

Pairing and unpairing electron densities in organic systems: [1.1.1]Propellane case

Rosana M. Lobayan^a, Roberto C. Bochicchio^{b,*}^aDepartamento de Física, Facultad de Ciencias Exactas, Naturales y Agrimensura, Universidad Nacional del Nordeste, 3400 Corrientes, Argentina^bDepartamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and Instituto de Física de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, 1428 Buenos Aires, Argentina

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ABSTRACT

We present a theoretical description of the case of the strained [1.1.1]propellane system by application of the local and nonlocal topological formalisms to the density decomposition into its effectively paired and unpaired contributions. The analysis is mainly focused on the nature of its carbon–carbon headbridge sequence and the existence of 2e–3c complex patterns of bonding. The results clearly indicate that the system only possess 2e–2c patterns, including a true carbon–carbon headbridge bond and no 3c–2e complex patterns of bonding appear.

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1. Introduction

[1.1.1]Propellane is the smallest and most strained system within the set of ring members strained organic compounds (Figure 1). It has a unique structure and a remarkable stability [1,2]. Also its electronic distribution is very intriguing because of two features: the nature of the bond connecting the two headbridge carbon atoms and the possibility of existence of 2e–3c patterns of bonding within its ring structure. Important work has been devoted to these aspects, the former one has been addressed in Refs. [3,4], while the latter, i.e., those dedicated to the existence of 2e–3c structure within its structure appeared in Refs. [1,5,6]. Nonetheless, the conclusions were not coincident between them. The aim of this Letter is to describe the electronic distribution of this molecule from the topological point of view for the electron density and its contributions from the exact decomposition recently reported into paired ($\rho^{(p)}(\mathbf{r})$) and unpaired ($\rho^{(u)}(\mathbf{r})$) ones [7,8]. Both of them possess a different physical character and hence it represents a quantum Lewis conjecture [7,8]. For such a goal, the information contained in the molecular state functions of N -electrons may be translated from the quantum mechanical point of view to the fundamental chemical concepts [9–13] for which the electron density constitutes the central tool in their qualitative and quantitative description [14–16]. Two main and complementary methodologies have been developed to deal with the density. One of these approaches, the *local formulation* relates the topological structure of the density $\rho(\mathbf{r})$ and its associated Laplacian field $\nabla^2\rho(\mathbf{r})$ described by the localization and classification of their critical points (cp) which characterize these fields and therefore permit to extract and interpret chemical information [17,18]. The other approach, the *nonlocal or integrated formulations*, is commonly known as

electronic population analysis and has several implementations [19,20]. The cp's are classified according to the information featured as (r, s) , where r is the *rank* (the number of nonzero eigenvalues of the Hessian matrix of the density $\rho(\mathbf{r})$) and s the *signature* (the sum of the signs of its eigenvalues). Such points are as $(3, -3)$, the nuclear critical point (ncp) and indicates a local maximum placed very close to the nuclear positions. A $(3, -1)$ point corresponds to a bond critical point (bcp) where the concentration of the electron density shows a bonding interaction between two atoms and with the existence of a bond path between the atoms involved defines a bond [17,18]. The remaining cp's, the *ring* (rcp) and *cage* (ccp) critical points, are indicators of more complex structures; and are noted as $(3, +1)$ and $(3, +3)$, respectively [17,18]. The sign of the Laplacian field, $\nabla^2\rho(\mathbf{r})$, i.e., the sum of the curvatures along the orthogonal coordinate axes indicates electron density locally depleted (positive) or locally concentrated (negative) is a valuable local indicator to describe the behavior of the density around a point [17,18]. Comparison of both contributions of the electron density with the total density itself, i.e., the main features that they share and those in which they differentiate has been also reported for systems with classical [7,8] and complex patterns of bonding [21,22]. Extension of the application of this methodology of description of the electron distributions to systems organic nature possessing special features, a strained structure in this case, are twofold, on one side to continue testing the method over different type of structures, and on the other side to get a more deep understanding of the electron distribution of these systems. As has been pointed out, the main purpose of this Letter is to study the capability of these tools to describe arbitrary electron distributions including as is obvious, nonconventional bonding as the $(3c-2e)$ ones. The organization of this Letter is as follows. The second section is devoted to a brief report of the theoretical framework of the methodology, partitioning of the electron density, relationships between the density gradients and Laplacian of

* Corresponding author.

