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ELF Analysis of Out-of-Plane Aromaticity and In-Plane Homoaromaticity in Carbo[*N*]annulenes and [*N*]Pericyclynes

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The aromaticity and homoaromaticity in ring carbomers of [*N*]annulenes and [*N*]cycloalkanes (i.e., [*N*]pericyclynes) are investigated using the topological analysis of the electron localization function (ELF). In a qualitative viewpoint, the ELF picture of aromaticity in carbo[*N*]annulenes is systematically "expanded" with respect to those of the parent [*N*]annulenes. The ELF analysis allows us to evaluate the weight of the various resonance forms of carbo[*N*]annulenes corresponding to (i) out-of-plane cyclic π electron delocalization and (ii) in-plane cyclic π electron homodelocalization. The latter is also quantified for the parent [*N*]pericyclynes. The chemical relevance of this evaluation is discussed by comparison with Bader's atoms-in-molecules topological analysis of the electron density and Hückel analysis. New criteria of homoaromaticity based on ELF analysis are proposed and further illustrated on the archetypes of homoaromaticity such as the homotropenylium cation and the cyclopropylcarbinyl cation.

Introduction

The carbomer structure of any given molecule is obtained by inserting a dicarbon C_2 unit into each bond of the representative Lewis structure of this molecule (and by reversing the whole charge in the case of a ionic molecule).[1] The symmetry, the shape, and the resonance properties of the original molecule are approximately retained in the carbomer structure, whereas the original molecule is almost homogeneously expanded by a factor of 3. This carbomerization process is illustrated in Scheme 1.

SCHEME 1

$$\mathrm{X{-}Y \rightarrow X{-}C{\equiv}C{-}Y \qquad X{=}Y \rightarrow X{=}C{=}C{=}Y \qquad X{\equiv}Y \rightarrow X{\equiv}C{-}C{\equiv}Y}$$

Aromaticity is expected to stabilize such highly unsaturated structures. Indeed aromatic derivatives of $[C,C]_6$carbobenzene of D_{6h} symmetry have been recently reported.[2,3] Density functional theory calculations performed at the B3PW91/6-31G** level have shown that the ring carbomer $(C_3H)_N$ of aromatic [*N*]annulenes $(CH)_N$ is aromatic according to structural (D_{Nh} symmetry), magnetic (nucleus independent chemical shift at the center of the ring (NICS)[4]), and energetic (Breslow resonance energy of the π_z electron system) criteria.[5,6]

In addition to the aromaticity already present in the parent [*N*]annulene, an "in-plane homoaromaticity" is envisionned in the carbo[*N*]annulene. This homoaromaticity would result from the in-plane interaction of the p orbitals of the C_2 units via the antibonding orbitals of C−H vertices. The term homoaromaticity was introduced by Winstein[7] in 1959 to describe compounds that display aromaticity-like properties despite one or more saturated linkages interrupting the formal cyclic conjugation, i.e., a homoconjugation resulting in electron or bond delocalization.[8] The Breslow-type π-resonance energy corresponding to homoaromaticity of carbo[*N*]annulenes has been calculated within the framework of the Hückel theory.[6] From this analysis, the stabilization resulting from in-plane homaromaticity is about 20 times smaller than the one resulting from out-of-plane aromaticity and thus appears as a second-order stabilizing effect with respect to the open-chain homoconjugated system. To support these results, cyclic electron homodelocalization is quantified here using a suitable tool.

The topological analysis of the gradient field of the electron localization function[9] (ELF) was recently introduced by Silvi and Savin as a mathematical model of the Lewis theory.[10] This method is in its principles independent of quantities such as molecular or atomic orbitals appearing as intermediates during the course of approximate procedures of solution of the many-body Schrödinger equation. It enables a partition of the molecular space into electronic domains. It has been successfully used in order to analyze the chemical bonds in molecular systems or materials.[11] The ELF analysis has already been carried out for academic examples of aromaticity such as benzene[12] or substituted benzene.[13,14] There is only one di-synaptic basin corresponding to the aromatic C−C bond with a population intermediate between that of a single and double bond.[12] As ELF is a totally symmetrical and global function, its analysis provides no evidence for any σ or π systems in benzene. ELF analysis has also been used to investigate the aromaticity in five-membered rings C_4H_4X.[15] A strong and smooth correlation between the populations of the basin corresponding to the formal single C−C bond facing the heteroatom and resonance energies was evidenced. In these structures, electron delocalization is evidenced by a significant variance of the population of the basins involved in the aromaticity.[16]

ELF appears therefore attractive in order to study the aromaticity and homoaromaticity of the new class of aromatic carbomers. In this work, this new tool is used to evaluate the weight of the various resonance forms of carbo[*N*]annulenes corresponding to (i) out-of-plane cyclic π electron delocalization and (ii) in-plane cyclic π electron homodelocalization. The in-plane cyclic π electron homodelocalization is also quantified for the parent [*N*]pericyclynes.

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Computational Details

Geometries were fully optimized at the B3PW91/6-31G** level using Gaussian 94[17] or Gaussian 98.[18] Vibrational analysis was performed at the same level in order to check that a minimum on the potential energy surface was obtained.

Atomic charges were derived from atoms-in-molecules[19] (AIM) analysis using TopMoD[20]

NICS (nucleus independent chemical shift) of the [*N*]-pericyclynes were computed according to the procedure described by Schleyer et al.[4] The magnetic shielding tensor was calculated for a ghost atom located at the center of the ring using the GIAO (gauge including atomic orbital)[21] method implemented in Gaussian 98.

ELF topological analysis was carried out with TopMoD.[20] Visualization of ELF isosurfaces and basins were done with the freeware SciAn.[22]

Topological Analysis of ELF

The electron localization function (ELF) was introduced in 1990 by Becke and Edgecombe.[9] It provides a probe of the efficiency of the Pauli repulsion at each point of the position space. Where electrons are single or form an antiparallel spin pair, ELF is close to 1, whereas it tends to 0 where the probability to find parallel spin electrons close to one another is high.

The topological analysis of the ELF gradient field yields a partition of the molecular space into electronic domains: the ELF basins and corresponding attractors (i.e., the local maxima of ELF). The latter are classified into core, valence bonding, and nonbonding basins. A core basin contains a nucleus X (except a proton) and will be referred to as C(X). A valence bonding basin lies between two or more core basins. Valence basins are further distinguished depending on their connectivity to the core basins. Each valence basin is characterized by its synaptic order which is the number of core basins with which it shares a common boundary. The monosynaptic basins therefore correspond to nonbonded pairs (referred to as V(X)), whereas the di- and polysynaptic ones are related to bi or multicentric bonds (referred to as V(X_1, X_2, X_3, ...).

The average populations of the basins may be obtained by integration of the electron density over the basin. They are not expected to have integral values, and the bond populations are about twice the topologically defined Lewis bond orders. The related variance, which is a measure of the quantum mechanical uncertainty of the basin population, may be calculated. The latter may be interpreted as a consequence of the electron delocalization.[16,23]

A localization domain is a region of space encompassed with an isoELF surface. The bifurcation tree diagram describing the evolution of the localization domains with the ELF value allows us to distinguish between the bonding modes and to predict the more reactive moieties of the studied system.

