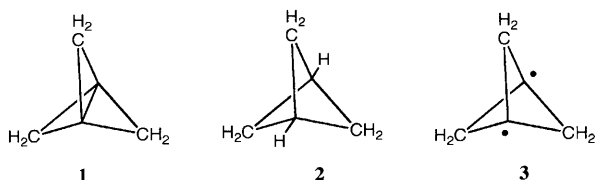# The Inverted Bond in [1.1.1]Propellane is a Charge-Shift Bond**

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The most intriguing feature of the family of small-ring propellanes is the nature of the central bond that connects the two inverted bridgehead carbons. The properties of the smallest member of the family, [1.1.1]propellane **1**, have been

predicted by an early ab initio study,[1] long before the successful synthesis by Wiberg and Walker.[2] This molecule has subsequently attracted considerable theoretical interest, and its "inverted bond" has remained, by and large, a mystery.[3–9] Compound **1** is remarkably stable despite its supposedly high strain energy, and it has a surprisingly short central bond of 1.60 Å.[4] From the enthalpy change of only 143 kcal mol^{-1} for the conversion of bicyclo[1.1.1]pentane **2** into [1.1.1]propellane plus two hydrogen atoms, a bond strength of 59–65 kcal mol^{-1} between the two bridgehead carbon atoms was deduced.[3,5] Another sign of the strength of the central bond is the stability of the singlet state **1** relative to the diradical triplet state **3**, which lies 79 kcal mol^{-1} higher in energy.[5] By contrast, other data have been presented that

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seemingly disprove the strength or even the very existence of a central bond in **1**, at least according to the traditional view of two-electron bonding. For example, [1.1.1]propellane was found to display a negative total overlap population between bridgehead atoms,[1] which was traced to the fact that the bond orbital is formed from hybrid atomic orbitals directed away from each other.[1,4,6] Furthermore, the inter-bridgehead regions of the total electron-density contour map of **2**, which is certainly devoid of C−C bonding, and of **1** are strikingly similar, thereby suggesting little bonding in **1**.[1] Additionally, experimental[10] and theoretical results[7] suggest that the deformation density associated with the central bond is much smaller than for a normal C−C bond. Considering all these contradictory data, Davidson concluded that "*all of the arguments put forward for the existence of a central bond in [1.1.1]propellane can be matched with a counterargument, except for the heat of formation*".[5] Finally, Luger et al. carried out an experimental study of a [1.1.1]propellane derivative,[11] and have shown that the "inverted bond" possesses a positive Laplacian of the density at the bond critical point (BCP), whereas, as expected from a normal covalent bond, the wing bonds have a negative Laplacian. So what kind of bonding do we have in the central bond of **1**? This is the central question of the present paper.

To answer this question, we recall that a positive Laplacian at a BCP is the signature of "charge-shift (CS) bonding";[12] a non-classical type of bonding in which the covalent–ionic resonance energy plays the major role.[13,14] As such, another typical characteristic of CS bonds is the depleted electronic density in the middle of the bond.[14] These two CS bond properties are reminiscent of the aforementioned electron density features of the bridge bond of **1**.[7,10] Another piece of this puzzle is the recent analysis of the electron localization function (ELF) of various propellanes by Polo et al.,[15] which showed strong similarities between the bridge bond of **1** and the single bond of F$_2$, a typical CS bond.[16] Thus, CS bonding might be the key feature that reconciles all of the seemingly contradictory data on the central bond of [1.1.1]propellane. Incidentally, Polo et al. interpreted their results in terms of an almost completely ionic bridge bond,[15] which would be unprecedented for a homonuclear bond. This intriguing conjecture of a completely ionic C−C bond, and Luger's recent data,[11] prompted us to characterize the nature of the "inverted bond" in [1.1.1]propellane. To obtain unequivocal insight on the nature of this enigmatic bond, we employed modern ab initio valence bond (VB) methods, which provide all the requisite key properties, such as the weights of the covalent and ionic components of the bond, the covalent–ionic resonance energy, the shape of the covalent dissociation curve.