E-mail address: rboc@df.uba.ar (R.C. Bochicchio).

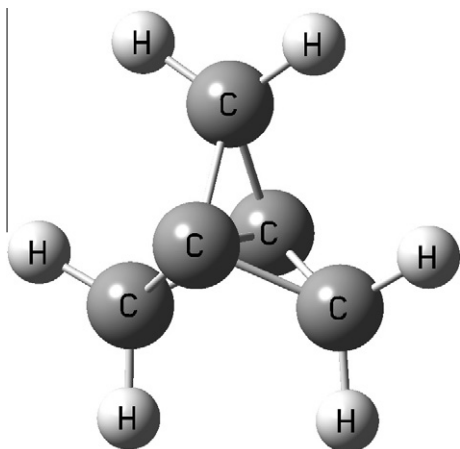


Figure 1. [1.1.1]Propellane structure.

both fields, as well as the tools used to carry out the studies of topological population analysis. The third section describes the computational details, the results and the discussion. Finally, the last section is dedicated to the concluding remarks.

2. Theoretical background

The electron density, $\rho(\mathbf{r})$, in an N -electron molecular system may be decomposed into two contributions [7,8]

$$\rho(\mathbf{r}) = \rho^{(p)}(\mathbf{r}) + \rho^{(u)}(\mathbf{r}) \quad (1)$$

where $\rho^{(p)}(\mathbf{r})$ and $\rho^{(u)}(\mathbf{r})$ indicate the effectively paired and unpaired densities, expressed by

$$\rho^{(p)}(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' {}^1D(\mathbf{r}|\mathbf{r}') {}^1D(\mathbf{r}'|\mathbf{r}), \quad \rho^{(u)}(\mathbf{r}) = \frac{1}{2} u(\mathbf{r}|\mathbf{r}) \quad (2)$$

respectively. ${}^1D(\mathbf{r}|\mathbf{r}')$ is the spin-free first-order reduced density matrix (1-RDM) in the coordinate representation [15,23], its trace (coordinate integration over the whole real space) is the number of electrons in the system, i.e., $tr({}^1D) = \int d\mathbf{r} {}^1D(\mathbf{r}|\mathbf{r}) = \int d\mathbf{r} \rho(\mathbf{r}) = N$. $u(\mathbf{r}|\mathbf{r})$ is the diagonal element of the effectively unpaired density matrix defined by $u(\mathbf{r}|\mathbf{r}') = 2 {}^1D(\mathbf{r}|\mathbf{r}') - {}^1D^2(\mathbf{r}|\mathbf{r}')$ where ${}^1D^2(\mathbf{r}|\mathbf{r}') = \int d\mathbf{r}'' {}^1D(\mathbf{r}|\mathbf{r}'') {}^1D(\mathbf{r}''|\mathbf{r}')$ [7,8,15], i.e., the densities are the diagonal part of the corresponding reduced density matrices. The physical meaning of the traces of the effectively paired and unpaired densities is the number of paired (opposite spins) and unpaired (far away) electrons. The unpaired density has two sources, one of them comes from the spin density (only present in non-singlet states) and the other corresponds to the many-body effects or correlation effects that are supported by the Coulomb interaction between the particles [24]. It may be noted that for state functions having all orbitals doubly occupied, as in the closed-shell Hartree-Fock or density functional theory (DFT) cases, $\rho^{(u)}$ is intrinsically zero [25–29] and such effects cannot be detected.

