Theoretical and (e,2e) Experimental Investigation into the Complete Valence Electronic Structure of [1.1.1]Propellane

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Abstract: An electronic structural study of the complete valence shell of [1.1.1]propellane is reported. Binding energy spectra were measured in the energy regime of 3.5–46.5 eV over a range of different target electron momenta, so that momentum distributions (MDs) could be determined for each ion state. Each experimental electron momentum distribution is compared with those calculated in the plane wave impulse approximation using both a triple-ζ polarized level SCF wave function and a further 13 basis sets as calculated using density functional theory. A critical comparison between the experimental and theoretical momentum distributions allows us to determine the optimum wave function for [1.1.1]propellane from the basis sets we studied. In general, the level of agreement between the experimental and theoretical MDs for this optimum wave function for all of the respective valence orbitals is fair. The determination of this wave function then allows us to derive the chemically interesting molecular properties of [1.1.1]propellane. A summary of these results and a comparison of them with those of other workers are presented with the level of agreement typically being good. In particular, we note that we confirm the existence of the C1–C3 bridging bond with a bond order of 0.70.

1. Introduction

Electron momentum spectroscopy (EMS), or (e,2e) coincidence spectroscopy, is now a well-developed tool for the investigation of the dynamic structure of molecules due to its unique ability to measure the orbital momentum profile for binding-energy-selected electrons. Furthermore, within the plane wave impulse approximation (PWIA) and, in many cases, the target Hartree–Fock (THFA) approximation, this measured momentum cross section may be directly compared with theoretical wave functions in quantum chemistry, and in this paper we report its application to the saturated hydrocarbon [1.1.1]propellane (C₃H₆).

The successful synthesis of [1.1.1]propellane, a truly remarkable hydrocarbon with “inverted” geometries at the bridgehead carbon atoms, opened the way to both experimental and theoretical studies of its properties. The structure, vibrational spectrum, total energy, strain energy, and heat of formation have all been investigated. In addition, an excellent study into its low-energy electron impact spectroscopy has also been reported. The compound was found to be remarkably stable and to have a surprisingly short bridgehead C₁–C₃ bond length (160 pm, of the order of only 9 pm longer than in cyclopropane), unexpected given the extreme deviation from tetrahedral geometry and the intuitively anticipated strain.

The above findings initiated a series of theoretical studies on the somewhat controversial nature of the C₁–C₃ bridging bond, a full description of which is found in Slee. Briefly, however, attempts to describe the character of the bridging bond of [1.1.1]propellane have concentrated on two main lines of investigation. In the first, orbital theories were employed either to describe the bonding as predictive models on their own or as a means of analysing ab initio wave functions, while in the second the nature of the C₁–C₃ bond was studied using the electron density or related quantities. In either approach, the fundamental questions being asked are there in fact a bridging
bond in [1.1.1]propellane, and if so, how can it be described and related to other bonds?

An orbital analysis of an ab initio wave function was performed by Jackson and Allen, who focused on the valence canonical molecular orbitals and decomposed them using an interaction scheme between a C2 fragment and the outer parts of the rings (CH2 groups). The highest-occupied molecular orbital (HOMO) was found to result from the in-phase combination of 2pσ orbitals on the bridgehead carbons, which has substantial density in the contributing regions. Jackson and Allen claimed that this orbital “contributed nil to holding C1 and C3 bridgehead bond to be sp^3. On the other hand in the more rigid bicyclic compound there is a ridge of maximum electron density connecting the two carbon nuclei while in the bicyclic compound there is not. Hence, the bridgehead carbons are bonded in [1.1.1]propellane but are not in bicyclo[1.1.1]pentane. Their second major conclusion was that there is also a quantitative difference between the electron density in the bridging region of [1.1.1]propellane and of the analogous bicyclic species, bicyclo[1.1.1]pentane. The latter showed a minimum in the center of the region while the former showed a bond point. Thus, in [1.1.1]propellane there is a ridge of maximum electron density connecting the two carbon nuclei while in the bicyclic compound there is not. Hence, the bridgehead carbons are bonded in [1.1.1]propellane but are not in bicyclo[1.1.1]pentane. Their second major conclusion was that there is also a quantitative difference between the electron density in the bridging region of [1.1.1]propellane and bicyclo[1.1.1]pentane. For instance, in [1.1.1]propellane the value of the electron density (ρ) at the bond point is ρ = 0.203 a₀⁻³, while in bicyclo[1.1.1]pentane it is only ρ = 0.098 a₀⁻³. We note at this time that Wiberg et al. found the bond order of [1.1.1]propellane to be n = 0.73. Finally, Wiberg et al. found that the HOMO does contribute to the bonding of C1 and C3. Indeed they noted that roughly one-third of the total electron density at the bond point is due to the HOMO with its principal contribution, at this point, being due to the overlap of 2s orbitals. The assignment by Jackson and Allen of the bonding as a result of off-axis density, and their claim that there is “very little charge density along the C1–C3 line of centers” is at variance with this observation of a bond point in the geometrical center of the [1.1.1]propellane molecule.