The interpretation of the ELF basin populations in terms of a superposition of weighted resonance structure contributions should provide a link between the topological approach and a more traditional way of thinking chemistry. For an *N*-electron system, it is possible to calculate the probability of finding *k* electrons in a given basin Ω_s,[24] hereafter denoted by $p_k(\Omega_s)$:

$$p_k(\Omega_s) = \frac{N!}{k!(N-k)!}\int_{\Omega_s}\boldsymbol{r}_1\cdots\int_{\Omega_s}\boldsymbol{r}_k\int_{\Omega}\boldsymbol{r}_{k+1}\cdots\int_{\Omega}\boldsymbol{r}_N\Gamma^{(N)}\times(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N) \quad (1)$$

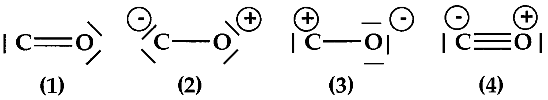
where $\Gamma^{(N)}(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N)$ is a diagonal element of the spinless *N*-particle density matrix and where Ω is the disjoint region complementary to Ω_s (the entire space minus Ω_s). The calculation of the $p_k(\Omega_s)$'s is difficult to handle because it requires the use of the full *N*-particle density matrix which tremendously increases the arithmetic complexity. Once the $p_k(\Omega_s)$ have been calculated for all of the *M* basins, it is not possible to recover the weight of all of the possible resonance structures in a rigorous fashion.

TABLE 1: Basin Populations ($\bar{N}$), Variance of the Basin Populations (σ^2), and Number of Electrons Per Basin of the Resonance Structures[a]

	ELF			Lewis structure			
	$\bar{N}$	scaled $\bar{N}$	σ^2	1	2	3	4
V(C)	2.60	2.62	0.81	2	4	2	2
V(C, O)	3.34	3.36	1.52	4	2	2	6
V(O)	3.99	4.02	1.49	4	4	6	2

[a] The scale factor is $10.0/\sum\bar{N}(\Omega_s) = 10.0/9.83 = 1.017$.

SCHEME 2



The interpretation of the basin populations in terms of superposition of resonance structures relies on the assumption that a resonance structure can be associated to each distribution of the *N* electrons in the *M* basins. The fact that the number $(N + M - 1)!/(M - 1)!N!$ of such distributions is usually larger than the number of $p_k(\Omega_s)$, $M(N + 1)$ severely hampers any rigorous approach. Moreover, the calculations of the *k*-electron basin populations requires a rather huge numerical complexity for $k > 2$. It is obvious that the weight of many distributions should be very low (for example those with all of the electrons in the same given basin). To attempt to determine the weights of a selection of reasonable intuitive resonance structures, we use and recommend the following procedure which only requires the one electron basin populations and their variance which are provided in the output of the TopMoD package. The interpretation is limited to the valence electrons or to a subset of the valence electron which are distributed in the valence basins or in a subset of the valence basins.

For example, the ELF analysis yields three valence basins for the carbon monoxide molecule, namely, V(C), V(C, O), and V(O), which are all used to localize the 10 valence electrons. Let *M* be the number of symmetry independent valence basins. In principle, it would be possible to calculate the weights of $M + 1$ symmetry independent valence structure contributions from the *M* basin populations provided that all other structures can be neglected by applying the following rules:

(1) The populations are scaled to the actual number of electrons involved in the resonance structures;

(2) Bond electrons are assigned to the relevant disynaptic basin;

(3) Lone pair electrons are assigned to the relevant monosynaptic basin if it exists, otherwise they are shared by the disynaptic basins involving the center bearing the lone pair;

(4) The resonance structures are chosen on the basis of chemical experience and also to account for the variance of the basin populations.

Table 1 reports the ELF population analysis of carbon monoxide and the number of electrons per basin of each proposed resonance structure. The four resonance structures considered are shown in Scheme 2.

Structure 1 corresponds to electron numbers close to the actual basin populations, structures 2 and 3 enable the V(C, O) population to be less than 4 and the variance of V(O) to be

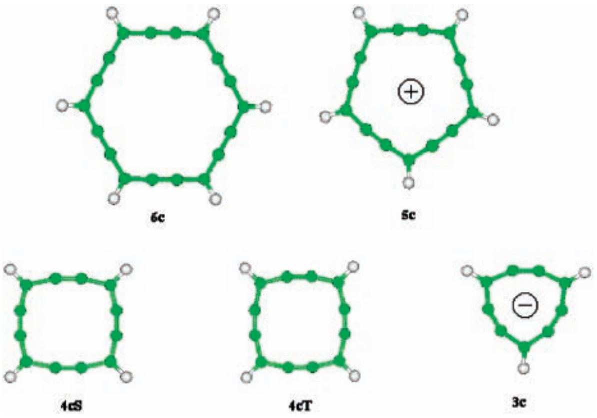


Figure 1. Optimized geometry at the B3PW91/6-31G** of the ring carbomers **Nc** of [*N*]annulenes.

rather large, and structure 4 is the structure which obeys the octet rule. Let w_i be the weights of the contributions of these resonance structures which can be calculated by the following system of four linear equations:

$$w_1 + \mathrm{w}_2 + w_3 + w_4 = 1.0$$
$$2w_1 + 4w_2 + 2w_3 + 2w_4 = 2.62$$
$$4w_1 + 2w_2 + 2w_3 + 6w_4 = 3.34$$
$$4w_1 + 4w_2 + 6w_3 + 2w_4 = 4.02$$

Unfortunately, the determinant of the linear system is zero because the average of the electron numbers of structures 3 and 4 corresponds to the distribution of structure 1. Nevertheless, one finds $w_2 = 0.31$, $w_1 + w_3 + w_4 = 0.69$ and $w_4 - w_3 = 0.01$.

To remove the indetermination, we now consider the variance of the V(O) basin whose "classical" expression is $w_1(4.02-4)^2 + w_2(4.02-4)^2 + w_3(6-4.02)^2 + w_4(4.02-2)^2$. Substituting w_1 and w_2 by their values and w_4 by $w_3 + 0.01$, one gets $\sigma^2 = 8.76w_3 + 0.02$. The calculated value 1.49 is an upper bound for this estimate because it contains contributions arising from all the possible arrangements of the electrons in the basins. Therefore, $0 < 8.76w_3 < 1.47$ which yields $0 < w_3 < 0.17$. A reasonable agreement between all of the calculated and estimated variances is thus achieved for $w_1 = 0.48$, $w_2 = 0.31$, $w_3 = 0.10$, and $w_4 = 0.11$.

Surprisingly, the two leading contributions (1) and especially (2) do not obey the octet rule. Structures 1, 3, and 4 are those considered by Pauling[25] on the assumption that the octet rule is the prominent criterion. Structure 4 was invoked to account for the electron-richness properties of the carbon atom (dipole moment orientation, coordinating ability). Theses properties are however also described by structure 2 despite it rules out the octet rule. The weight of (2) + (4) is 0.42 which is close to the value of 0.40 proposed by Pauling assuming $w_2 = 0$.