The electron density topology description [17,18] can also be straightforwardly applied to both of the scalar fields components, to describe bonding features in a precise manner. The fundamental information is obtained from the nature and localization of the cp's of each contribution to the electron density and their local accumulation/depletion in physical regions of the system. The cp's of the total density are determined throughout the gradient of the field by

$$\nabla \rho(\mathbf{r})|_{\mathbf{r}^c} = 0, \quad \nabla \rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c} + \nabla \rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c} = 0 \quad (3)$$

where $\mathbf{r}^c = \{\mathbf{r}_i^c; i = 1, \dots, M\}$ indicates the set of critical points of the total density $\rho(\mathbf{r})$ and Eq. (1) has been considered. Then it follows,

$$\nabla \rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c} = -\nabla \rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c} \quad (4)$$

whose physical meaning is that each density field component increases/decreases its value in opposite direction, i.e., when $\rho^{(p)}(\mathbf{r})$ increases its value, the other part of the density, the unpaired contribution, properly does it in the opposite direction [7]. The Laplacian field of Eq. (1) yields

$$\nabla^2 \rho(\mathbf{r})|_{\mathbf{r}^c} = \nabla^2 \rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c} + \nabla^2 \rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c} \neq 0 \quad (5)$$

Eq. (5) clearly show that both, $\nabla^2 \rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c}$ and $\nabla^2 \rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c}$ contributions do not necessarily follow opposite trends, as the above mentioned ones for the density gradient, i.e., both density may concentrate or deplete at the neighborhood of a cp, simultaneously. It is worthwhile to note that within this context $\rho^{(p)}(\mathbf{r})$ and $\rho^{(u)}(\mathbf{r})$ densities possess a shell structure as the $\rho(\mathbf{r})$ one [8,30].

The nonlocal or integrated formalism is the complementary to the above mentioned local one. It deals with classical chemical concepts like atomic charges, bond orders and valences, etc. [9–13] We will refer to the nonlocal AIM topological population analysis. Let us summarize the relations defining the relevant magnitudes to our goal, which have been previously stated within that approach [11–13,31–33]. The covalent bond order (two-center bond index) has been defined as

$$I_{\Omega_A \Omega_B} = \sum_{i,j,k,l} {}^1D_j^i {}^1D_l^k S_{il}(\Omega_A) S_{kj}(\Omega_B) \quad (6)$$

where Ω_A and Ω_B stand for Bader's atomic domains in the physical space [17,18], ${}^1D_j^i$ the first-order reduced density matrix elements and $S_{ij}(\Omega_A)$ the elements of the overlap matrix over the region Ω_A , in the orthogonal molecular basis set $\{i, j, k, l, \dots\}$ [32,33]. Within the same context, the three-center bond population (or three-center bond index) is defined by

$$I_{\Omega_A \Omega_B \Omega_C} = \sum_{i,j,k,l,m,n} {}^1D_j^i {}^1D_l^k {}^1D_n^m S_{in}(\Omega_A) S_{kj}(\Omega_B) S_{ml}(\Omega_C) \quad (7)$$

giving raise to the three-center topological bond order as [32,33]

$$\Delta_{\Omega_A \Omega_B \Omega_C}^{(3)} = \frac{1}{4} \sum_{P(\Omega_A \Omega_B \Omega_C)} I_{\Omega_A \Omega_B \Omega_C} \quad (8)$$

where $P(\Omega_A \Omega_B \Omega_C)$ stand for the permutations of the three domain contributions. Finally, the unpaired population is quantified by [11,25–29]

$$u_{\Omega_A} = 2 \sum_{ik} {}^1D_k^i \langle i|k \rangle_{\Omega_A} - \sum_{ijkl} {}^1D_l^i {}^1D_k^j \langle i|k \rangle_{\Omega_A} \langle j|l \rangle_{\Omega_A} - \sum_{B \neq A} \sum_{ijkl} {}^1D_l^i {}^1D_k^j \langle i|k \rangle_{\Omega_A} \langle j|l \rangle_{\Omega_B} \quad (9)$$