The nature of the hybridization of the C1–C3 bond in [1.1.1]propellane has also been examined. In their earlier work, Newton and Schulman found the hybridization of the inter-bridgehead bond to be sp^3. On the other hand in the more recent study of Jarret and Cusumano, in which the Cl–Cl coupling constant in [1.1.1]propellane was measured to be 9.9 ± 0.1 Hz, the hybridization of the C1–C3 bridgehead bond was estimated to be sp^3.5.

The outer-valence structure of [1.1.1]propellane was previously studied with photoelectron spectroscopy (PES) using He-I radiation by Honegger et al. In this work, five valence states were identified and classified, consistent with their expectation based on the results of the molecular orbital calculations that assumed the validity of the Koopmans theorem, as being due to the respective 3a′′, 1e′′, 3e′, 1a′, and 2e′ orbitals. We note that while no PES investigation of the inner valence 1a′′, 2a′′, 1e′, and 1a′ orbitals has been reported, there is our preliminary report of some aspects of our investigations into [1.1.1]propellane which indicates binding energies and spectroscopic factors for the inner-valence orbitals. In addition, this work confirmed the ordering of the outer-valence states as given by Honegger et al. The molecular orbital nomenclature that we have adopted in this paper is consistent with that employed by Honegger et al. in that the numbering of the symmetry labels within each irreducible representation refers to the valence-shell orbitals only (i.e., those of carbon 2s and 2p and hydrogen 1s parentage).

The only previous EMS study into [1.1.1]propellane reported experimental binding energy spectra at two azimuthal angles, φ = 0° and 10° (see section 2) and the results of a Green’s function calculation, to third order, in the algebraic diagrammatic construction (ADC(3)) method.

In section 2 we briefly discuss some of the experimental aspects of the EMS technique used in our work, while in section 3 details of our structure calculations are presented. In section 3 a brief discussion of the UniChem package and density functional theory (DFT) employed extensively in this investigation is provided. The results of the experimental and theoretical MDs are presented and discussed in detail in section 4. This is the first time these data have been reported in the literature for [1.1.1]propellane. The significance of the present application of the EMS technique to this molecule is that by comparing the experimental and theoretical MDs, for the relevant valence orbitals, we can independently determine which of the SCF or DFT basis sets of states we have studied provides the most physically reasonable representation of the [1.1.1]propellane molecule. Standard UniChem features then allow us to utilize this optimum wave function to extract the chemically important molecular property information for the [1.1.1]propellane system including bond lengths, bond orders, electron density (3D), and electron density contour (2D) plots and its infrared spectra. These data and a comparison with previous work are given and discussed in section 5 of this paper. Finally, in section 6, conclusions from the results of the present study are drawn.

