Aromaticity and homoaromaticity of annulene ring carbomers

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A simple electron count shows that the ring carbomers of (anti)aromatic [N]annulenes are (anti)aromatic according to the formal criterion of the Hückel rule. Basic VSEPR theory suggests that the ring carbomers of (anti)aromatic [N]annulenes should be (anti)aromatic according to the structural criterion, namely (dis)symmetry with respect to D_{Nh}. These predictions are here confirmed by DFT geometrical optimization at the B3PW91/6-31G** level. Calculations of the NICS at the center of the rings produce negative (respectively positive) values for singlet $4n + 2$ (respectively $4n$) and triplet $4n$ structures. The structural and magnetic aromaticity criteria are thus correlated. A relevant measure of energetic *topological* aromaticity is based on the Hückel method. The DFT π_z levels are shown to vary with the corresponding HF levels with a universal slope and to closely correlate with the Hückel MO analysis. Values of the resonance integrals β are derived and Breslow's resonance energy (RE) is calculated. The latter is emphasized to represent the energetic effect of the ring-closing π overlap and thus the switch-on of a π ring current. The RE values of [N]annulenes vary with those of their carbomers in accordance with the Hückel rule. The π_{xy} system in the carbomer rings thus has minimal effect with respect to the π_z system. However, the DFT π_{xy} levels are also correlated with the corresponding HF and Hückel levels: the weak degeneracy lifting with respect to the ideally isolated π_{xy} MOs indicates a weak in-plane homoaromaticity.

Owing to their functional, theoretical and aesthetic attractivness, carbon-rich molecules are the subject of intense investigations.[1] A class of such structures is rigorously defined by inserting C_2 units into each bond of any Lewis structure (Scheme 1): the resulting so-called "carbomer" structures merely differ from the originals in size and the number of carbon atoms.[2] Indeed, this generalization of the interatomic topology preserves the connectivity (the chemical nature of the connections being carbon pairs instead of electron pairs), the symmetry, the shape[3] and the resonance, but modifies the size of the original structure, by increasing the *formal* covalent radii *ca.* $2r \approx 1.3$ Å, where r is the mean covalent radius for sp carbon atoms.

The general question is as follows: as carbomerization grossly preserves basic features of molecular models, it might also preserve or systematically transpose physicochemical properties, for example: specific optical rotation, NMR chemical shifts, dipole moments, polarizability, hyperpolarizability, crystal packing, density, stability and related valence electron energy. The introduction of two high energy π-electron pairs per connection should *a priori* make a carbomer molecule more reactive than its antecedent. However, the non-additive bond energy scheme of aromaticity can be sought in order to restore some stability and identify reasonable synthetic targets.[4] Such a stabilization could correlate with structural and magnetic properties and with the formal $4n/4n + 2$ Hückel rule. The Hückel rule was formulated early on for the [N]annulenes $(CH)_N$, and we thus naturally considered their ring carbomers $(C_3H)_N$, which are also 1, 2, 4, 5 ..., $3N - 2,3N - 1$-dehydro-[$3N$]annulenes. In 1995, while we reported our efforts towards the synthesis of a carbomer of the benzene ring $C_{18}H_6$ ($N = 6$),[5] Ueda *et al.* described the new dehydro-[18]annulene derivatives $C_{18}R_3Ar_3$ (R = H, Ar′) (Scheme 2).[6] On the basis of X-ray diffraction data, these authors recently confirmed the D_{6h} symmetry of the ring of what can be called "hexaphenyl-[C,C]$_6$carbobenzene" **1**.[7] The aromatic character of the latter was also supported by a strong diatropic ring current (^{1}H and ^{13}C NMR data) and by thermal stability up to 250 °C.[7]

$X{-}Y \Rightarrow X{-}C{\equiv}C{-}Y$

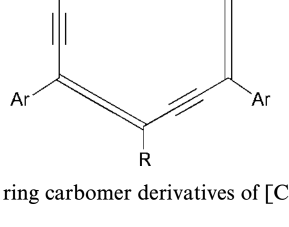
$X{=}Y \Rightarrow X{=}C{=}C{=}Y$

$X{\equiv}Y \Rightarrow X{\equiv}C{-}C{\equiv}Y$

Scheme 1 Basic processes in the definition of carbomers.