3. Computational details, results and discussion

The state functions has been calculated at the level of configuration interaction with single and double excitations (CISD) with the basis sets 6-31G** using the GAMESS04 package [34]. The geometries for all systems were optimized within this approximation. The densities, their critical points and their Laplacian fields $\nabla^2 \rho^{(p)}(\mathbf{r})$ and $\nabla^2 \rho^{(u)}(\mathbf{r})$ were determined by modified AIMPAC modules [35]. The numerical results of populations analysis were obtained with our own codes mentioned in Refs. [9–13] For practical reasons, we will use the function $L(\mathbf{r}) = -\nabla^2 \rho(\mathbf{r})$ in the discussion of the results as an indicator of local concentration (positive value) or local depletion (negative value) of the number of electrons at the point \mathbf{r} [17,18,30]. The terms accumulation and depletion have been proposed for the description of maxima and minima in $\rho(\mathbf{r})$ [17,18,30]. Because of the complex structure of the $\rho^{(u)}(\mathbf{r})$ topology, we will only deal with critical points

associated with its valence shells (vs) in the corresponding systems and no reference will be made to those of the inner shells of this density; in fact, only the former ones are involved in bonding phenomena. The terminology vs (3, -1) cp, vs (3, +1) cp and vs (3, +3) cp will refer to (3, -1), (3, +1) and (3, +3) critical points of $\rho^{(u)}(\mathbf{r})$ valence shell, in analogy with the bcp, rcp and ccp's of the total density. Nevertheless, it is important to note that such points are not *sensu strictu* bcp, rcp or ccp's because only the cp's of the total density are able to define a bond in the AIM topological formalism [17,18]. The discussion of the results about the existence of the complex 2e-3c patterns of bonding will be considered in the light of the quantum rule we have successfully built on the basis of well known systems possessing such bonding patterns, like boron hydrides and then applied to some evolved structures, the closo-boranes [21,22]. Because of the above mentioned controversy in the literature about the [1.1.1]propellane electron structure, it is a privileged system for testing the rule in organic compounds which are natural candidates to possess 2e-3c complex patterns. Let us begin the discussion by enunciating the quantum rule and getting its result about this question for this organic compound: *in borane systems a (2e-3c) bond between atoms ABC exists if there is a vs (3, -1) cp of $\rho^{(u)}$ between each pair of atoms involved in the three-center ABC sequence and a vs (3, +1) cp defined only by the atoms involved in the three center bond*, hereafter called the *local rule*. Despite of being implicit in the rule, it must be remarked that at least two of the atoms involved in the 3c bond can not be classically bonded, i.e., there will not be a bcp and a bond path between them. This result seems to be the local version of the criterion of the integrated formalism of population analysis for detecting three-center bonding, hereafter: *the integrated or nonlocal rule*. That criterion settles down the existence of a (2e-3c) bond between atoms ABC when fractional bond orders $I_{\Omega_A\Omega_B}$ appear between all possible pairs of atoms AB, BC and AC and the covalent 3c population $\Delta_{\Omega_A\Omega_B\Omega_C}^{(3)}$ is appreciable [21,22].

Figure 1 shows the molecular structure of [1.1.1]propellane. Table 1 shows a detailed description of the electronic distribution from the topological (local and nonlocal) point of view for this system. Note that no reference to the effectively paired density $\rho^{(p)}(\mathbf{r})$ is made in Table 1 because as shown in previous articles, its structure is similar to that of $\rho(\mathbf{r})$ and therefore it does not introduce any new information [21,22]. Table 2 is devoted to the topological structure of $\rho^{(u)}(\mathbf{r})$ and its associated chemical descriptor u_{Ω} . Table 3 shows the numerical values for each density and its $L(\mathbf{r})$ field at bcp's and vs (3, -1) cp's.