2. Experimental Details

The EMS technique and its theoretical analysis have been discussed in detail elsewhere. In the present work, noncoplanar symmetric kinematics is employed, with the two outgoing electrons, denoted by A and B, having essentially equal energies (500 eV) and making equal polar angles (θ = 45°) with respect to the incident electron beam. The incident electron energy E₀ is 1000 eV plus the binding energy εᵣ of the struck electron.

\[ E₀ = E_A + E_B + εᵣ \]  

The ion recoil momentum q (and thus the momentum p of the target electron) is varied by varying the out-of-plane azimuthal angle φ.

\[ q = p₀ - p_A - p_B \]  

At high enough energies and momentum transfer |p₀ − pᵣ|, momentum is transferred to the outgoing electrons only by a collision of the incident electron with a moving target electron of momentum p. In this case,


approximated by evaluating orbitals at the equilibrium geometry of the molecule. Final rotational and vibrational states are eliminated by closure. The momentum-space target-ion overlap \( S_{ij} \) can be evaluated using configuration interaction (CI) descriptions of the many-body wave functions, but usually the weak-coupling approximation is made. Here, the target-ion overlap is replaced by the relevant orbital of, for example, the Hartree–Fock or Kohn–Sham ground state \( \Phi_0 \), multiplied by a spectroscopic amplitude, which is the coefficient, in the CI description of the ion state, of the configuration representing a hole in the appropriate ground state orbital. With these approximations, eq 5 reduces to
\[
\sigma = S^{f(0)}(q) \int d\Omega (\Phi(q))^2
\]
where \( \Phi(p) \) is the momentum space orbital. The spectroscopic factor \( S^{f(0)} \) is the square of the spectroscopic amplitude for orbital \( j \) and ion state \( f \). It satisfies the sum rule
\[
\sum_f S_j^{f(0)} = 1
\]
Hence, it may be considered as the probability of finding the one-hole configuration in the many-body wave function of the ion.

The target-ion overlap is a one-electron function called the quasi-particle orbital. A quasiparticle equation, the Dyson equation, can be constructed from the electronic Schrödinger equations for the target and ion. \(^{23} \) Formally this is a one-electron Schrödinger equation with target and ion structure details contained in the potential operator. The quasiparticle energies are given by the poles in the Greens function of this equation, which can be evaluated using diagrammatic perturbation theory. \(^{25} \) An example of this calculation, which omits diagrams above the third order, is the third-order algebraic diagrammatic construction, or ADC(3), method.

The Kohn–Sham equation \(^{26} \) of DFT may be considered as an approximate quasiparticle equation, with the potential operator approximated by the exchange-correlation potential. \(^{23} \) Recently, \(^{26} \) the physical significance of the valence orbitals of DFT has been shown by their ability to describe EMS data that are not well described by SCF calculations that omit electron-correlation considerations, but are well described by full CI calculations.

In order to compute the coordinate-space Kohn–Sham orbitals \( \psi_i \), we employed DGauss, a program developed for CRAY Research by Andzelm and co-workers. \(^{22,23} \) DGauss is itself a part of UniChem, a suite of computational quantum-chemistry programs from CRAY Research Inc. \(^{29} \) Using DGauss and UniChem, we employed various basis sets to build a model of \([1.1.1]\)propellane molecule and then we minimized the energy. The molecular coordinates at the optimum geometry (minimum energy) and the Gaussian molecular orbital parameters (coefficients and exponents) were next treated as an input to the Flinders-developed program AMOLD, which computes the momentum space spherically-averaged molecular-structure factor \(^{20} \) and the \((a,2c)\) cross section or momentum profile.

The comparisons of calculated momentum profiles with experiment (see section 4) may be viewed as an exceptionally-detailed test of the quality of the basis set. In this study, we have used thirteen basis sets in the DFT (DGauss) computations (Table 1). The notations DZ and TZ denote basis sets of double-, or triple-\( \zeta \) quality. \( V \) denotes a calculation in which such a basis is used only for the valence orbitals

\[ p = -q \] (3)

The complete valence region of \([1.1.1]\)propellane was studied in several experimental runs using the Flinders symmetric noncoplanar electron momentum spectrometer. \(^{22} \) Both electron energy analyzers have position sensitive detectors in their energy-dispersing planes. A full description of the coincidence spectrometer and the method of taking the data can be found in McCarthy and Weigold, \(^{1} \) although we note that since their report there has been a major upgrade in the data acquisition and computer control system. Specifically, the obsolete PDP-11/23 computer and its associated CAMAC control units were replaced by a PC 486D computer with a \( \mu \)-ACE MCA card and a National Instruments LabPC+ card. The benefits of this upgrade in terms of data handling, processing, and storage and hardware reliability were manifest, in particular, by greatly reducing down time in the experiment.