The generalization of this process is here envisioned from a theoretical viewpoint for other N values. First of all, to preserve the Hückel rule, the ring carbomer of a charged annulene $[(CH)_N]^q$ is formally defined as $[(C_3H)_N]^{-q}$: thus, if a ring sustains $m = 4n + a$ π_z electrons ($a = 0, 2$; π_z = out-of-plane π MO), then its carbomer does as well. Then, we propose to evaluate the aromatic character of the ring carbomers $[(C_3H)_N]^{-q}$ (***N*b**) of the simplest [N]annulene derivatives $[(CH)_N]^q$ (***N*a**) for N = 3, 4, 5, 6 (Scheme 3). The singlet state is assumed by default, and owing to the long debated relative stability of singlet and triplet states of cyclobutadiene **4a**, the triplet state of its ring carbomer **4b** is also envisaged: singlet structures are denoted as **4aS** and **4bS**, while triplet structures are denoted as **4aT** and **4bT**.[8]

Although aromaticity is one of the most essential notions in



Scheme 2 Known ring carbomer derivatives of [C,C]$_6$carbobenzene: R = H, aryl.[7]

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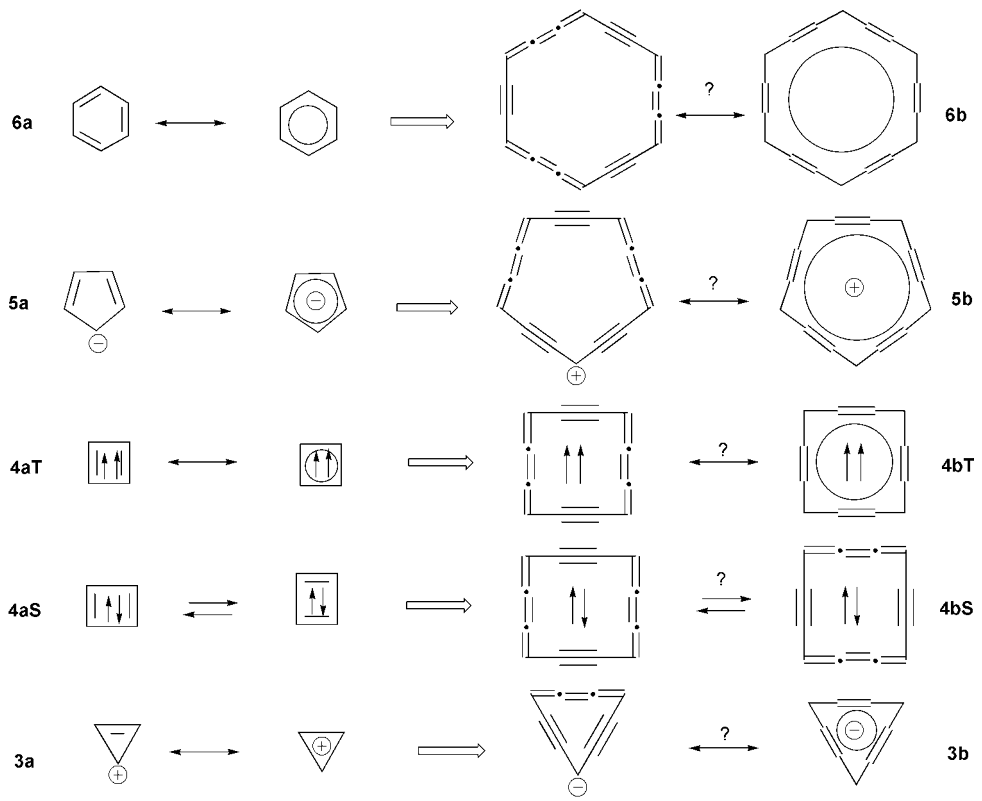


Scheme 3 [*N*]annulenic species and their ring carbomers.

chemistry, it is not univocally appraised. This molecular characteristic is revealed by three types of properties, namely structural, magnetic and energetic, which are more or less correlated. On the basis of a factor analysis, Katritsky *et al.* showed that aromaticity is a two-dimensional notion in a statistical sense.[9] Later, Schleyer and coworkers showed that particular measures of each of the three criteria are not necessarily orthogonal, and can even be accurately correlated over a homogeneous set of molecules.[10] Within this context, structural and magnetic criteria were selected as descriptors of the aromaticity of ring carbomers.[11] As for the set of parent [*N*]annulenic molecules, and following Schleyer's report,[10] symmetry and NICS proved to be locally parallel measures of structural and magnetic aromaticities, respectively.[11] The complete results are discussed here with respect to a relevant measure of energetic aromaticity.