Results

The geometries of the ring carbomer of [*N*]annulenes (referred to as **Nc**) were fully optimized at the B3PW91/6-31G** level (Figure 1).[5,6] Some of the structural parameters of their D_{Nh} calculated structures are presented in Table 2.[5,6]

Two types of carbon atoms may be distinguished: (i) C_α is an sp^2 carbon atom located at the vertices, whereas (ii) C_β is an sp carbon atom located in the edges. The orbital analysis allows to distinguish two classes of π molecular orbitals (MO): (i) the π_z MO system results from the cyclic overlap of 2p(C) atomic orbitals out of the ring plane, and (ii) the π_{xy} MO system results from the cyclic overlap of 2p(C_β) atomic orbitals in the ring plane. The former, presented in Figure 2 for **6c**, may be associated with aromaticity that has been evidenced through structural, magnetic, and energetic criteria.[5,6] In the π_{xy} MO system, presented in Figure 3 for **6c**, the overlap formally occurs via the σ^*(C_α-H) orbitals. The splitting of bonding π_{xy} MOs is rather small (about 0.005 au) suggesting that the stabilizing effect expected from the related homoconjugation is rather small. The aromaticity of the ring carbomers of [*N*]annulenes has been studied in the framework of Hückel analysis by assuming a single Coulomb integral α and a single averaged resonance integral β for C_α, C_β (Figure 4a).[6] The homoaromaticity has been studied similarly using the same resonance integral β for $C_\beta-C_\beta$ in-plane interaction than the one determined for the $C_\beta-C_\beta$ out-of-plane interaction. An additionnal resonance integral β' related to the transannular $C_\beta-C_\beta$ interactions (Figure 4b) was also determined.[6]

TABLE 2: Selected Geometric Features of the Calculated Structures of Carbo[*N*]annulenes (Distances in Å)

	$C_\alpha-C_\beta$	$C_\beta-C_\beta$	1,3 transannular $C_\beta-C_\beta$
6c	1.369	1.239	2.401
5c	1.369	1.238	2.353
4cT (triplet)	1.378	1.241	2.327
4cS (singlet)	1.428, 1.334	1.218, 1.267	2.233
3c	1.389	1.253	2.275

TABLE 3: Average Population (*N*) and Variance (σ^2) of the ELF Basins of Carbo[*N*]annulenes

	$C_\alpha-C_\beta$		$C_\beta-C_\beta$	
	N	σ^2	*N*	σ^2
6c	2.90	1.37	4.71	1.57
5c	2.83	1.32	4.68	1.56
4cT (triplet)	2.91	1.33	4.69	1.59
4cS (singlet)	2.24	1.12	5.41	1.50
	3.54		4.25	1.50
3c	2.91	1.37	4.60	1.62
	V(C_α) = 0.48[a]			
C_6H_6	2.80	1.31		

[a] V(C_α) corresponds to a separate nonbonding valence basin.

The ELF analysis of carbo[*N*]annulenes is illustrated below for the ring carbomer of benzene **6c**. The bifurcation tree diagram[12] and some selected localization domains are presented in Figure 5a. In a qualitative viewpoint, the ELF picture of **6c** is "expanded" with respect to that of the parent benzene.

The basin partition map in the molecular plane (Figure 5b) exhibits a D_{6h} symmetry. There is one disynaptic basin V(C_α, C_β) associated to each $C_\alpha-C_\beta$ bond. The corresponding population of 2.90 is in agreement with a partial double bond similar to the one of benzene. The $C_\beta-C_\beta$ bond is associated with two disynaptic basins V(C_β, C_β) that may be gathered in a superbasin with a total population of 4.71 in agreement with the relative expected bond order of 2.5.

The variance $\sigma^2 = 1.37$ of the V(C_α, C_β) population is very close to the one of V(C, C) population in benzene[12] thus indicating a comparable electron delocalization (Table 3). In the classical limit, σ^2 is the square of the standard deviation, and therefore, a V(C_α, C_β) population of 2.9 ± 1.17 is consistent with the resonance of the Kekule structures. The variance of the V(C_β, C_β) population of 1.57 is slightly higher than the one of the V(C_α, C_β) population. The excess is mostly due to the electron delocalization with the two adjacent basins (vide infra).

Both, the absence of attractor corresponding to transannular $C_\beta-C_\beta$ bond and the long 1,3 transannular $C_\beta-C_\beta$ distances (Table 2) suggest a weak homoconjugation and thus a weak

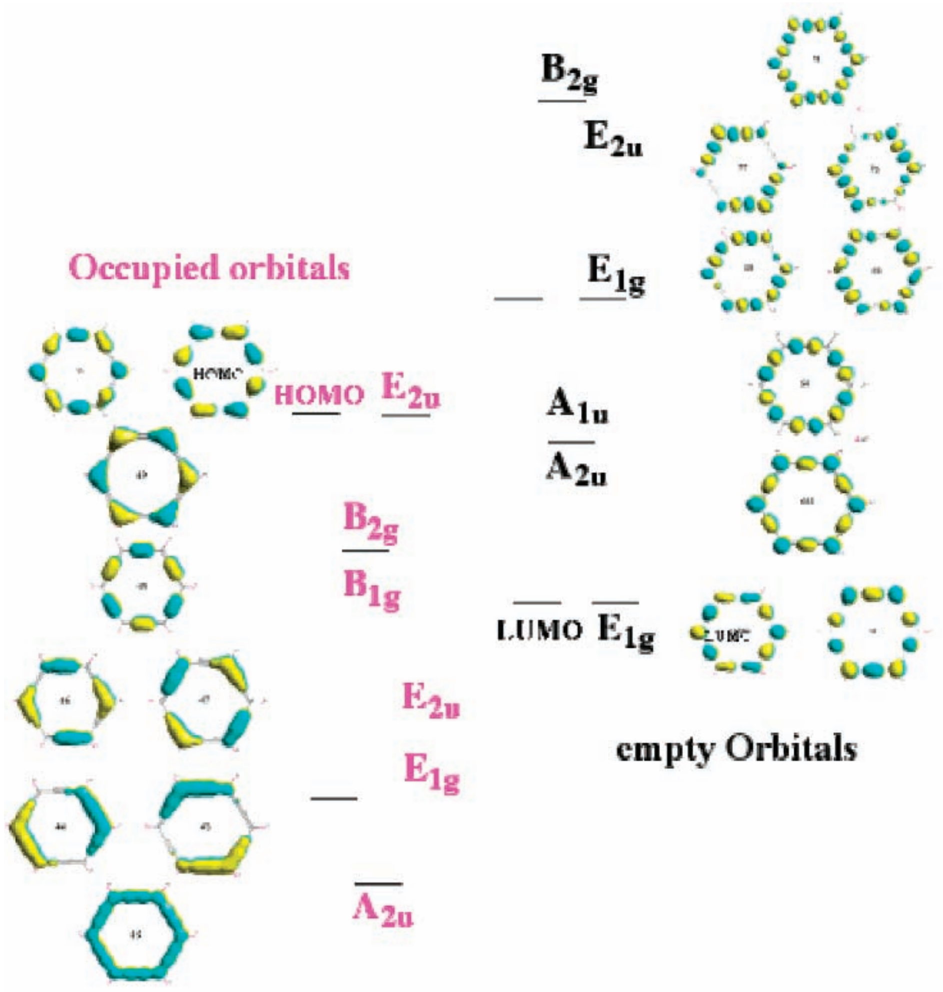


Figure 2. Out-of-plane π_z MOs system of ring carbomer of benzene **6c**.