In the current study, the binding energy range of interest (\( \epsilon_i = 3.5-46.5 \) eV for \([1.1.1]\)propellane) is stepped through sequentially at each of a chosen set of angles \( \phi \) using a binning mode through the entire set of azimuthal angles \( \phi \). Scanning through a range of \( \phi \) is equivalent to sampling different target electron momenta (see eqs 2 and 3) as
\[
p = [2p_A \cos \theta - p_0]^2 + 4p_A^2 \sin^2 \theta \sin^2(\phi/2)]^{1/2}
\] (4)

The energy resolution of the present work, as determined from measurements of the binding energy spectrum of helium, is 1.38 eV (fwhm). However, due to the natural line widths of the various transitions, as estimated from the relevant PES spectrum, \(^{20} \) the fitted resolutions of the spectral peaks for \([1.1.1]\)propellane varied from 1.42 to 2.60 eV (fwhm). The angular resolution was \( \Delta \phi = 1.2^\circ, \Delta \theta = 0.6^\circ \), as determined from the electron optics and apertures and from a consideration of the argon 3p angular correlation. \([1.1.1]\)Propellane of very high purity was introduced into the interaction region via a variable leak valve. The \([1.1.1]\)propellane was prepared free of solvent from 1,3-diiodobicyclo[1.1.1]pentane by a procedure outlined by Alber and Szeimies, \(^{22} \) although we note that the original synthesis of \([1.1.1]\)propellane was due to Wiberg and Walker. \(^{7} \) Since the EMS technique is very sensitive to impurities, great care was exercised to minimize the possibility of sample contamination both during its synthesis and in its transportation from the storage reservoir to the interaction region. With regard to the latter point, the \([1.1.1]\)propellane sample was always initially condensed by liquid \( N_2 \) and any \( N_2, O_2, H_2O \) etc., contaminants pumped off. The sample was kept at 15 °C and its vapor introduced through a 0.7 mm diameter single capillary into the interaction region. Note that the \([1.1.1]\)propellane driving pressure was too low to cause any significant clustering by supersonic expansion. Since we were unsure as to the long-term stability of gas phase \([1.1.1]\)propellane, and indeed how it interacts with the walls of its storage reservoir and stainless steel gas transport lines, the results of each scan were carefully monitored for any signs of sample degradation. Furthermore, our \([1.1.1]\)propellane samples were regularly changed to additionally minimize the possibility of sample degradation.

3. Theoretical Analysis

The PWIA is used to analyze the measured cross sections for high-momentum transfer \((a,2c)\) collisions. \(^{2} \) Using the Born–Oppenheimer approximation for the target and ion wave functions, the \((a,2c)\) differential cross section \( \sigma \), for randomly-oriented molecules and unresolved rotational and vibrational states, is given by
\[
\sigma = K \int d\Omega \left| \langle \Psi_f^{N-1} | \Psi_i^N \rangle \right|^2
\]
where \( K \) is a kinematical factor which is essentially constant in the present experimental arrangement, \( \Psi_i^N \) and \( \Psi_f^{N-1} \) are the electronic many-body wave functions for the final \((N-1) \) electron ion and target \((N)\) electron ground states, and \( p \) is the momentum of the bound electron at the instant of ionization. The \( d\Omega \) denotes an integral over all angles (spherical averaging) due to the averaging over all initial rotational states. The average over the initial rotational state is well

\[(22) \text{Alber, F.; Szeimies, G. Chem. Ber. 1992, 125, 757.}\]
Table 1. Basis Sets Used in the Present Study for the DGauss Computations

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Table 2. Local Spin-Density-Optimized Basis Sets Used in the DGauss Computations

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DFT result with the TZ94.bspp basis is only marginally in better agreement with the experimental momentum distribution than that obtained with the TZ94 basis, we can infer that in this case the more exact nonlocal exchange-correlation functionals afforded by the Becke–Stoll–Preuss–Pavlidou corrections are not really necessary.