To investigate the inverted bond, we optimized the geometry of **1** using the MP2 and CASPT2 methods, and

performed subsequent VB calculations on these geometries (see the Methods Section). Indeed, the singlet state **1** of [1.1.1]propellane (Figure 1) has a single minimum with a short central bond of 1.596 Å (CASPT2/6-31G*), in good agreement with earlier calculations and with experiment. The
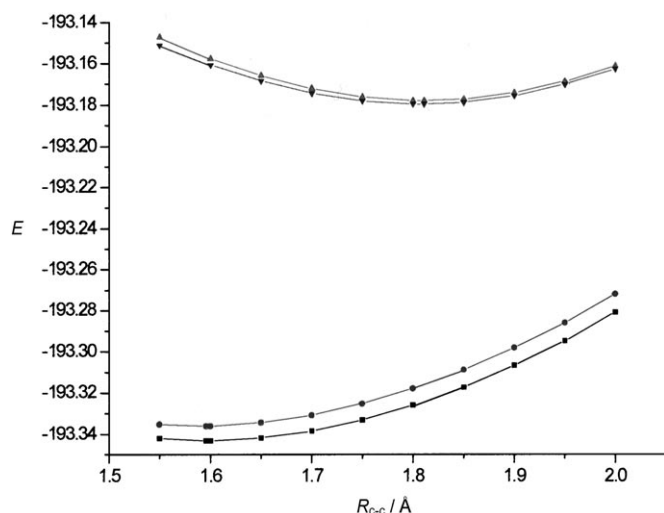

Figure 1. Energies *E* (in hartree) of the singlet (bottom curves) and triplet states (top curves) of [1.1.1]propellane as a function of the bridge bond distance calculated at the MP2/6-31G* and CASPT2/6-31G* levels. Singlet state: ■ MP2, ● CASPT2; triplet state: ▲ MP2, ▼ CASPT2.

triplet minimum **3** lies 98.1 kcal mol^{-1} higher, in general agreement with the previously reported high value, calculated at a lower level.[5] At the singlet optimum geometry, the vertical singlet–triplet energy gaps amounts to 109.1 kcal mol^{-1}, which is a sufficiently large value to rule out a putative diradical nature of the ground state.

The hybrid atomic orbitals (HAOs) located at the bridgehead of **1** are outwardly directed, which is in agreement with the general consensus that there is a degree of hybridization lying in between the classical sp and sp^2 hybrid orbitals, or more precisely, sp$^{1.57}$. Does the stability of **1** then arise from a direct σ bond between these two HAOs or, as has also been suggested, from bonding multicenter orbitals involving both the pair of bridgehead carbons and the methylene wing groups?[3] VB theory can settle the question, since it enables one to calculate the bonding strength in situ by focusing on the central bond by itself.

In VB theory and in the chemist's language, a bond is regarded as an interaction between two localized HAOs. In the homonuclear case, this interaction always takes the form of a combination of a major covalent structure and two minor ionic ones (Scheme 1). Note that the covalent structure is itself a combination of two neutral components that differ from each other by an exchange of spins.[14] It is this exchange that causes bonding in the covalent structure. On the other hand, any one of these neutral components defines, by itself, a so-called "quasiclassical (QC) state" that is nonbonding and can serve as reference for gauging the bond strength.

Using the QC state as a nonbonded reference, the energy difference between the QC state and the ground state is a
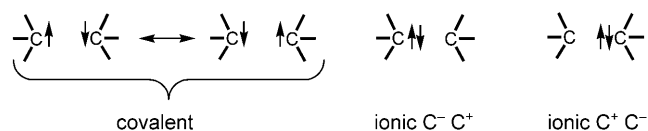
Scheme 1. The three VB structures that completely describe a C—C bond.

direct measure of the stabilization associated to the exchange of the two electrons in the covalent VB structure, and is complemented by the resonance energy stabilization owing to the mixing of the ionic structures into the covalent structure (Scheme 1). This energy difference measures the in situ bonding energy, which is a vertical quantity and is generally larger than the thermochemical bond dissociation energy (BDE). This is because as one brings together two fragments from infinity to a bonding distance, the bonding interaction is weakened by the repulsions between the adjacent bonds or lone pairs of the fragments facing each other. This repulsion is accounted in the BDE quantity but not in the in situ bond strength. However, the latter gives a reliable measure of the bonding interaction strength. For example, in ethane, the in situ bonding energy is 138.5 kcal mol^{-1}, and the BDE is 96.1 kcal mol^{-1}, as calculated at the breathing orbital valence bond (BOVB) level (Table 1). In [1.1.1]propellane, the in situ bonding energy of the central C—C linkage is 119.1 kcal mol^{-1}, which is only 19.4 kcal mol^{-1} less than in ethane, thus clearly indicating a significant σ-bonding direct interaction between the bridgehead HAOs.

Table 1: Some BOVB/6-31G*-calculated energies in kcal mol^{-1} for ethane and [1.1.1] propellane **1** at the ground-state equilibrium geometries.