TABLE 4: Relative Weight of Resonance Forms of Carbo[*N*]annulenes Derived from ELF Analysis

	no. of π_z electrons	no. of π_{xy} electrons	$x + y$ (aromaticity)	$z + w$ (homo-aromaticity)	β'^6 (in ha)
6c	18	12	0.97	0.04	−0.01081
5c	14	10	0.87	0.13	−0.02005
4cT	12	8	na[a]	na[a]	−0.03543
4cS	12	8	1.00	0	−0.03533
3c	10	6	0.84	0.16	−0.05333

[a] na: not available.

π_{xy} electron homodelocalization. Indeed, a much shorter 1,3 transannular distance is observed in the homotropylium cation (1.906 Å calculated at the MP2/6-31G*[26] or 1.948 Å at the B3PW91/6-31G** (this work)), one of the archetypes of homoaromatic systems.

Quantification of the Resonance Forms of Carbo[*N*]annulenes Using the ELF Analysis. Let us apply the principles set out above to quantify resonance forms (ELF topological analysis section) to **6c** with M = 2 (V(C_α, C_β), V(C_β, C_β)). Four main nonpolar resonance forms may be considered (Figure 6). Two of them are related to the cyclic out-of-plane π_z electrons delocalization and have the same weight (x/2) because of the D_{6h} symmetry. Two other apolar resonance forms account for the in-plane π_{xy} electrons homodelocalization and have the same weight $(1 - x)/2$ as well.

From the scaled ELF populations of V(C_α−C_β) and V(C_β−C_β) on one hand and the formal bond population in each Lewis resonance form on the other hand, two identical equations may be written. The solution $x = 97\%$ (Table 4) suggests that the electron homodelocalization in **6c** is low.

TABLE 5: Atomic Charges of 5c and 3c Derived from AIM Analysis at the B3PW91/6-31G Level of Calculation**

	AIM atomic charges
5c C_α	+0.18
5c C_β	−0.04
3c C_α	−0.07
3c C_β	−0.13

The same procedure applied to **4cS** yields four resonance forms of respective weight x, y, z, w (Figure 7) and a system of four equations involving four unknowns. The corresponding solutions (Table 4) indicate the absence of electron homodelocalization in this compound.

It is not possible to quantify the resonance forms of **4cT** using the ELF analysis. Too many radical resonance forms have to be considered with respect to the single available equation. Moreover, ELF or Mulliken analysis of the spin densities suggests that these radical resonance forms all have a significant weight, ruling out any approximate resolution.

In the case of ionic carbo[*N*]annulenes **5c** and **3c**, at least five resonance forms may be considered (Figures 8 and 9). Again, The ELF populations allow us to derive two identical equations involving three unknowns x, y, z with $w = 1 - x - y - z$.

For **5c**, the atomic charges derived from the AIM analysis (Table 5) suggest that y may be neglected as compared to x. In

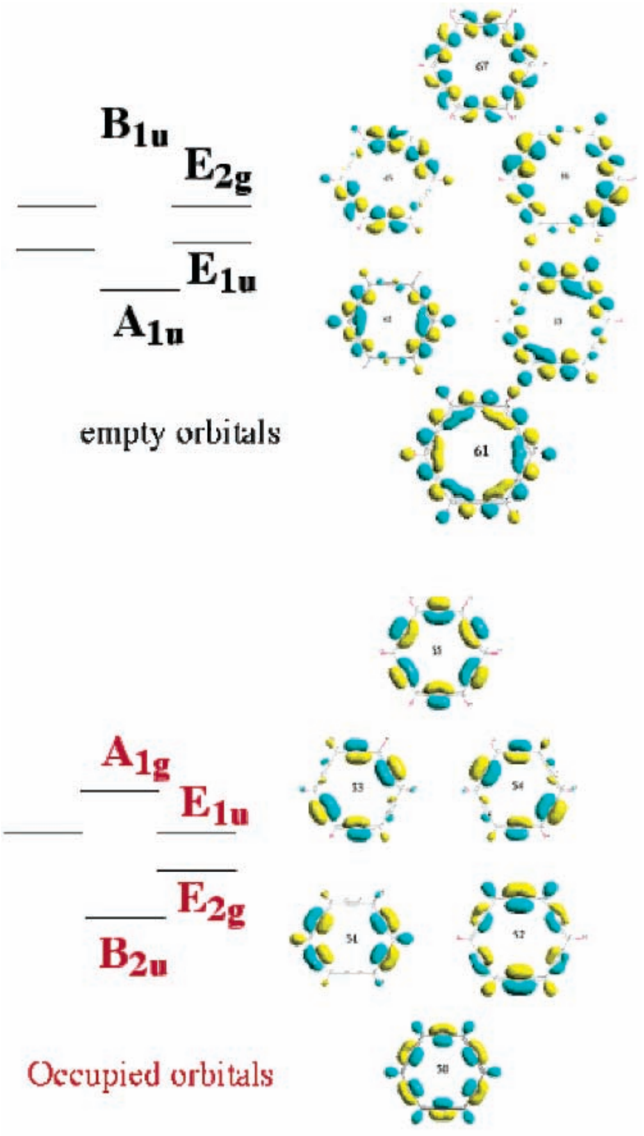


Figure 3. In-plane π_{xy} MOs system of ring carbomer of benzene **6c**.

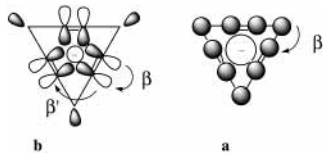


Figure 4. (a) Out-of-plane π_z conjugation associated with aromaticity. β is the out-of-plane resonance integral in the Hückel analysis of aromaticity. (b) In-plane π_{xy} homoconjugation. The same resonance integral β as for aromaticity is used in the Hückel analysis of in-plane homoaromaticity. A weaker in-plane resonance integral β' is used for through space homoconjugation.

5c, the propargylium−allenylium resonance is displaced toward the cationic propargylic form by contrast to what is observed in acyclic relative cations such as $C_3H_3^+$, $C_5H_3^+$, and $C_6H_7^+$ (Table 6). Moreover, as the homoaromaticity of ring carbomers of [*N*]annulenes exibits second-order stabilizing effects,[6] the weight of the corresponding resonance forms is expected to be low. z can therefore may be neglected as compared to *x*. The following solutions results: $x + y = 87\%$ and $z + w = 13\%$ (Table 4).

For **3c**, the AIM charges (Table 5) suggest that $y = x$. As the homoaromaticity is a second-order phenomenon,[6] *z* may therefore again be neglected as compared to *x*. The following solutions results: $x = y = 42\%$ and $z + w = 16\%$. The π electron homodelocalization is thus greater in the ionic carbo-[*N*]annulennes.