The 3e' state at a binding energy of 12.6 eV and the 1a2' state at a binding energy of 13.4 eV are only separated by 0.8 eV. Consequently, given our coincident energy resolution of ΔE_{coin} = 1.38 eV (fwhm), we were not confident of uniquely resolving them in our deconvolution of the measured spectra.

**Figure 1.** Typical binding energy spectra from our 1000 eV noncoplanar symmetric EMS investigation into [1.1.1]propellane. The curves show the fits to spectra at φ = 0°, φ = 10°, and φ = 0° + 10° using the known energy resolution function. We thank Elsevier Science for permission to reproduce this figure from ref 21.

Figure 2. The 1000 eV noncoplanar symmetric momentum distribution for the 3a1' state of [1.1.1]propellane. The present data (●) are compared against the results of our PWIA-SCF triple-ζ basis (—), PWIA-DFT 6-31G Pople basis (— —), and PWIA-DFT TZ94.bspp basis (— — —) calculations. Also shown is the result of the PWIA-DFT TZ94.bspp basis (— — — —) scaled by a factor of 0.89.

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**Figure 3.** The 1000 eV noncoplanar symmetric momentum distribution for the 1e'' state of [1.1.1]propellane. Legends are the same as in Figure 2. Also shown is the result of our PWIA-DFT TZ94 basis (— — —). Thus, a combined momentum distribution for the 3e' and 1a2' states (peaks 3 and 4 of Figure 1) is presented in Figure 4. If we now consider Figure 4 in more detail, then it is clear that
none of our PWIA-SCF and PWIA-DFT calculations exactly reproduce the measured MD. In particular the TZ94p.bp (not plotted) and TZ94p.bspp basis sets lead to momentum distributions which completely fail to predict the first peak in the measured (e,2e) cross section, strongly suggesting that they are totally inadequate in providing a realistic physical picture for these states. With regard to the remaining basis sets, while they all lead to a quite good qualitative representation of the measured momentum distribution, there are differences in some of the fine details between them and the experimental cross section. Specifically the PWIA-SCF and PWIA-DFT results, with 6-31G Pople, TZ94, DZ94, and TZ94.bspp basis sets, all predict the first peak in the 3e' + 1a' state cross section to occur at a value of momentum $p \approx 0.40$ au, which is too large compared to our experimental observation for this peak of $p \approx 0.33$ au. The additional experimental flux at small momentum, compared to the theoretical results, suggests that the orbitals for the 3e' + 1a' states are somewhat more diffuse in coordinate space than those afforded by the basis states considered in this investigation. Nonetheless we consider that, across the current experimental range of momentum, the present PWIA-DFT results using the respective 6-31G Pople and TZ94.bspp basis sets provide a fair level of agreement with the measured data for the 3e' + 1a' states.

In Figure 5 we plot the experimental momentum distribution for the 2e' orbital (peak 5 of Figure 1), at binding energy $\epsilon_f = 15.7$ eV, along with our theoretical PWIA-SCF and PWIA-DFT results. It is quite clear from this figure that none of the calculations, for any of the basis sets considered, provides an (e,2e) cross section in agreement with the experimental result. This is particularly apparent for momenta less than 0.76 au, where the measured cross section increases in value until reaching a maximum at $p \approx 0.16$ au (i.e., it is s-like in nature), while all of the theoretical cross sections tend to 0 as $p$ approaches 0.16 au (i.e., they are all p-like in nature). For $p > 0.76$ au, we see from Figure 5 that, to within the errors on the momentum distribution data, there is fair agreement between all the 2e' orbital PWIA-SCF and PWIA-DFT calculation results and the experiment, although it is perhaps interesting to note that the magnitude of the measured data still lay above the theoretical cross section for all $p > 0.76$ au. In Adcock et al.\textsuperscript{21} we previously noted that our ADC(3) calculation found that the 2a_1' orbital was severely split, with a significant 2a_1' pole strength (55% contribution allowed here) using the TZ94.bspp basis, then very good qualitative agreement is found between theory and experiment for this combined momentum distribution. This is well illustrated by our plot in Figure 5 for the 2e' + (0.55)2a_1' states. Obviously the level of agreement for the (e,2e) cross section, between the theory result that incorporates a 2a_1' contribution to the 2e' state and the measured data, is not perfect, perhaps reflecting a limitation in our 2a_1' orbital. Nonetheless this agreement is still quite good with the present analysis providing the first unequivocal supporting evidence for the ADC(3) 2a_1' orbital spectroscopic strength splitting result of Adcock et al.\textsuperscript{21} If we now consider the 1a_2'' state (peak 6 of Figure 1), then the level of agreement between the present experimental momentum distribution and the MDs from the results of the PWIA-SCF and PWIA-DFT calculations, with the respective 6-31G Pople basis, TZ94 basis, TZ94.bspp basis, and DZ94 basis, is excellent across the entire range of measured momentum (see Figure 6). Both the experimental MD and these theoretical MDs accurately predict that the peak in the 1a_2'' cross

