at preexisting sequences, usually the recognition sites for restriction endonucleases.[16] We are currently investigating the effects of this discrete platinum adduct upon replication, repair, and mutagenesis, in order to further our understanding of the mechanism of action of platinum anticancer drugs.

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Generalized Valence Bond Description of the Bonding in [1.1.1]Propellane

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There has been considerable interest, both experimental[1] and theoretical,[2-6] in the propellane family of molecules ever since the synthesis of the first compound of this kind was carried out 18 years ago.[7] The smallest member of this series of compounds and the one generally believed to have the highest strain energy is [1.1.1]propellane. In light of some predictions that the moelcule should not even exist,[4] the recent preparation of this compound[8] and the discovery that it is, in fact, more stable than a number of its family members is particularly interesting. This has stimulated renewed activity toward the understanding of the bonding in [1.1.1]propellane and related compounds.[5,6,9] Many molecular orbital calculations have been carried out on these molecules; in this paper we report the first comprehensive valence bond calculations for a propellane. The results, we believe, offer a new perspective on the bonding between bridgehead carbon atoms and illustrate the simple way the valence bond approach accounts for crucial electronic correlation effects ignored in the molecular orbital treatments.

It recently has been shown[10,11] for multiple bonds in a number of molecules that Ω–bonds (multiple equivalent bent bonds) are energetically more favorable than the traditional σ- and π-bonds. Although this may be of some intrinsic interest, a more significant issue is whether any conceptual advantage can be derived from the description of multiple bonding in terms of Ω–bonds. That is, does this description aid in making new connections and provide fresh insight into the understanding of novel situations? In the present context, it appears that the concept of Ω–bonds provides a way to establish a natural relationship between the bonding in the C_2 molecule in its ground state and the [1.1.1]propellane molecule and thereby allows one to gain some new insight into the bonding of the latter molecule.

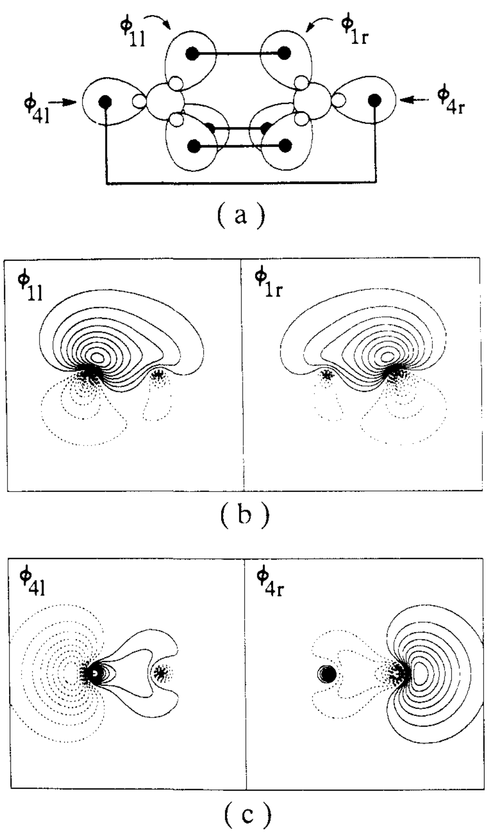

Figure 1. (a) Schematic representation of the many-electron wave function of C_2. Dots denote the electron occupancy of the orbitals and lines show which orbitals overlap to form bonds. (b) Two orbitals which form one of the three equivalent Ω-bonds. (c) The two orbitals which form the fourth pair in C_2.

In the present work, the generalized valence bond (GVB) approach with the perfect pairing (PP) restriction is used.[12] Although GVB-PP finds Ω-bonds as the energetically favored description of bonding in many cases,[10,11] restrictions in this wave function actually bias it against the Ω-description.[11] Rather than attempting to obtain a more sophisticated wave function that removes this bias toward the σ,π-description in C_2, we adopt the expedient of starting with the Ω-bond description at the perfect pairing level of approximation. This allows us to make a simple connection to [1.1.1]propellane, which is the molecule of chief interest here.

In Figure 1, some results of a GVB-PP (four GVB pairs) calculation[13] for C_2 are presented. Panel a gives a schematic representation of the many-electron wave function of the molecule, illustrating the approximately tetrahedral hybrid orbitals on each of the carbon atoms. Three of these orbitals on the left atom

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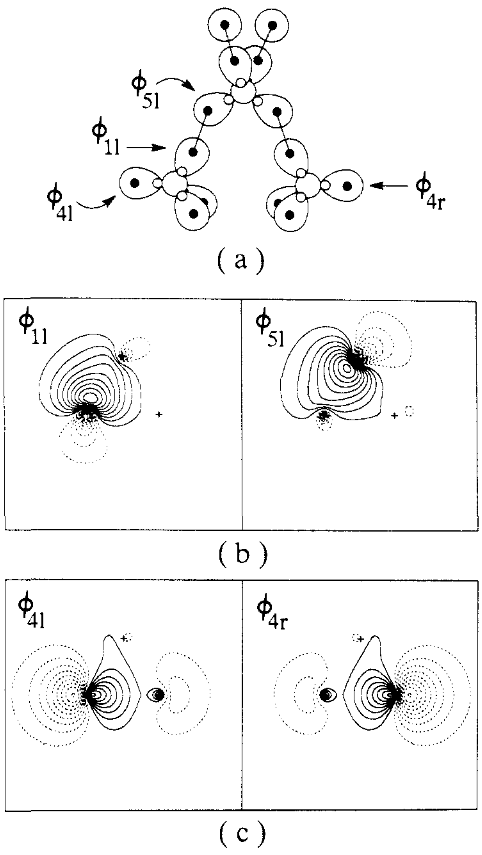