TABLE 6: Relative Weight of Propargylium and Allenylium Resonance Forms Derived from ELF Populations Analysis for Various Acyclic Cations

	allenylium resonance form	propargylium resonance form	other resonance forms
$C_3H_3^+$	59%	41%	
$C_5H_3^+$	16%	30%	54%
$C_6H_7^+$	24%	38%	38%

TABLE 7: Selected Bond Length (in Å) and Angles (in Degrees) of the Calculated Structures of [*N*]Pericyclynes at the B3PW91/6-31G Level**

	symmetry	$C_\beta-C_\beta$	$C_\alpha-C_\beta$	transannular $C_\beta-C_\beta$	$C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta-C_\beta$
6P	D_{3d}	1.208	1.466	2.451	113.5	179.4
5P	D_{5h}	1.208	1.466	2.432	112.1	177.9
4P	D_{4h}	1.209	1.469	2.378	108.1	171.0
3P	D_{3h}	1.216	1.474	2.280	101.3	159.3

The ELF analysis results are gathered in Table 4 and compared to the corresponding quantitative Hückel analysis of homodelocalization of carbo[*N*]annulenes[6] through the resonance integral β' (Figure 4b). The approximate Hückel analysis of DFT molecular orbitals suggests that the π_{xy} electron homodelocalization grossly increases from **6c** to **3c**, whereas the finer ELF analysis suggests that π_{xy} electron homodelocalization is more important for ionic structures involving $4q + 2$ π_{xy} electrons in the MO description.

ELF Analysis of [*N*]Pericyclynes. [*N*]Pericyclynes (that will be referred to as **NP**) may be envisionned as ring carbomers of [*N*]Cycloalkanes (Figure 10). These "exploded alkanes" designed by Scott et al.[27] are carbon rich compounds. Only peralkylated pericyclynes were known[28] until recently where oxygen substituents were introduced.[29,30] The latter compounds may be synthetic precursors of carbo[*N*]annulenes.

The optimized geometries of [*N*]pericyclynes calculated at the B3PW91/6-31G** level are described in Table 7. They are all planar of D_{Nh} symmetry except **6P** which exhibits a more stable D_{3d} chair conformation. To the best of our knowledge, **3P** and **4P** have not been described to date;[28] however, similar calculated structures as the one described here using molecular mechanics[31] or semiempirical methods[32] were reported for these compounds. The planar D_{5h} geometry of **5P** is calculated to be more stable than the envelope conformation exhibited by the crystallographic structure of decamethyl-[5]-pericyclyne.[31]

Two types of carbons atoms may be distinguished in the calculated pericyclyne structures. C_α is an sp^3 carbon atom located at the vertexes, whereas C_β is an sp carbon atom located in the edges. Two sets of π orbitals may also be distinguished: (i) the π_z MO system (Figure 11a-**5P**), results from the out-of-plane overlap of $2p(C_\beta)$ atomic orbitals via the bonding orbitals of C−H bonds that materializes the homoconjugative interruptions, and (ii) the π_{xy} MO system (Figure 11b-**5P**), results from the through space interaction of $2p(C_\beta)$ atomic orbitals in the ring plane.

Early studies[32] pointed out the existence of these two modes of cyclic homoconjugation, in-plane and out-of-plane, and thus raised the question of the existence of homoaromaticity. The latter point has been controversial in the literature concerning **5P** involving 10 in-plane and/or 10 out-of-plane π electrons. Thermochemical calculations performed on decamethyl-[5]-pericyclyne allowed Scott et al.[33] to estimate a weak homoaromatic stabilization energy of about 6 kcal/mol, suggesting that

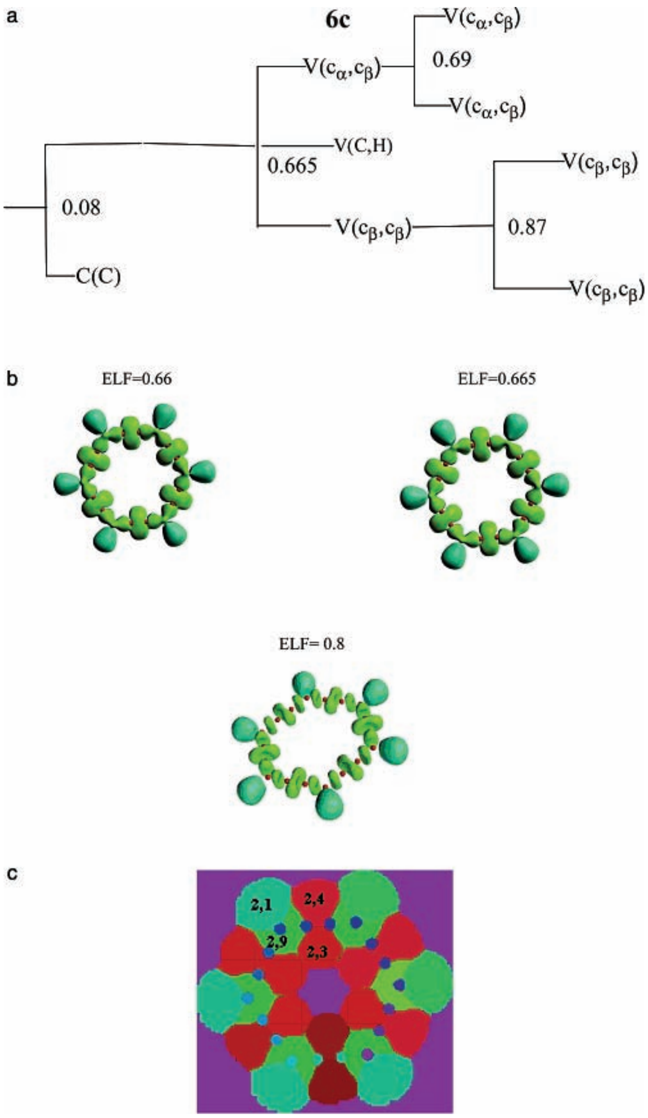
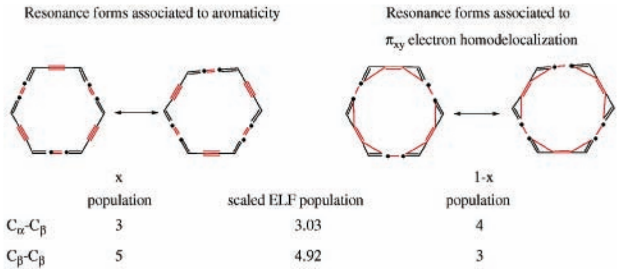
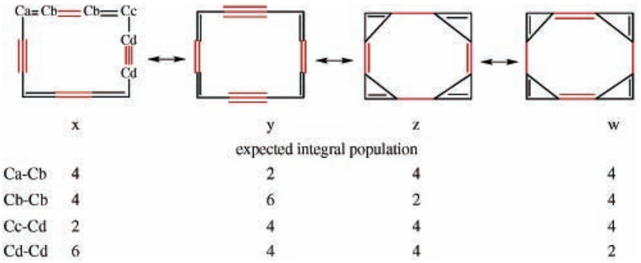


Figure 5. (a) Bifurcation tree diagram and localization domains (ELF = 0.66, 0.665, and 0.8) of **6c**. (b) ELF basins partition map in the molecular plane of **6c**. Carbon cores are in blue, $C_\alpha-C_\beta$ basins in green and $C_\beta-C_\beta$ basins in red. ELF basins populations are given in black.