Results and discussion

Structure

The ring carbomer structure **6b** served as a test for the validation of the calculation method. Since *ab initio* Hartree–Fock geometry optimization of **6b** did not reproduce the experimental D_{6h} geometry of the ring of the hexaphenyl derivative of **6b**, a DFT method was used. Using GAUSSIAN 94,[12] the geometries of **6a**–**3a** and **6b**–**3b** have been fully optimized at the B3PW91/6-31G** level. These calculations yielded the known equilibrium geometries of **6a**–**3a**. Moreover, starting from highly disymmetrical nonplanar structures, geometry optimization reproduced the experimental structure of the central 18-membered ring of the hexaphenyl derivative of **6b**. D_{Nh} structures were also produced for **5b**, **4bT** and **3b** (Fig. 1, Table 1): thus the carbomer ***N*b** of an aromatic molecule ***N*a** is aromatic according to a qualitative structural criterion and in accordance with the Hückel $4n + 2/4n - \pi_z$ electron count, depending on the spin state. Quantitative criteria of structural aromaticity are based on measures of bond length equalization between formal single and double bonds.[13] Classical methods (Julg's parameter *A*,[14] Krygowski's HOMA,[15] *etc.*), however, are not parametrized for triple bonds and thus not straightforwardly relevant for the ring carbomers ***N*b**. Nevertheless, the Csp–Csp *vs.* Csp–Csp^2 bond length alternation in D_{Nh} structures ***N*b** (N = 6, 5, 4T, 3)

Table 1 Optimized geometries at the B3PW91/6-31G** level of the [*N*]annulene derivatives ***N*a** and their ring carbomers ***N*b**

	Symmetry	sp^2–sp^2/Å	sp–sp/Å	sp–sp^2/Å	d_{ccm}[a]/Å	sp$^{(2)}$–sp^2–sp$^{(2)}$/°	sp^2–sp–sp/°
6a	D_{6h}	1.394	—	—	1.394	120	—
6b	D_{6h}	—	1.239	1.369	1.325	122.6	178.7
5a	D_{5h}	1.419	—	—	1.419	108	—
5b	D_{5h}	—	1.238	1.369	1.325	118.5	174.8
4aT[b]	D_{4h}	1.437	—	—	1.437	90	—
4bT[b]	D_{4h}	—	1.241	1.378	1.332	115.2	167.4
4aS[c]	D_{2h}	1.572, 1.334	—	—	1.453	90	—
4bS[c]	D_{2h}	—	1.267, 1.218[d]	1.334, 1.428[d]	1.335	115.2	167.3
3a	D_{3h}	1.365	—	—	1.365	60	—
3b	D_{3h}	—	1.253	1.391	1.345	109.7	155.1

[a] Mean C–C bond length in the ring. [b] Triplet state. [c] Singlet state. [d] Two types of non-equivalent bonds.

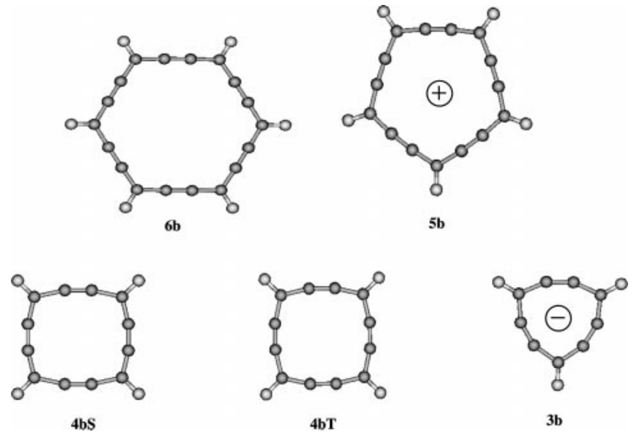


Fig. 1 Optimized geometries at the B3PW91/6-31G** level of ring carbomers **_N_b**.

is 0.13 Å: this is slightly shorter than the mean value (0.15 Å) of the bond length alternation in butatriene (0.04 Å) and 2-butyne (0.25 Å), showing that the cyclic conjugation has a weak but significant aromatic structural effect.

