) but has σ character at the zone edge ($k = \pi/a$). In fact, the three bands labeled as σ, n_{xg}, and n_{xu} mix and switch their orbital characteristics on going from the zone center to the zone edge. The form of these bands results from the crossing of a wide band (σ) through two narrow bands (n_{xg} and n_{xu}). The switch of orbital character with wavevector is a result of mixing between orbitals of overlapping bands of the same symmetry (i.e., the noncrossing rule[5]). As indicated in Figure 2, the orbital at the top of the valence band has σ-bonding character within each unit

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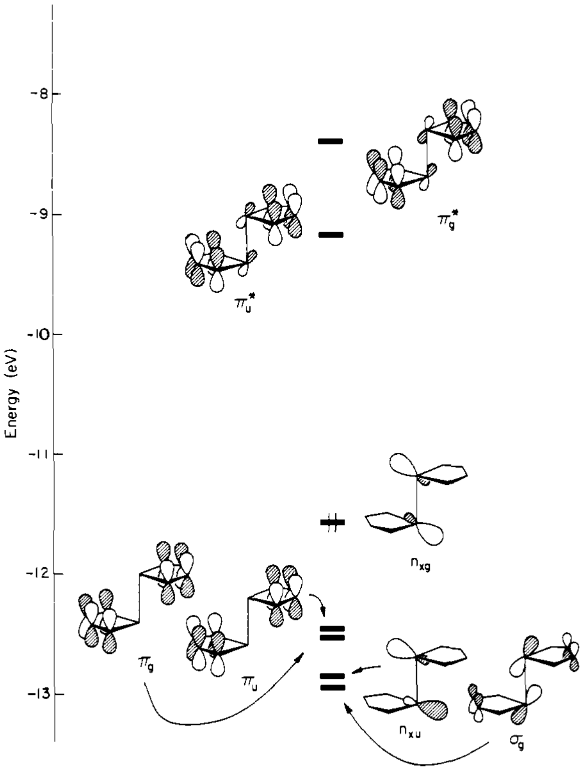


Figure 1. Molecular orbitals for the bistibole molecule **1**.

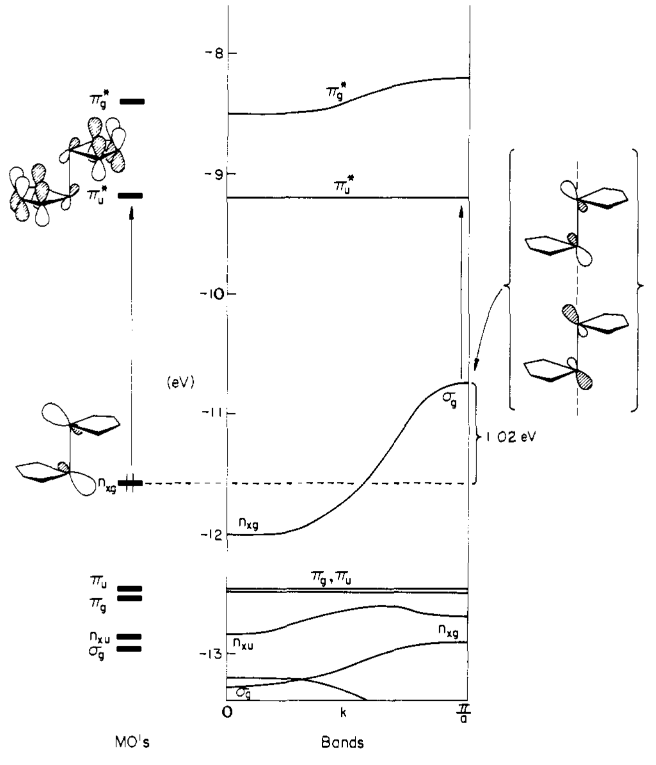
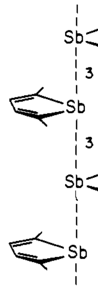


Figure 2. One-dimensional band structure for the observed chain **2**. The molecular orbitals of **1** are shown for purposes of comparison.

cell and σ-antibonding character between neighboring unit cells. As shown, the top of the valence band is pushed 1.02 eV above the HOMO of **1**. Therefore, crystallization is predicted to provide a red shift of this magnitude, in good agreement with experiment. The observed shift is 1.2 eV, assuming that the long wavelength shoulder in the solution spectrum and the broad band maximum in the crystal both correspond to the HOMO → LUMO transition.