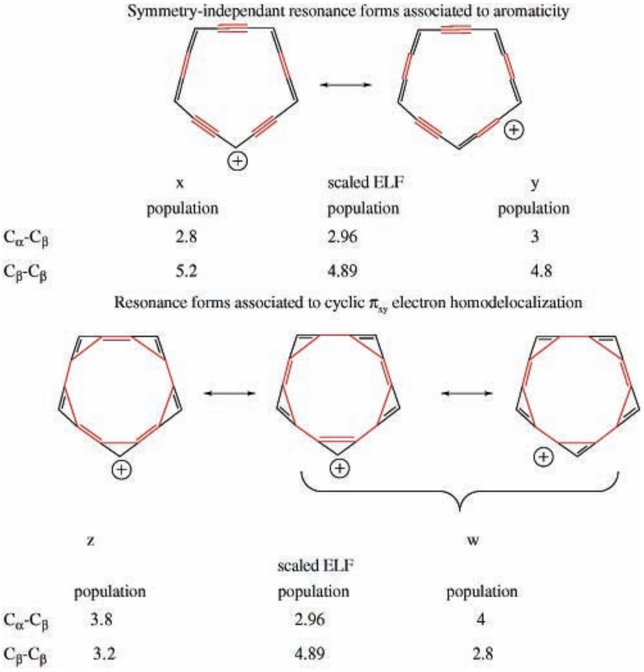
	x population	scaled ELF population	1-x population
C_α-C_β	3	3.03	4
C_β-C_β	5	4.92	3

Figure 6. Resonance forms of **6c**. Corresponding weight and bond populations.



	x	y	z	w
		expected integral population		
Ca-Cb	4	2	4	4
Cb-Cb	4	6	2	4
Cc-Cd	2	4	4	4
Cd-Cd	6	4	4	2

Figure 7. Resonance forms of **4cS**. Corresponding weight and bond populations.



	x population	scaled ELF population	y population
C_α-C_β	2.8	2.96	3
C_β-C_β	5.2	4.89	4.8

	z population	scaled ELF population	w population
C_α-C_β	3.8	2.96	4
C_β-C_β	3.2	4.89	2.8

Figure 8. Resonance forms of **5c**. Corresponding weight and bond populations.

it is homoaroamatic. However, Williams et al.,[34] and more recently a DFT theoretical study of Schleyer et al.,[35] showed that [5]pericyclynes may be regarded as nonhomoaromatic according to the usual magnetic, geometric, and energetic criteria of aromaticity. Indeed, their chemical properties are very similar to those of other cyclic oligoacetylenes.[36]

The ELF analysis has been performed and is in agreement with the D_{Nh} symmetry of the [*N*]pericyclynes ($3 \leq N \leq 5$). As an illustration, the bifurcation tree diagram[12] and some selected localization domains are displayed in Figure 12 in the case of **3P**. From a qualitative viewpoint, the ELF picture of **[*N*]P** is *expanded* with respect to those of the parent cycloalkane. The C_2 unit may be easily distinguished at ELF = 0.64 (Figure 12) before it separates into the $V(C_\alpha, C_\beta)$ and $V(C_\beta, C_\beta)$ disynaptic basins corresponding to the $C_\alpha-C_\beta$ and $C_\beta \equiv C_\beta$ bonds of respective bond order 1 and 3, thus suggesting very low cyclic electron delocalization. The corresponding ELF populations and variance are given in Table 8.

The variance of both $V(C_\beta, C_\beta)$ and $V(C_\alpha, C_\beta)$ (respectively $\sigma^2 = 1.47$ and 1.05) is larger than one suggesting a large electron delocalization. It however appears from the analysis of covariances that this electron delocalization does not extend over the ring but is rather limited to two adjacent basins. A similar $\sigma^2 = 1.21$ value for the triple C−C bond is indeed observed for 2-butyne (Table 8). This delocalization may be analyzed in terms of σ delocalization as emphasized by Shaik et al.[37]

Although the ELF populations suggest that π electron homodelocalization is very low, four resonance forms may be considered for [*N*]pericyclynes as illustrated in Figure 13 for **5P**. Two equations involving the scaled ELF populations and the formal bond orders of each resonance form may be written. These two equations are again identical and yield a linear equation with two independent variables x and y, with $z = 1 - x - y$. The results in the best agreement with the low cyclic electron delocalization[38] suggested from the ELF analysis are

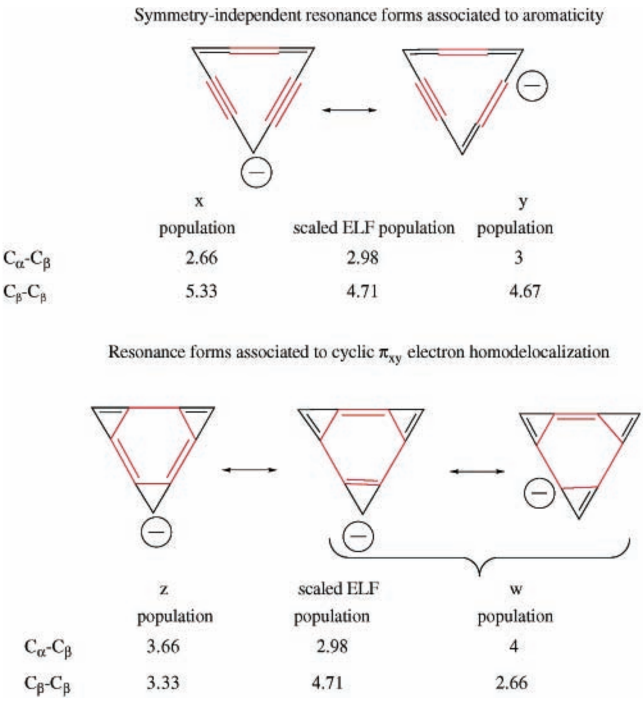


Figure 9. Resonance forms of **3c**. Corresponding weight and bond populations.

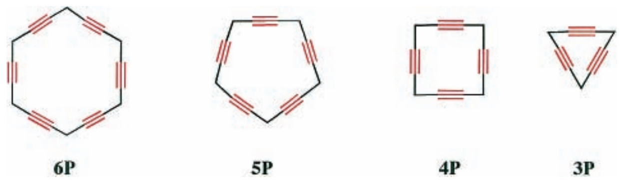


Figure 10. [*N*]Pericyclynes or ring carbomer of cycloalkanes ($N = 3-6$).

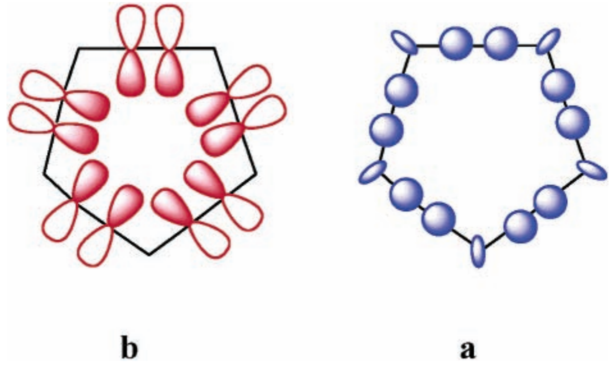


Figure 11. Through-space and through-bond homoconjugation in **5P**.