Figure 4. The 1000 eV noncoplanar symmetric momentum distribution for the 3e' + 1a' states of [1.1.1]propellane. Legends are the same as in Figure 2. Also shown is the result of our PWIA-DFT TZ94p.bspp basis (--- - - -).

Figure 5. The 1000 eV noncoplanar symmetric momentum distributions for the 2e' state of [1.1.1]propellane. Legends are the same as in Figure 2. Also shown is the result for the PWIA-DFT TZ94.bspp basis (- - - - - - -) when a (0.55)2a_1' pole strength contribution is added to that for the 2e' state.
section occurs at a momentum $p \approx 0.62$ au. The PWIA-DFT results with TZ94p.bp and TZ94p.bspp (not plotted) basis states also predict that the peak in this cross section occurs at $p \approx 0.62$ au, but they significantly underestimate the magnitude of the $(e,2e)$ cross section at the peak ($\approx 33\%$ too small in magnitude). This result adds further weight to what we have previously observed for the $1e'$ magnitude). This result is in itself not alarming if we recall that the ADC(3) calculation predicted a pole strength for the $2a'_1$ orbital, at the binding energy $\epsilon_l = 19.07$ eV (i.e., within the binding energy region encompassed by peaks 7–10 of Figure 1), to be only $S_{2a_1'}^{\text{ADC(3)}} = 0.43$. Hence, on this basis, we should $a$ priori expect the full PWIA-DFT $2a'_1 + 1e'$ momentum distribution to overestimate the magnitude of the measured cross section, particularly at small values of $p$ where the $2a'_1$ contribution dominates, which is exactly what we see in Figure 7. If we now consider the theoretical MD which results when only a 43% $2a'_1$ contribution is added to the $1e'$ cross section, in particular within the PWIA-DFT framework for a TZ94.bspp basis, then the level of agreement between the experimental MD and the (0.43)$2a'_1 + 1e'$ PWIA-DFT MD is generally quite good, the exception being at values of momenta $p < 0.35$ au. This lack of agreement between the calculated MD for (0.43)$2a'_1 + 1e'$ and the experimental MD at small values of $p$ is possibly indicative of a limitation of the current $2a'_1$ orbital in the TZ94.bspp basis. Alternatively, it is also possible that there is some $1a_1'$ flux under peaks 7–10 of Figure 1 which we have not accounted for. Certainly the ADC(3) result of Adcock et al.21 shows that the $1a'_1$ orbital spectroscopic strength is severely split among numerous poles. Thus, the possibility of about a 20% $1a'_1$ contribution to the measured MD cannot be discounted here.