Table 1
Electronic structure of [1.1.1] propellane. Local and integrated (nonlocal) topological features of $\rho(\mathbf{r})$ density at CISD/6-31G** level of approximation. All quantities are in atomic units.

cp type	ρ sequences ^a	Bond	$I_{\Omega_A\Omega_B}$	$\Delta_{\Omega_A\Omega_B\Omega_C}^{(3)}$
[1.1.1]propellane				
ncp	one on each C, H atoms			
bcp ^b	one for the $C_{bh}C_{bh}$ ^c sequence	$C_{bh}C_{bh}$	0.673	
	one for each $C_{bh}C_b$ sequence	$C_{bh}C_b$	0.946	
	one per each of C_bH sequence	C_bH	0.931	
rcp	one for each $C_{bh}C_bC_{bh}$ sequence	$C_{bh}C_bC_{bh}$		0.146
ccp	no present	$C_bC_{bh}C_b$		0.047

^a Indicate the nucleus at which the **ncp** is located; for **bcps**, the atoms defining the bond; for **rcps**, the atoms giving rise to the ring; for **ccps**, the atoms defining the cage.

^b Each bcp reported indicates also the existence of the corresponding bond path between these atoms both defining the bond, otherwise it will be specified in the text.

^c C_{bh} and C_b stand for a *bridgehead* and *bridging*-carbon atoms, respectively.

Table 2

Electronic structure of [1.1.1] propellane. Local and integrated (nonlocal) topological features of $\rho^{(u)}(\mathbf{r})$ density at CISD/6-31G** level of approximation. All quantities are in atomic units.

cp type	$\rho^{(u)}$ sequences ^a	Atom	u_{Ω_A} ^c
[1.1.1]propellane			
vs (3, -3) cp	one on each C, H atoms	C_{bh}	0.190
		C_b	0.160
		H	0.060
vs (3, -1) cp	one for the $C_{bh}C_{bh}$ ^b sequence		
	one for each $C_{bh}C_b$ sequence		
	one per each of C_bH sequence		
vs (3, +1) cp	one for each $C_{bh}C_bC_{bh}$		
vs (3, +3) cp	no present		

^a Indicate the nucleus at which the **vs (3, -3) cp** is located; for **vs (3, -1) cps**, the atoms defining the corresponding bond; for **vs (3,+1) cps**, the atoms giving rise to the ring; for **vs (3,+3) cps**, the atoms defining the cage.

^b C_{bh} and C_b stand for a *bridgehead* and *bridging*-carbon atoms, respectively.

^c Effectively unpaired atomic electron index.

The topological structure of the total density ρ shown in Table 1 exhibits one ncp located on each nucleus. Let us note, C_{bh} and C_b the *bridgehead* and *bridging*-carbon atoms, respectively. The $C_{bh}C_b$ and C_bH sequences are bonded and show accumulation and depletion at the bcp and vs (3, -1) cp for the paired and unpaired densities, respectively as reported in Table 3 which stand for a typical covalent interactions except for the greater ellipticity than in those cases because of the strain of the system [7,8].

The covalent bond orders in Table 1 are very close to one, which confirms this result and state for single bonds. The absence of bcp's between C_b atoms indicates that the C_b atoms are not bonded (cf. Table 1). Table 3 show that ρ and $\rho^{(u)}$ has similar values at bcp and vs (3, -1) cp for $C_{bh}C_b$ sequences indicating that both cps are not appreciable displaced between them; on the contrary in C_bH sequence the displacement is appreciable as shown by the different values of the densities. Table 2 shows that each nucleus exhibits a vs (3, -3) cp and also a vs (3, -1) cp for each $C_{bh}C_{bh}$, $C_{bh}C_b$ and C_bH sequences. The total density shows a **rcp** for each $C_{bh}C_bC_{bh}$ sequence and no **ccp**, as expected because the system posses a ring but no a cage structure.