	Ground state	QC state[a]	Covalent–ionic resonance energy[b]	BDE[c]
ethane	0	138.5	36.3	96.1
propellane **1**	0	119.1	72.2	–

[a] The difference between the energy of the QC state and that of the ground state gives the "in situ" bonding energy. [b] RE$_{c-i}$ is calculated relative to the covalent-only structure. [c] Bond dissociation energy as calculated in the traditional way as the difference between the energy of the molecule and that of the separate fragments.

Having established the strength of the central bond in **1**, the next question is what the nature of this bond is: classically covalent, ionic, or charge-shift? Knowledge of two quantities will settle this assignment: The first is the ratio of the respective weights of ionic versus covalent structures. The second is the resonance energy arising from the mixing of covalent and ionic structures (RE$_{c-i}$), defined as the energy difference between the ground-state and the major VB structure. The covalent and ionic weights in the central bond of **1** are quite comparable to those of the C—C bond in ethane (Table 2). In both cases, the covalent structure contributes ca. 60% of the wave function of the ground state, whereas the ionic structures have smaller weights. As

Table 2: Weights of the covalent and ionic components in the C—C bond of ethane and in the central bond of [1.1.1]propellane **1**.

|	Covalent	Ionic C$^-$C$^+$	Ionic C$^+$C$^-$
ethane[a]	55%	23%	23%
propellane[b]	62%	19%	19%

[a] Ref. [14]. [b] This work.

was shown before,[13,14] such a predominance of the covalent structure may characterize covalent and CS bonds, but certainly not ionic bonds. Thus, the present VB calculations do not support the statement of Polo et al. that the central bond of [1.1.1] propellane is predominantly ionic.[15]

As the covalent structure is definitely established as the major contributor in both ethane and propellane, the resonance energy RE_{c-i} will simply be the energy difference between the covalent structure and the ground state (Table 1, column 3). By definition, a bond is considered to be of the charge-shift type if RE_{c-i} contributes more than 50% to the overall bonding energy.[14] Table 1 shows that ethane, with an RE_{c-i} of only 36.3 kcal mol^{-1} (BDE = 96.1 kcal mol^{-1}), is a classical covalent bond. In contrast, the RE_{c-i} of the central bond of propellane is exceptionally large (72.2 kcal mol^{-1}), which is to our knowledge the largest RE_{c-i} ever calculated for a homonuclear bond. By comparison, the RE_{c-i} value of F$_2$, the most typical CS bond to date, is 5.5 kcal mol^{-1} smaller.[14] RE_{c-i} can also be compared to the BDE of the bridge bond that we estimated from considerations of in situ bonding energies, to be about 20 kcal mol^{-1} smaller than that of the C—C bond of ethane; that is, about 70 kcal mol^{-1}. By any measure, this estimation shows that RE_{c-i} contributes more than 50% to the bond strength of the bridge bond of **1**, thus definitely putting this bond in the CS-bonding category.[14]

Another general feature of CS bonding in homonuclear bonds is the shape of the covalent dissociation curve, which, in contrast with a deep covalent potential well in the case of a classical covalent bond, is only weakly bonding or even repulsive.[14] Schematic energy profiles of the ground state, covalent VB structure, and QC state for ethane and propellane as a function of the C—C distance are given in Figure 2. It is seen that the covalent structure of ethane has, as expected, an attractive profile that is close to the ground-state profile and accounts for most of the bonding energy, whereas the covalent structure of the bridge bond of [1.1.1]propellane is repulsive and rises in energy from 1.6 Å to 1.8 Å, in close analogy with difluorine.[13d,14]