TABLE 8: Average Population (*N*) and Variance (σ^2) of the ELF Basins of [*N*]Pericyclynes and 2-Butyne

	$C_\beta-C_\beta$		$C_\alpha-C_\beta$	
	N	σ^2	N	σ^2
6P	5.69	1.47	2.07	1.05
5P	5.65	1.47	2.07	1.05
4P	5.61	1.47	2.08	1.05
3P	5.53	1.47	2.10	1.05
2-butyne	5.77	1.21	2.03	1.02

reported in Table 9 and compared to the NICS calculated at the center of the ring.

6P, **5P**, and **4P** exhibit parallel ELF and NICS behavior. The NICS is positive, and the electron homodelocalization is very low confirming that these compounds are not homoaromatic in agreement with previous reports.[34,35] **3P** exhibits a slightly higher electron homodelocalization character and a slightly negative NICS suggesting the presence of stronger homoconjugative interactions, as anticipated from the increased geometrical constraint to transannular π-orbital overlap.

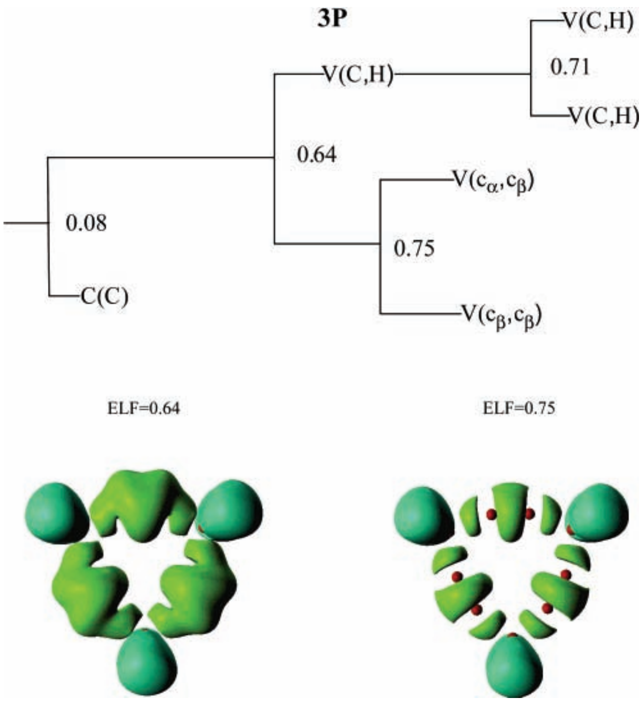


Figure 12. Bifurcation tree diagram and localization domains (ELF = 0.64 and 0.75) of **3P**.

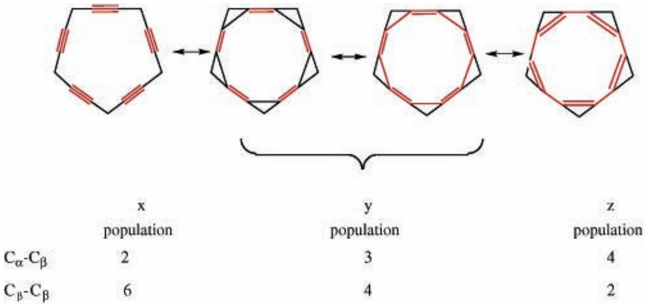


Figure 13. Resonance forms of **5P**. Corresponding weight and bond populations.

TABLE 9: Relative Weight of Resonance Forms of [*N*]Pericyclynes Derived from ELF Analysis

	x	*y* + *z* electron homodelocalization	NICS (HF/6-31+G*) in ppm
6P	0.95	0.05	+0.6
5P	0.95	0.05	+0.6
4P	0.94	0.06	+0.7
3P	0.92	0.08	−6.6

Discussion

The term homoaromatic was introduced by Winstein[7] in 1959 to describe compounds that display aromaticity-like properties despite one or more saturated linkages interrupting the formal cyclic conjugation. Since that time, homoaromaticity has been an area of intense activity.[8,39,40] Homoaromaticity is well established in cationic systems, whereas it is often controversial in neutral and anionic systems.[40] The term homoaromaticity is

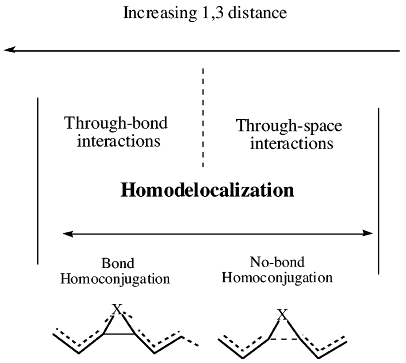


Figure 14. Various types of homoconjugation and homoaromaticity. From ref 8.

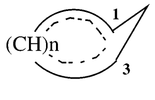
used to designate homoconjugation resulting in electron or bond delocalization.[8] The properties of the homoaromatic molecule can therefore not be explained in terms of bond or group contributions of the two homoconjugated systems.

Homoaromaticity like any homoconjugative interactions may be classified according to (i) the number of interruptions in the conjugated chain, (ii) the nature of orbital interactions classified by Winstein,[41] and (iii) the charge, the spin multiplicity, and the state (ground or excited) of the molecule.[8] Two main types of homoconjugation (homoaromaticity) may be distinguished (Figure 14): (i) bond homoconjugation when a cyclopropyl group is formed as the interacting centers are connected by a bond and (ii) no-bond homoconjugation when the conjugative interaction is mediated through space by appropriate orbital overlap.

Clearly no-bond homoconjugation with *N* interruptions resulting from σ/σ overlap is involved in carbo[*N*]annulenes, whereas in [*N*]pericyclynes, π/π overlap and σ/σ overlap are respectively responsible for out-of-plane (Figure 11a) and in-plane (Figure 11b) no-bond homoconjugation.

Several criteria of homoaromaticity have been already proposed. In the late sixties, Winstein's definition[41] of homoaromaticity involved four requirements and covered both bond and no-bond aromaticity. A cyclic system involving $(4q + 2)$ π-electrons was said to be homoaromatic if (1) the system is closed by electron delocalization across the homoconjugatively connected atoms; (2) the interaction or bond index of the 1,3 link ranges between 0 and 1; (3) Orbital overlap of the participating p-atomic orbitals (AOs) at center 1 and 3 is neither σ nor π but intermediate between these two (Scheme 3); (4) The $(4q + 2)$ π-electrons are fully delocalized over the resulting closed cycle, thus leading to net stabilization.

SCHEME 3



This definition calls for experimental or theoretical tools in order to assess the requirements and clearly identify homoaromatic molecules. Orbital overlaps,[42] bonds orders, and NBO analysis were tentatively used to investigate homoaromaticity but with always some drawbacks.[8] Dewar resonance energies or resonance energies (RE) extracted from isodesmic or homodesmotic formal reactions have been calculated.[8] However, as for determination of aromatic stabilization energies,[43] the suitable reference molecule to obtain meaningful stabilizing energies is not straightforward, and the low RE values obtained are often ambiguous.