An analog structure is found for $\rho^{(u)}$ where a vs (3, +1) cp is present for each $C_{bh}C_bC_{bh}$ ring sequence but no vs (3, +3) cps are present. The sequences $C_{bh}C_{bh}$, $C_{bh}C_b$ and C_bH exhibit a vs (3, -1) cp $\rho^{(u)}$ and each C_{bh} and C_b nucleus show a high concentration of unpaired electrons as indicated for the u_{Ω_A} values, 0.19 and 0.16, respectively. These results enable us to interpret these bonds as a nonelectron deficient, i.e., they do not transfer charge to any other part of the system and this results are compatible with a 2c-2e type bonding system in agreement with the local view of the unpairing density depletion at the bcp's as mentioned above (cf. Table 3).

All these results may be globally appreciated from Figure 2 where $L(\mathbf{r})$ is shown for the paired and unpaired density at $C_{bh}C_bC_{bh}$ plane; Figure 2a shows a strong concentration of the paired density which gives rise to the onset of the bcp between all carbon atoms; Figure 2b shows that a very slight spillage of $\rho^{(u)}$ appears between $C_{bh}C_bC_{bh}$ in agreement with the high unpaired electron populations around the nucleus. As was expressed above, the sequence formed by the *headbridge* carbon atoms $C_{bh}C_{bh}$ has been matter of a wide discussion. The controversies range from its existence as a *true* bond to its very nature [1-5].

The information about this sequence reported in Table 1 show one bcp and an associated bond path between the atoms, hence it confirms the existence of a true bond featured by a high covalent bond order. Figure 3 shows the electron density map of the natural orbital defined by the two C_{bh} atoms at the same plane of Figure 2 which clearly shows its bonding character [5]. From Table 3 it may

Table 3

Density and $L(\mathbf{r})$ of the total density ρ and $\rho^{(u)}$ for [1.1.1] propellane at bond critical points of the total density at CISD/6-31G** level of calculation^a. All quantities are in atomic units.

System ^b	Bond	$\rho(\mathbf{r}) _{bcp}$	$\rho^{(u)}(\mathbf{r}) _{bcp}$	$-\nabla^2\rho(\mathbf{r}) _{bcp}$	$-\nabla^2\rho^{(u)}(\mathbf{r}) _{bcp}$	ε^c
[1.1.1]propellane	$C_{bh}C_b$	0.2475	0.0044	0.4832	-0.0064	0.4890
		0.2475	0.0044	0.4751	-0.0064	0.0544
	$C_bC_b^{df}$					
	$C_{bh}C_{bh}$	0.1963	0.0042	-0.0636	-0.0039	0.0002
		0.1963	0.0042	-0.0636	-0.0039	0.0000
	C_bH	0.2942	0.0041	1.1131	-0.0041	0.0128
		0.2949	0.0041	1.1798	-0.0035	0.0953
rcp		0.1927	0.0036	-0.0953	-0.0088	
		0.1988	0.0033	-0.0526	-0.0125	

^a Second line in Columns 3 to 7 for each bond indicates the densities and $L(\mathbf{r})$ at $\rho^{(u)}(\mathbf{r})$ vs (3, -1) cp.

^b See Figure 1 for atoms labeling.

^c Ellipticity.

^d There are no bcp points for $\rho(\mathbf{r})$ between these atoms.

^f There are no vs (3, -1) cp's for $\rho^{(u)}(\mathbf{r})$ between these atoms.

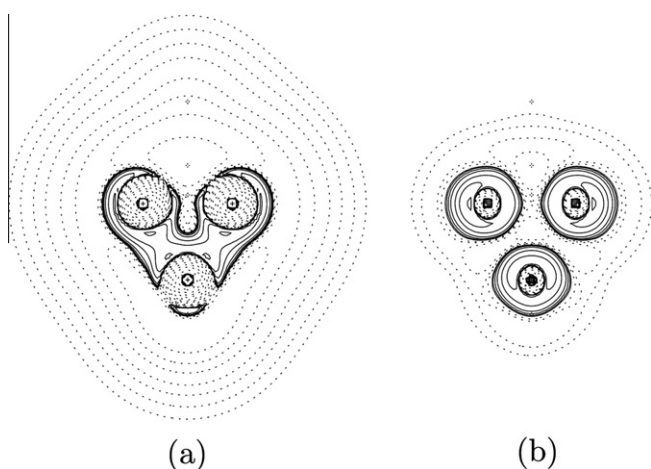


Figure 2. $L(\mathbf{r})$ contour maps for effectively paired (a) and effectively unpaired densities (b) in the plane defined by $C_{bh}C_bC_{bh}$ atoms. Positive and negative values are denoted by solid and dashed lines, respectively.