The innermost-valence $1a'_1$ state is seen to be severely split among many poles, consistent with the ADC(3) result of Adcock et al.,21 due to final state correlation effects so that two rather broad Gaussians (peaks 11 and 12 of Figure 1) were needed to fit the observed spectral strength for $\epsilon_f \approx 31.5$ eV. Comparing our experimental MD to those calculated within the PWIA-SCF and PWIA-DFT frameworks, it is then apparent from Figure 8 that all the calculations overestimate the magnitude of the $(e,2e)$
Our calculations using the optimum TZ94.bspp basis set gave good agreement between experimentally-determined molecular properties and compared favorably with the results from other MO calculations. In particular, the interbridgehead carbon–carbon distance was 1.59 Å, in excellent agreement with the experimental value of 1.596 Å. The DFT calculations indicated considerable negative charge on the methylene carbons (Mulliken net atomic charge of $-0.538$, Löwdin net atomic charge of $-0.265$) with the bridgehead carbons remaining essentially neutral (Mulliken net atomic charge of $-0.016$, Löwdin net atomic charge of $-0.093$). The results are summarized in Table 3.

From the DFT calculations we were also able to calculate the frequencies of the vibrational modes of [1.1.1]propellane with reasonable accuracy. In addition, the calculated intensities of the transitions are in reasonable agreement with the observed experimental infrared spectrum of [1.1.1]propellane. The main discrepancy is with the intensity of the CH stretching vibrations near 3000 cm$^{-1}$, which are predicted to be weaker than observed. Other theoretical work on the vibrational spectrum of [1.1.1]propellane includes the 6-31G$^*$MP2 calculations of Riggs et al. which yielded excellent agreement with experiment and useful predictions of the properties and stability of the sulfur analogue, trithia[1.1.1]propellane.

It is of particular interest to investigate the electron density in the interbridgehead region of [1.1.1]propellane. We performed a study analogous to that of Wiberg to estimate the electron density ($\rho$) at the bond critical point (midway between the two bridgehead carbons). We obtained a value of $\rho_b = 0.173 \times 10^{-3}$, compared to the Wiberg value of 0.203 $\times 10^{-3}$. We then used the Wiberg empirical method to calculate bond orders from electron densities at the bond critical points derived from the TZ94.bspp basis calculations. The relation between the bond order $n$ and the bond critical point electron densities $\rho_b$ is

$$n = \exp[7.004(\rho_b - 0.224)] \quad (8)$$

This relationship yielded a bond order for the interbridgehead bond in [1.1.1]propellane of 0.70, very similar to the Wiberg value of 0.73. We also calculated the bond order of the interbridgehead bond using Mulliken and Mayer populations analysis. The Mayer bond order of 0.55 was in reasonable agreement with our value of 0.70. The Mulliken value of $-0.11$ reflects the well-known deficiencies of this method of orbital decomposition.

In order to assess the claim of Newton and Schulman that the electron density in the interbridgehead region of [1.1.1]-propellane is little different from that in bicyclo[1.1.1]pentane, we also calculated the electron density and bond order for the latter compound using the same basis set and nonlocal functional as the [1.1.1]propellane calculations. We obtained a value of 0.097 $\times 10^{-3}$ for the electron density midway between the bridgehead carbon atoms of bicyclo[1.1.1]pentane, very similar to the value of 0.098 $\times 10^{-3}$ reported by Wiberg. The bond order from the above empirical relationship (see eq 8) for bicyclo[1.1.1]pentane was 0.40 (for this relationship zero electron density gives a bond order of 0.21), indicating little or no interbridgehead bond in this compound. Mayer population analysis from our DFT calculation of bicyclo[1.1.1]pentane yielded a bond order of 0.075, again consistent with negligible bonding between the bridgehead carbons and markedly different to the value of 0.55 for [1.1.1]propellane.

The present experiment and its analysis contribute to the understanding of the bonding between the bridgehead carbon

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momentum profile. The antibonding s and p contributions to the bridgehead, both of head, and the p contribution is bonding. The 3e character. There is essentially no s contribution to the bridgehead p contribution. The degenerate 1e phase (bonding). There is also a strong out-of-phase (bonding) and methylene carbons. The bridgehead s contributions are in- s character, due to strong s contributions from the bridgehead bridgehead methylene bonds and much larger s character (sp 0.5 ).