The nature of a two-electron bond can also be deduced from considerations of electron densities. As we have shown in a VB study of a series of two-electron bonds,[12] a classically covalent bond has a large-density ρ and a negative Laplacian $\nabla^2\rho$ at BCP, whereas homonuclear CS bonds have large densities and positive or zero Laplacians. In their experimental study of a [1.1.1]propellane derivative, Luger et al. reported values for ρ and $\nabla^2\rho$ at BCP for the wing bonds and for the central bond.[11] They obtained values of $\rho = 1.55$ and $\nabla^2\rho = -13.0$, and $\rho = 1.31$ and $\nabla^2\rho = 10.3$ for the central bond. Clearly, according to our recent study,[12] these results classify the wing bonds as classically covalent and the central
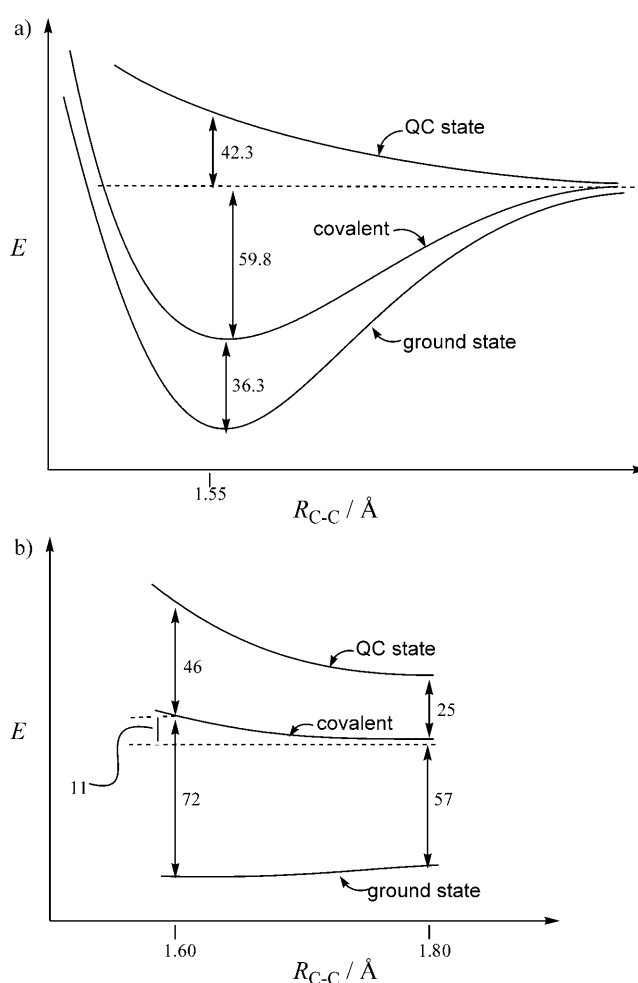
Figure 2. Energy profiles of the ground state, covalent VB structure, and quasi classical state as a function of the C—C distance for a) ethane and b) [1.1.1]propellane, and calculated at the BOVB level. Energies are given in kcal mol^{-1}.

bond as a CS bond. Another indication that arises from ELF analyses of the CS character of a bond is the absence of a disynaptic basin in the middle of the bond and the presence of two separate monosynaptic basins, as was found in F$_2$ and Cl$_2$.[14] Precisely this observation was made by Polo et al., who found an extremely low disynaptic basin population (0.13) between bridgehead carbon atoms of **1**, and two monosynaptic basins (population 1.27 each) on these atoms outside the [1.1.1]propellane cage.[15]

In summary, we have shown herein that the bridgehead carbons of [1.1.1]propellane are linked by a direct two-electron σ bond having significant strength that is very close to the C—C bond in ethane, but being very different in its nature. This homonuclear bond is neither classically covalent nor classically ionic, but is rather distinctly a CS bond, and is very similar to the F—F bond. All the criteria that may be used to probe the nature of a two-electron bond (covalent–ionic resonance energy, repulsive covalent curve, density and its Laplacian at the BCP, and ELF studies) converge to this very same conclusion. This description resolves the longstanding question of more than two decades. Based on the repulsive

nature of the covalent curve, it can be predicted that analogues of [1.1.1]propellane, in which the CH_2 groups at the wings are replaced by powerful electron donors, such as NH, O, and S, if they can be synthesized, will have a greater CS character and even shorter "inverted" C−C bonds.[17] The present analysis of [1.1.1]propellane and the future testing of the prediction about its heteroatomic analogues[17] will further demonstrate that CS bonding constitutes a unique and significant class of bonding.

Methods Section

A many-electron wave function is expressed in terms of VB functions Φ_K [Eq. (1)], where each Φ_K corresponds to a VB structure. In the

$$\Psi = \sum_K C_K \Phi_K \tag{1}$$

present work, the VB wave functions are calculated by the BOVB method,[18] in which the coefficients C_K and the orbitals are optimized simultaneously, and each VB structure Φ_K is allowed to have its unique set of orbitals. This condition is important in obtaining accurate bonding energies (see the Supporting Information for a more detailed description of the method). The 6–31G* basis set was used for all calculations. The geometry optimizations were performed at the MP2 level with the Gaussian 03 program,[19] and at the CASPT2 level with MOLPRO.[20] A complete description of the geometry of [1.1.1]propellane is provided in the Supporting Information. The XMVB program[21] was used for the BOVB calculations.

[1] M. D. Newton, J. M. Schulman, *J. Am. Chem. Soc.* **1972**, *94*, 773.

[2] K. B. Wiberg, F. H. Walker, *J. Am. Chem. Soc.* **1982**, *104*, 5239.

[3] J. E. Jackson, L. C. Allen, *J. Am. Chem. Soc.* **1984**, *106*, 591.