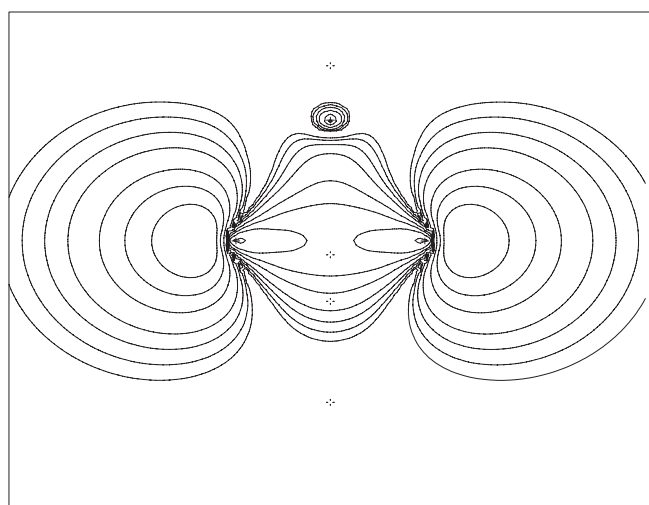


Figure 3. Total electron density map of the natural orbital localized at the $C_{bh}C_{bh}$.

be noted, that both, the total and the unpaired densities deplet at the bcp for this sequence. This result is similar to the cases of F_2 [7] and $CINa$ [8] systems, except that in the present case there are a very slight $\rho^{(u)}$ spillage which does not appear at the other

cases. Some authors have included this type of bond in the so called 'charge-shift bond' (CSB) defined by the density depletion at the bcp [4] or *deficient covalent bond* [36]. Our calculations confirm this character for this bond and in this particular case a depletion of the unpaired density is also noted from Table 3. Hence it permits to open a question if that this specificity may be extended as a general character of this CSB, i.e., not only for the decrement of the total density but for the paired and unpaired densities as well at the bcp, as an indicator of important energetic interaction of covalent and ionic structures. There also exist a rcp formed by the two *headbridge* carbons C_{bh} and the bridge one C_b , which is characterized by a high three-center population, 0.146.

The features of all bonds analyzed here indicate the molecular structure of this system may be considered as formed by 2e–2c interactions although one of them, i.e., the $C_{bh}C_bC_{bh}$ is a nontypical one. This is consistent with the view of the structure from the quantum rule. Table 2 indicate that the electron distribution fulfills all conditions for the rule, except that the $C_{bh}C_{bh}$ is bonded and it breaks the implicit feature indicated above that at least two of the atoms must not be bonded [7,8], and hence no 2c–3e bonding patterns are present in this system. Otherwise the bonding structure would be reducible to 2e–2c bonds and complex 2e–3c pattern would be senseless.

4. Concluding remarks

In this Letter, we have dealt with the most stable strained organic molecule which has devoted a wide spectra of opinions about the nature of its electronic distribution. Some results in the literature interpreted that this systems has 2e–3c patterns of bonding and/or that the two carbon headbridge atoms were not bonded. Other opinions were in controversy with those ones. It is well-known that 2e–3c bonds tends to appear at electron-deficient compounds, emblematic examples of such systems are boron hydrides. Our results show that the present system has enough additional electrons and therefore such electron deficiency is broken. We may conclude, in view of the application of the topological local rule, that the electronic distribution of [1.1.1]propellane has only 2e–2c patterns, and no 3c–2e complex patterns of bonding appear. Finally, we may note that organic compounds with well-known 2e–3c patterns are being considered in our laboratories as the natural continuation of this investigation.

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