Finally, Cremer et al.[8] proposed more rigorous criteria of homoaromaticity. Using the Bader topological analysis of the electron density[19] and its molecular parameters (bonds orders, interaction indices, and π-character indices), they translated Winstein early requirements into density language for bond homoaromaticity.[44]

According to Cremer et al.,[8] a cyclic system involving $(4q + 2)$ π-electrons will be homoaromatic if the following exist: *(1) a partial 1,3 bond* (Scheme 3), i.e.: the system is closed by a 1,3 bond path with a bond critical point $\mathbf{p}(1,3)$ at which the energy density distribution is stabilizing: $H(\mathbf{p}) < 0$, and the bond order of the 1,3 bond ranges between 0 and 1 thus indicating a partial bond with a π character, as measured by the bond ellipticity $\epsilon(1,3)$, larger than that of cyclopropane; *(2) cyclic electron delocalization* characterized by the following: (a) a large degree of bond equalization; (b) calculated bond orders and bond ellipticities approaching those of an aromatic system; (c) major axes of $\epsilon(1,3)$ overlapping effectively with those of the neighboring bonds; (d) in the case of ions, positive or negative charge delocalized throughout the cyclic system; *(3) resonance energy of the homoaromatic molecule higher than 2 kcal/mol* typical values range between 2 and 10 kcal/mol.

This definition of bond homoaromaticity may be extended to no-bond homoaromaticity.[8,44]

A bond may be easily evidenced using ELF analysis. Moreover, as illustrated above, electron delocalization may also be easily quantified using ELF analysis. Much concise criteria of homoaromaticity especially for quantifying electron homodelocalization may therefore now be proposed from ELF analysis.

Without a priori requiring a $4q + 2$ electron count, a cyclic system is claimed to be bond-homoaromatic if the following characteristics exist: *(1) a partial 1,3 bond*, i.e.: the system is closed by a 1,3 bond evidenced by an attractor and the corresponding disynaptic V(1,3) basin whose population ranges between 0 and 2 thus indicating a partial bond; *(2) electron delocalization* in the cyclic system that is characterized by the relative weight of possible resonance forms describing the homoconjugation higher than 10%.

These ELF criteria of bond homoaromaticity may be extended to no-bond homoaromaticity. A cyclic system will be no-bond homoaromatic if there is *(1) no 1,3 bond*, i.e.: there is no attractor between 1 and 3 but through space interactions are confirmed by the AIM covariance between interacting basins involved in the homoconjugative internuclear 1,3 gap higher than 0.05; (2) *electron delocalization* in the cyclic system is characterized by the relative weight of possible resonance forms describing the homoconjugation higher than 10%.

These criteria of homoaraomaticity defined from ELF analysis are validated below for the cyclopropylcarbinyle cation $C_4H_7^+$ in the case of bond-homoaromaticity and homotropenylium $C_8H_9^+$ in the case of no-bond homoaromaticity.

The optimized geometry of cyclopropylcarbinyl cation (B3PW91/6-31G** level) of C_s symmetry is presented Figure 15a. Similar results were obtained at the Hartree−Fock level.[45] The existence of an attractor between C_1 and C_2 as well as between C_2 and C_4 indicates the existence of partial 1,2 and 2,4 C−C bonds involving one bonding electron. The ELF populations are in agreement with almost equivalent three resonance forms displayed in Figure 15b. This supports the existence of π-bond homoaromaticity. This ELF analysis is in agreement with previous AIM analysis.[8]

The optimized geometry of homotropenylium (B3PW91/6-31G** level) of C_s symmetry is in agreement with previous MP2/6-31G* calculations[26] and is given in Figure 16a. There

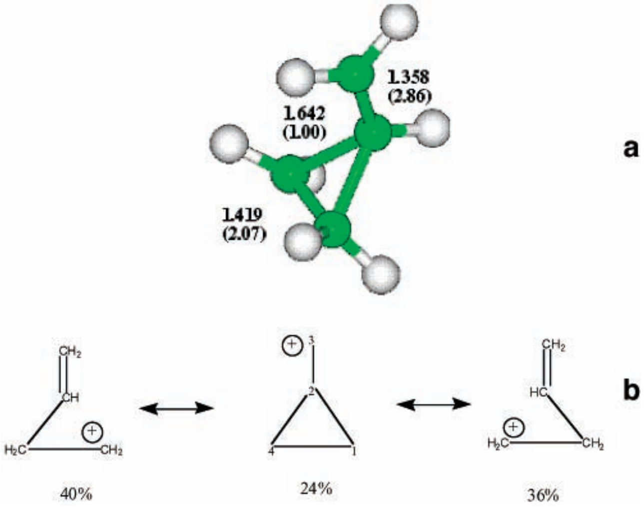


Figure 15. (a) Optimized geometry at the B3PW91/6-31G** level of cyclopropylcarbinyl cation. C−C distances are given in angstroms and corresponding ELF populations in parentheses. (b) Resonance forms of cyclopropylecarbinyl cation and relative weights calculated from ELF analysis.

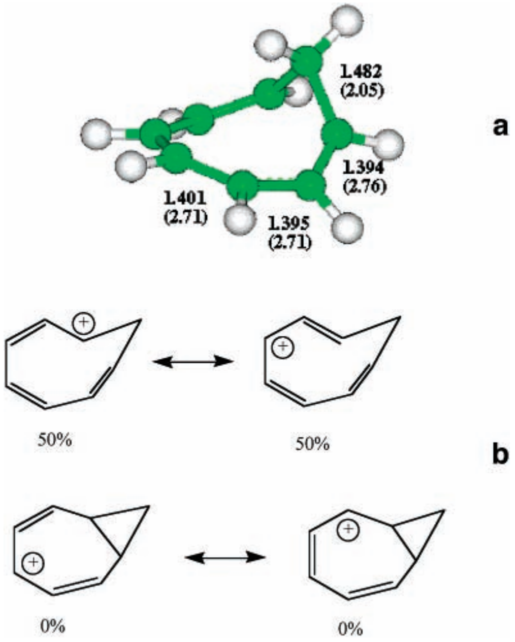


Figure 16. (a) Optimized geometry at the B3PW91/6-31G** level of homotropenylium. C−C distances are given in angstroms and corresponding ELF populations in parentheses. (b) Resonance forms of homotropenylium and relative weights calculated from ELF analysis.

is no attractor between C_1 and C_3; however, the ELF populations are in agreement with complete cyclic electron delocalization thus suggesting no-bond homoaromaticity as expected (Figure 16b).

Conclusions

ELF analysis has been used to investigate aromaticity and homoaromaticity of carbo[*N*]annulenes and [*N*]pericyclynes. It appears as a simple and unique tool to quantify electron delocalization through the weight of the corresponding resonance forms. More generally, it provides a simple quantitative treatment of mesomerism.

New criteria of homoaromaticity based on ELF analysis have been proposed and validated on the archetypes of homoaromaticity such as the homotropenylium cation and the cyclopropylcarbinyl cation.

Only the ionic carbo[*N*]annulenes **5c** and **3c** are homoaromatic. **3P** is one of the few examples of neutral homoaromatic molecules, whereas **5P** is not homoaromatic as already reported.[34,35]

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