In contrast to the previous studies, 17,46 they found much higher propellane, the most-strained example.17,46,19 The most recent study by Jarret and Cusumano 19 estimated the hybridization at

by several workers give contradictory results for [1.1.1-

the carbon 2s and 2p orbitals. The 3a1 functions of the TZ94.bspp model, which are loosely related to atoms in terms of the hybridization of the atom-centered basis functions of the TZ94.bspp model, which are loosely related to the carbon 2s and 2p orbitals. The 3a1 HOMO has very strong s character, due to strong s contributions from the bridgehead and methylene carbons. The bridgehead s contributions are in-phase (bonding). There is also a strong out-of-phase (bonding) bridgehead p contribution. The degenerate 1e'' orbitals have p character. There is essentially no s contribution to the bridgehead, and the p contribution is bonding. The 3e' orbital has antibonding s and p contributions to the bridgehead, both of which are responsible for the p-like character of the 3e' momentum profile. The 1a2' orbital has essentially no contribution from the bridgehead carbons.

The studies of hybridization in [l.m.n]propellanes performed by several workers give contradictory results for [1.1.1]-propellane, the most-strained example.17,46,19 The most recent study by Jarret and Cusumano19 estimated the hybridization at the bridgehead carbons using 13C−13C NMR coupling constants. In contrast to the previous studies,17,46 they found much higher p character (sp8.6−sp4.8) in the three hybrids forming the three bridgehead methylene bonds and much larger s character (sp0.5) for the hybrids forming the bridgehead bond. Since the HOMO makes a substantial contribution to the interbridgehead bond, a point in agreement with the very recent results of Kar and Jug,47 and as we have previously seen that the HOMO is very s-like in nature (see Figure 2), the present results are not inconsistent with the observation of Jarret and Cusumano19 in respect to the hybrid nature of the interbridgehead bond.

6. Conclusions

Using EMS techniques we have been able to a priori assess, for the extensive range of basis states investigated, the quality of these basis states and therefore the validity of the physical representation provided by our respective [1.1.1]propellane wave functions. This procedure enabled us to select our optimum wave function for [1.1.1]propellane, in this case a wave function calculated within a density functional theory framework at the triple-ζ level with Becke, Stoll, Pavlidou, and Preuss nonlocal functionals, from which the subsequently determined molecular properties were found to be in good accord with the available experimental data and other calculations. In particular, we confirmed the existence of the C1−C3 bridging bond with a bond order of n = 0.70.

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Table 3. A Comparison between the Present Results and the Results of Other Calculations and Experiments for Some of the Important Molecular Properties of [1.1.1]Propellane

<table>
<thead>
<tr>
<th>propertya</th>
<th>experimental</th>
<th>theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(Cb−Cb), Å</td>
<td>1.522 ± 0.002</td>
<td>1.518</td>
</tr>
<tr>
<td>r(Cb−Cb), Å</td>
<td>1.60 ± 0.02</td>
<td>1.586</td>
</tr>
<tr>
<td>r(C−H), Å</td>
<td>1.06 ± 0.005</td>
<td>1.094</td>
</tr>
<tr>
<td>∠Cn−Cb−Cn, (deg)</td>
<td>63.1 ± 0.2</td>
<td>62.69</td>
</tr>
<tr>
<td>∠Cb−Cb−Cn, (deg)</td>
<td>95.1 ± 0.1</td>
<td>95.81</td>
</tr>
<tr>
<td>Mulliken charge</td>
<td>Cb</td>
<td>−0.016</td>
</tr>
<tr>
<td></td>
<td>Cn</td>
<td>−0.538</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.274</td>
</tr>
<tr>
<td>Lowdin charge</td>
<td>Cb</td>
<td>−0.093</td>
</tr>
<tr>
<td></td>
<td>Cn</td>
<td>−0.265</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.163</td>
</tr>
<tr>
<td>Cb−Cb bond order</td>
<td>Mulliken</td>
<td>−0.11</td>
</tr>
<tr>
<td>Mayer</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>n (ED)</td>
<td>0.70</td>
<td>0.73</td>
</tr>
</tbody>
</table>

a Cb = bridgehead (axial) carbon atoms; Cn = methylene (equatorial) carbon atoms; ED = from electron density at the bond critical point.

b Mean value.