The outward bending angle at the sp carbon atoms increases as N decreases: the ring strain is thus partly transferred from the vertices of the ideal $D_{N\mathrm{h}}$ polygon to the middle of the edges. The extreme bending of the edges (with respect to 180°) in structure **3b** (24.9°) is almost identical to the experimental value (24.3°) obtained for dibenzocyclooctadiyne.[16] Whereas the global $D_{N\mathrm{h}}$ symmetry of ring carbomers can be analyzed in terms σ- and/or π_z-delocalization,[17] transannular p_{xy} overlaps and possible in-plane homoaromaticity are not sufficient to prevent the local outward bending of the edges as N decreases.

Similarly to **4aT** and **4bT**, singlet cyclobutadiene **4aS** and its ring carbomer **4bS** are planar, but exhibit a $D_{2\mathrm{h}}$ symmetry: this structural antiaromatic character is in accord with their Hückel $4n$ π_z electron count. The overall bond length alternation of **4bS** is obviously more important than in **4bT** ($D_{2\mathrm{h}}$ instead of $D_{4\mathrm{h}}$ symmetry): this can serve to quantify a reduced structural aromaticity or even a structural antiaromaticity effect of the cyclic conjugation in **4bS**.

It is also noteworthy that the relative stability of $D_{2\mathrm{h}}$ singlet cyclobutadiene **4aS** *vs.* $D_{4\mathrm{h}}$ triplet cyclobutadiene **4aT** calculated at the B3PW91/6-31G** level [E(**4aT**) − E(**4aS**) = +4.6 kcal mol^{-1}] is preserved in the ring carbomer series [E(**4bT**) − E(**4bS**) = +2.1 kcal mol^{-1}].

Magnetic properties

A magnetic response is generated by a ring current resulting from the application of a magnetic field on the cyclic conjugated π-electron system. The response thus reveals the nature of the ring current (diatropic or paratropic), which is linked to the aromatic character (strictly aromatic or antiaromatic).[18] Magnetic susceptibility exaltation and NMR chemical shifts of various nuclei located near the ring are widely used as experimental or computed indicators of the nature and the magnitude of the ring current.

The $\delta\,^1$H chemical shifts of **_N_a** and **_N_b** were first calculated at the HF level of theory and eventually compared with experimental data in solution: as anticipated from the Hückel rule, singlet $4n+2$ and triplet $4n$ π-electron rings give deshielded ^{1}H NMR signals (Table 2).

However, many factors other than aromaticity do influence the NMR chemical shift of the peripheral nuclei. A universal and more specific NMR measure of aromaticity has been proposed by Schleyer, namely the Nucleus Independent Chemical Shift (NICS).[19] The relevance of the NICS obtained by DFT (B3LYP) calculations has been evaluated by comparison with the values obtained from HF calculations with the same basis set (6-31+G*) (Table 2).[20] Most of the HF- and DFT-computed NICS values are almost identical (except for **4bS**), and accurately correlate according to:

$$\mathrm{NICS(HF)} = \mathrm{NICS(B3LYP)} - 2.02\ \mathrm{ppm} \qquad (1)$$

Negative NICS values indicate an aromatic character, while strongly positive values indicate an antiaromatic character. From Table 2, it appears that the NICS values qualitatively correlate with the $4n+2$ Hückel rule for singlet and triplet molecules. Furthermore, the more an annulene is magnetically aromatic, the more its ring carbomer is magnetically aromatic too.

As previously emphasized by Schleyer *et al.*, the order of magnitude of the NICS does not depend much on the size of the ring.[19] The NICS lies in the range 20–60 ppm for $4n$ π electron rings, and in the range 0– −30 ppm for $4n+2$ π electron rings. Nevertheless, the NICS of a molecule **_N_a** is generally smaller than that of its ring carbomer **_N_b** (Table 2).

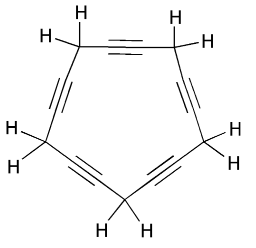
The NICS can be split into several components corresponding to the ring σ contribution, the ring π contribution and other minor contributions:[21] NICS ≈ NICS(σ) + NICS(π). Whereas NICS(σ) and NICS(π) generally tend to cancel each other out in the absence of π delocalization, large NICS values result from enhanced NICS(π) components due to the occurrence of π ring currents. Two orthogonal π_z and π_{xy} systems are present in ring carbomers **_N_b**. The NICS can therefore be expanded as: NICS ≈ NICS(σ) + NICS(π_z) + NICS(π_{xy}). The total NICS value should reflect the effect of two ring currents, namely the out-of-plane aromaticity of the π_z system and the in-plane homoaromaticity of the π_{xy} system. In order to estimate the magnetic influence of in-plane homoaromaticity *vs.* that of the out-of-plane aromaticity in **5b**, the NICS of [5]pericyclyne **7** in its optimized geometry has been