We now digress briefly and discuss the likely effect of including Sb(5d) orbitals in our picture. Since the 5d orbitals will lie considerably above 5p, it should suffice to consider the addition of d functions as a small perturbation to the above analysis. It is likely that the *xy* and $x^2 - y^2$ orbitals interact with the deeply occupied Sb–C σ manifold but probably have only a moderate effect in the regime of energies which concerns us. The *yz* orbitals will be destabilized by mixing with the occupied π orbitals. However, the in-phase combination of the *xz* and z^2 orbitals are of the proper symmetry to interact with the π_u* (LUMO) orbital, and indeed this mixing is likely to be significant since the energy match is probably good. The net effect upon our previous schemes is that the LUMO in Figure 1 will be somewhat lowered and the valence band in Figure 2 will be likewise stabilized and will acquire some dispersion. The presence of low-lying d orbitals may also explain why a thermochromic effect is observed for tetramethyl- and tetraethyldistibene[12] (Sb_2R_4, R = CH_3, C_2H_5); in these compounds no ring π* orbitals are available to play the role of LUMO. Calculations without d orbitals on $Sb_2(CH_3)_4$ yield a HOMO–LUMO gap which is too large to explain the yellow color of this compound. With d orbitals the σ* orbital is appreciably stabilized and the gap becomes more reasonable, if still somewhat too large. We suggest that the yellow color of these compounds may be due to the tail of a σ → σ* transition where the σ* orbital has appreciable d orbital contributions. We have not found in the literature any definitive assignment of this transition. In band structure calculations (assuming an isostructural relationship between $Sb_2(CH_3)_4$ and $Sb_2(C_4H_4)_2$), inclusion of d orbitals seems to overestimate the stabilization of the σ* band. This is probably a consequence of our uncertainty regarding a proper set of parameters for these orbitals. In what follows we shall ignore the possible d orbital contributions though d orbital mixing may play some role in the valence band.

The Sb–Sb···Sb–Sb alternation along the chain of **2** may be viewed as a distortion from a regular structure as in **5**, where we have chosen the Sb–Sb lengths as the average of the lengths in the observed structure. Examination of the electronic structure



5

of **5** would be useful, were it only because it sheds light upon the electronic structure of the "distorted" material. However, it is also of interest to inquire as to whether this structure can be stabilized to the extent that it is lower in energy than the observed structure or at least such that it is an energetically accessible way point between equivalent "distorted" structures. The band structure for the regular chain is shown in Figure 3. On the left-hand side of this figure are the molecular orbitals for the $Sb(C_4H_4)$ fragment. As in the case of the alternating structure, **2**, the π bands of **5** are virtually unperturbed by "crystallization". The σ and π bands are clearly changed in moving from **2** to **5**, and it is to the origin of the changes that we now turn our attention.

In the electronic structure of **2**, the Sb–Sb σ and σ* bands can be clearly made out (although the latter band is too high in energy to be included in Figure 2). The σ and σ* bands are distinguishable because of the unequal Sb–Sb contacts in the chain; the top of the σ band is bonding *within* the unit cell and antibonding *between* neighboring cells while for the σ* band precisely the opposite obtains. Obviously then, in the regular chain the top of the "σ band" must be degenerate with the bottom of the "σ* band" since *inter-* and *intramolecular* Sb–Sb contacts are equal. Since the σ and σ* bands of **2** were respectively well below and well above the π* bands, the latter orbitals were only weakly perturbed by interaction with the former. As discussed, however,