Figure 2. (a) Schematic representation of how the many-electron wave function of [1.1.1]propellane is derived from those of C_2 and three CH_2 groups. (b) Two orbitals forming a bond between a bridgehead carbon and a methylene carbon. There are six equivalent bonds of this form. (c) The two orbitals which form the bond between bridgehead carbon atoms. Note the significant increase in overlap as compared to C_2. There are also six equivalent carbon–hydrogen bonds (orbitals not shown).

overlap with the corresponding orbitals on the right atom to form the Ω-bonds of C_2. Contour plots of one of these bonds (made up of orbitals $\phi_{1\ell}$ and ϕ_{1r}) are shown in Figure 1b. The fourth orbital pair of C_2 is composed of two hybrids which point away from the molecule; the contour plots of these two orbitals are shown in Figure 1c. The overlap of $\phi_{4\ell}$ and ϕ_{4r} is 0.31,[15] while that of the orbitals making up an Ω-bond is 0.82.[16]

From the above description of C_2, the [1.1.1]propellane molecule[17] is related simply by the insertion of a CH_2 species into each of the three Ω-bonds of C_2, such as schematically depicted in Figure 2a for one CH_2 group. Three equivalent C–C bonds (of C_2) are broken, but six equivalent new (and somewhat less strained) C–C bonds are formed. One of these bonds, formed from orbitals $\phi_{1\ell}$ and $\phi_{5\ell}$ (with overlap 0.84), is displayed via the orbital contour plots in Figure 2b. Note that the orbital $\phi_{1\ell}$ of propellane contains less p-character than $\phi_{1\ell}$ of C_2; it is less sp^3-like and more sp^2-like. As a consequence, there is significantly more p-character available for the orbital $\phi_{4\ell}$ (an approximate hybridization of $sp^{4.5}$ as opposed to $sp^{0.8}$ for C_2). The additional p-character in orbitals $\phi_{4\ell}$ and ϕ_{4r} results in a favorable overlap (0.62)[15,16] as shown in the orbital contour plots of Figure 2c. Thus $\phi_{4\ell}$ and ϕ_{4r} of [1.1.1]propellane actually contribute significantly to the bonding and stability of the molecule in contrast to the situation in C_2.[18] This conclusion regarding the bonding is quite different from previous work using uncorrelated wave functions.[6] The use of simple correlated wave functions (GVB-PP) allows a clear physical picture of the bonding to emerge—a picture not unlike that pioneered by Slater and Pauling many years ago.[19]

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(15) The negative relative phase of $\phi_{4\ell}$ and ϕ_{4r} (Figure 1c) in C_2 indicates dominant antibonding character (by examining the natural orbital representation of the pair, 78% antibonding and 22% bonding), detrimental to C–C bonding. For propellane the orbitals are in phase, indicating a positive contribution to the bonding (95% bonding, 5% antibonding).

(16) For reference it is useful to consider H_2 at the same level of theoretical approximation: at $R = 2.0$ Å, the overlap (S) is 0.30 and the binding energy (BE) is 0.47 eV; at $R = 1.25$ Å, $S = 0.62$, and BE = 2.46 eV; at $R = 0.74$ Å (the equilibrium value), $S = 0.80$, and BE = 3.96 eV.

(17) The calculations employed a standard valence double-ζ basis set[13] and used the experimental geometry (Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257). The calculated total energy using 13 GVB pairs is −192.78914 hartree.

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Simple and Selective Method for RCHO → (*E*)-RCH=CHX Conversion by Means of a CHX_3-$CrCl_2$ System

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Many methods are now available for the stereocontrolled preparation of alkenyl halides from acetylenic precursors.[1] However, the one-carbon homologation of an aldehyde to an alkenyl halide is quite limited.[2] For example, treatment of an aldehyde with the Wittig reagent $Ph_3P{=}CHX$ usually gives a mixture of *Z* and *E* isomers and preparation of the ylide is rather complicated.[3] Here we introduce a simple and stereoselective method for the conversion of aldehydes to the corresponding (*E*)-alkenyl halides by an organochromium reagent.[4]

Anhydrous $CrCl_2$[5] (0.74 g, 6.0 mmol) is suspended in THF (10 mL) under an argon atmosphere. A solution of benzaldehyde (0.11 g, 1.0 mmol) and iodoform (0.79 g, 2.0 mmol) in THF (5 mL) is added dropwise to the suspension at 0 °C. After stirring at 0 °C for 3 h, the reaction mixture is poured into water (25 mL) and extracted with ether (3 × 10 mL). The combined extracts are dried over Na_2SO_4 and concentrated. Purification by column chromatography on silica gel (hexane) affords 0.20 g (87%, *E*/*Z* = 94/6)[6] of β-iodostyrene (**1**) as a colorless oil. The chromium(II)

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(6) The *E*/*Z* isomer ratios were determined by NMR and/or GLPC.

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