[4] K. B. Wiberg, W. P. Dailey, F. H. Walker, S. T. Waddell, L. S. Crocker, M. D. Newton, *J. Am. Chem. Soc.* **1985**, *107*, 7247.

[5] D. Feller, E. R. Davidson, *J. Am. Chem. Soc.* **1987**, *109*, 4133.

[6] a) R. P. Messmer, P. A. Schultz, *J. Am. Chem. Soc.* **1986**, *108*, 7407; b) R. M. Jarret, L. Cucumano, *Tetrahedron Lett.* **1990**, *31*, 171; c) A. Ebrahimi, F. Deyhimi, H. Roohi, *J. Mol. Struct. (Theochem)* **2003**, *626*, 223; d) M. Pecul, H. Dodziuk, M. Jaszunski, O. Lukin, J. Leszczynski, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1986; e) L. B. Krivdin, *Magn. Reson. Chem.* **2004**, *42*, 1.

[7] K. B. Wiberg, *J. Am. Chem. Soc.* **1983**, *105*, 1227.

[8] K. B. Wiberg, R. F. W. Bader, C. D. H. Lau, *J. Am. Chem. Soc.* **1987**, *109*, 985.

[9] K. B. Wiberg, *Chem. Rev.* **1989**, *89*, 975.

[10] a) P. Chakrabarti, P. Seiler, J. D. Dunitz, A.-D. Schluter, G. Szeimies, *J. Am. Chem. Soc.* **1981**, *103*, 7378; b) P. Seiler, J. Belzner, G. Szeimies, *Helv. Chim. Acta* **1988**, *71*, 2100.

[11] M. Messerschmidt, S. Scheins, L. Grubert, M. Pätzel, G. Szeimies, C. Paulmann, P. Luger, *Angew. Chem.* **2005**, *117*, 3993; *Angew. Chem. Int. Ed.* **2005**, *44*, 3925.

[12] For example, the Laplacian of the density at the BCP amounts to 0.58 for the CS bond of F_2, versus −0.62 for the classical C−C bond of ethane. See: L. Zhang, F. Ying, W. Wu, P. C. Hiberty, S. Shaik, *Chem. Eur. J.* **2008**, in press.

[13] a) S. Shaik, P. Maître, G. Sini, P. C. Hiberty, *J. Am. Chem. Soc.* **1992**, *114*, 7861; b) A. Shurki, P. C. Hiberty, S. Shaik, *J. Am. Chem. Soc.* **1999**, *121*, 822; c) P. C. Hiberty, C. Megret, L. Song, W. Wu, S. Shaik, *J. Am. Chem. Soc.* **2006**, *128*, 2836; d) P. C. Hiberty, R. Ramozzi, W. Wu, S. Shaik, *Faraday Discuss.* **2007**, *135*, 261.

[14] S. Shaik, D. Danovich, B. Silvi, D. Lauvergnat, P. C. Hiberty, *Chem. Eur. J.* **2005**, *11*, 6358.

[15] V. Polo, J. Andres, B. Silvi, *J. Comput. Chem.* **2007**, *28*, 857.

[16] R. LLusar, A. Bertran, J. Andres, S. Noury, B. Silvi, *J. Comput. Chem.* **1999**, *20*, 1517.

[17] We are thankful to one of the referees for inducing us to make this prediction.

[18] a) P. C. Hiberty, J. P. Flament, E. Noizet, *Chem. Phys. Lett.* **1992**, *189*, 259; b) P. C. Hiberty, S. Humbel, C. P. Byrman, J. H. van Lenthe, *J. Chem. Phys.* **1994**, *101*, 5969; c) P. C. Hiberty, S. Shaik, *Theor. Chem. Acc.* **2002**, *108*, 255.

[19] M. J. Frisch et al., Gaussian 03, Revision D.01; Gaussian, Inc.: Wallingford CT, **2004** (see Supporting Information).

[20] H.-J. Werner et al., MOLPRO, a package of ab initio programs, Version **2002**.1 (see Supporting Information).

[21] a) L. Song, Y. Mo, Q. Zhang, W. Wu, XMVB: An Ab Initio Nonorthogonal Valence Bond Program, Xiamen University, Xiamen, **1999**; b) L. Song, Y. Mo, Q. Zhang, W. Wu, *J. Comput. Chem.* **2005**, *26*, 514.

[22] For example, a pentagerma[1.1.1]propellane has been synthesized: See D. Nied, W. Klopper, F. Breher, *Angew. Chem.* **2009**, *121*, 1439; *Angew. Chem. Int. Ed.* **2009**, *48*, 1411.