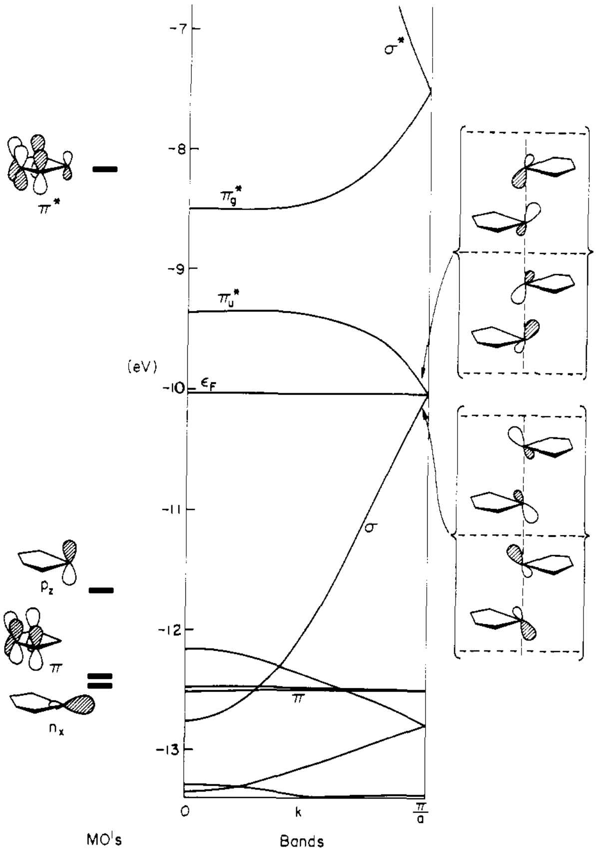


Figure 3. The band structure for the regular chain **5** with the MO's for $Sb(C_4H_4)$ included for comparison. The Fermi level is indicated by the horizontal line marked with ϵ_F.

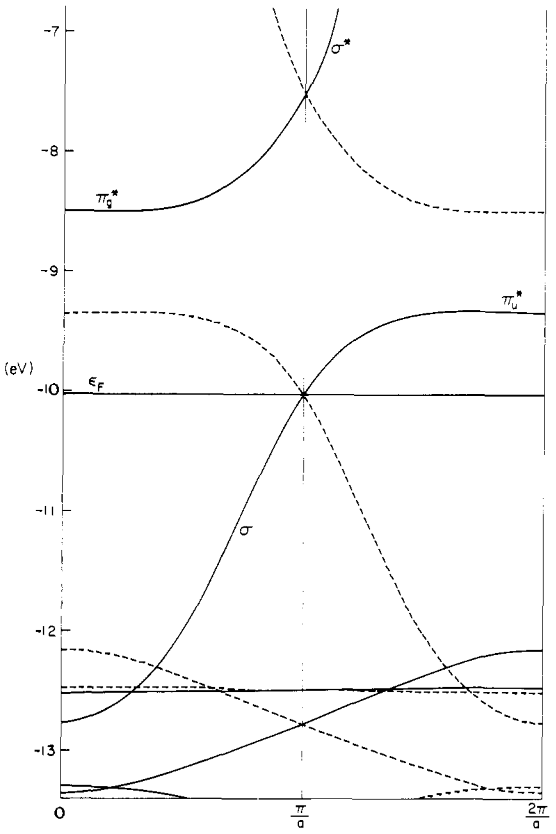


Figure 4. Bands for **5** in the extended zone scheme. Dotted lines indicate "redundant" bands which contain no additional information.

Table I

	χ_μ	ζ_μ	$H_{\mu\mu}$, eV
Sb	5s	2.323[9]	−18.8[10]
	5p	1.999	−11.7
C	2s	1.625	−21.4
	2p	1.625	−11.4
H	1s	1.3	−13.6

in **5**, the σ and σ^* bands must meet (at the zone edge as it turns out) and therefore must pass through the π^* bands. Since these "σ-type" bands are of the same symmetry as the "π^*-type" bands, mixing between the orbitals occurs and an avoided crossing results. This avoided crossing can be most easily discerned in the extended zone scheme[11] (i.e., by "unfolding" the bands) pictured in Figure 4. The extended zone scheme is often the most useful way of looking at the band structure for a crystal with a twofold screw axis.[4]

The highest occupied band of **5**, shown in Figure 3, is an example of a half-filled band which typically results from a regular chain with an odd number of electrons per unit. When the width of such a band is narrow, its magnetic insulating state may become more stable than the metallic state, because of electron–electron repulsion.[13] Since the width of the highest occupied band of **5** is quite substantial (i.e., about 3.5 eV according to Figure 3), we will assume in the present work that the ground electronic state of the regular chain **5** is metallic, as indicated in Figure 3.

The observed preference for a distorted structure is easily rationalized by examining the two crystal orbitals shown in Figure 3 which lie at the Fermi level. By shortening the bond within the unit cell and lengthening the bond between cells, the (occupied) orbital shown at bottom will be stabilized and the (unoccupied) orbital at top will be destabilized, leading to net stabilization of the crystal and to the band picture we have seen for **2**. This "Peierls distortion" is an obvious analogue to the well-known Jahn–Teller distortion. In our calculations we find the observed alternant structure about 9 kcal/mol more stable than the regular chain. Since EH calculations are generally unreliable in dealing with bond length distortions, this number should be used for comparison with values cited below only.

How can we stabilize the regular structure? One way may be to oxidize the chain as is done for the tetracyanoplatinate chain.[3] In this case oxidation will empty electrons from higher lying levels in the regular chain than for the alternant chain—implying a trend toward stabilization of the former. For example, when we remove 0.4 e^-/unit cell (0.2 e^-/Sb atom), the alternating structure is only 5 kcal/mol more stable than the regular chain. Another stratagem we may employ is to add acceptor substituents to the ring to lower the "π^*" band. Since the levels in **5** at the Fermi level include a larger fraction of π^* character than those at the Fermi level of **2**, we hoped the inclusion of substituents such as cyano groups would reduce the energy difference between **5** and **2**. Calculations performed with cyano substitutents at the 2,2′,5,5′ sites led to energy difference of 7 kcal/mol between **5** and **2**, only 2 kcal/mol better than with hydrogens. However, the π^* orbital in **1** was lowered by about 1 eV and the band gap in **2** is comparably reduced. The magnitude of alternation is also expected to decrease under pressure,[6] as in the case of Wolfram's red salts[7] and NbX_4,[8]

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leading to a smaller band gap.

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Appendix

The exponents ζ_μ and the valence state ionization potentials $H_{\mu\mu}$ of the Slater-type atomic orbitals χ_μ employed in our calculations are summarized in Table I.

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Criteria of Maximum Overlap and Minimum Orbital Energy in Molecular Orbital Studies of Conformations of Transition-Metal Carbene and Carbyne Complexes

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Abstract: We carried out nonparameterized molecular orbital calculations on various conformations of several transition-metal complexes containing carbene or carbyne ligands. In the preferred conformations of $CpMn(CO)_2CMe_2$ and $CpMn(CO)_2C(OMe)Ph$ ($Cp = \eta^5\text{-}C_5H_5$), the carbene lies in the symmetry plane of the metal fragment; in the latter compound, the Cp and Ph rings tend to be anti. In the preferred conformation of $BzCr(CO)_2C(OMe)Ph$ ($Bz = \eta^6\text{-}C_6H_6$), however, the carbene is perpendicular to the symmetry plane of the metal fragment. The rotation about the metal–carbyne triple bonds in $CpMn(CO)_2CPh^+$ and $BzCr(CO)_2CPh^+$ is very facile. These theoretical findings agree with crystal structures and NMR spectra of the complexes. We found that conformational preferences of certain organometallic compounds can better be explained and predicted by the criterion of minimum orbital energy than by the criterion of maximum metal–ligand overlap. Stabilizing and destabilizing effects of nonbonding molecular orbitals, as well as those of bonding and antibonding orbitals, need to be considered in the study of conformational preferences. A striking example is $BzCr(CO)_2C(OMe)Ph$. It adopts a conformation with smaller chromium–carbene π overlap because this leaves the more stable of the two π-type metal orbitals as the nonbonding HOMO for the whole complex molecule. $CpMn(CO)_2CMe_2$ and $CpMn(CO)_2C(OMe)Ph$ also adopt conformations that minimize total orbital energies. The maximum overlap criterion cannot be applied without ambiguity to molecules in which several bonds are appreciably affected by internal rotation. On the basis of calculations, we expect the heterocarbene complexes to undergo frontier-controlled nucleophilic additions.

From ethane to biological macromolecules, experimental and theoretical chemists have sought to explain and predict relative stabilities of different conformations, to measure and calculate barriers to rotation about chemical bonds, and to understand the physical origin of these barriers.[1] Theoretical studies have been carried out with various nonempirical and semiempirical methods of quantum chemistry and empirical methods based on classical mechanics. The rigor of such studies depends mainly on the size and complexity of the molecules in question and upon the computational requirements of the problem. Not surprisingly, conformational studies of transition-metal complexes began only several years ago. Since even small organometallic molecules are still too large to allow close approach to the Hartree–Fock limit in ab initio calculations,[2] less rigorous methods are indispensable for studying chemically interesting and practically important compounds. Roald Hoffmann and his co-workers have systematically examined conformations of various transition-metal compounds with extended Hückel calculations in conjunction with overlap and symmetry arguments.[3] They concluded that barriers to rotation of organic ligands about their bonds to metal atoms stem mainly from electronic causes.[3i] Others have also examined conformations of transition-metal complexes by qualitative theory and by calculations, emphasizing electronic effects.[4] A single

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