Table 2 NMR data for [N]annulenic molecules and ions and their ring carbomers

	NICS[a] (B3LYP)	NICS[a] (HF)	$\delta\,^1$H[a] (B3LYP)	$\delta\,^1$H (expt)
6a	−8.0	−9.7	7.3	7.27[b]
6b	−17.9	−19.6	11.4	9.87[b]
5a	−12.5	−14.2	5.7	5.59[c]
5b	−16.9	−18.5	10.9	—
4aT	−2.0	−7.7	7.1	—
4bT	−15.8	−17.5	8.0	—
4aS	28.2	27.6	5.5	—
4bS	*53.0*	*20.1*	−3.6	—
3a	−22.4	−27.6	10.4	11.1[d]
3b	−22.3	−23.5	5.7	—

[a] NICS at the ring center and $\delta\,^1$H values are calculated within the framework of the GIAO formalism[36] using 6-31+G* basis sets from B3PW91/6-31G** optimized geometries. [b] Measured in CDCl$_3$. The value associated to **6b** has been reported for a triphenyl derivative.[7] [c] H. O. House, A. V. Prabhu and W. V. Phillips, *J. Org. Chem.*, 1976, **41**, 1209. [d] G. A. Olah, J. S. Staral and G. Liang, *J. Am. Chem. Soc.*, 1974, **96**, 6233.

calculated at the HF/6-31+G* level: NICS(**7**) = +0.6 ppm. This weak value confirms the absence of homoaromaticity claimed by Schleyer and de Meijere for [5]pericyclynes.[22] Since the calculated ring geometry of **7** is quasi-D_{5h} [with d(C≡C) = 1.208 and d(C–C) = 1.466 Å, at the B3PW91/6-31G** level] and thus similar to that of **5b**, it can be approximated that **7** and **5b** have similar NICS(σ) and NICS(π_{xy}) contributions. The high NICS value of **5b** is thus merely due to a π_z aromaticity, while in-plane homoaromaticity plays a minor role.



7

Energetic criterion of aromaticity

Whereas delocalization is a stabilizing factor, aromaticity corresponds to the specific stabilization due to the cyclic component of the delocalization. Topological aromaticity is therefore measured by the difference in energy between the studied cyclic fully conjugated structure and that of a reference acyclic structure with the same spin state and the "same geometry" (in the restricted sense of bond lengths), but not the same topology of conjugation:

$$\Delta = E(\text{cyclic conjugated molecule}) - E(\text{reference}) \quad (2)$$

Aromatic stabilization energies (ASE) based on isodesmic, homodesmotic or isogyric equilibria call for real, optimized reference structures.[23] Besides the drawback of requiring additional computation time for these auxiliary references, ASEs do not allow for a specific analysis of *topological* aromaticity. Nevertheless, nonparametric measures of energetic aromaticity can be designed without resorting to somewhat arbitrary external molecules: the reference is then a fictitious structure constructed on the sole basis of the properties of the cyclic molecules. Shaik and other authors showed that in both cyclic and acyclic conjugated structures, the delocalized geometry is dictated by the σ framework.[17,24] In particular, the structural aromaticity criterion of the ***N*b** structures (D_{Nh} symmetry) could be explained by the delocalization of σ electrons. More generally, however the proposal of Shaik *et al.* entails that the reference for topological aromaticity must have the same properties of the σ framework. On the basis of a σ/π separation, topological aromaticity is thus measured by the effect of the *ring-closing π overlap*. This definition of topological aromaticity is therefore consistent with the formal aromaticity criterion (Hückel $4n + 2/4n$ π_z electron count) and with the magnetic aromaticity criterion (π ring current). On the other hand, the energetic effect of the *ring closing π overlap* is exactly measured by the Breslow resonance energy (RE),[25] in which the reference is a finite acyclic conjugated structure treated by the Hückel (HMO) method, and thus assumed to have the same σ properties and the same α and β values as the cyclic structure:[26]

$$\mathrm{RE} = E_{\pi,\,\text{cyclic}}(\alpha, \beta) - E_{\pi,\,\text{acyclic}}(\alpha, \beta) \quad (3)$$

where α denotes the Coulomb integral and β the resonance integral.

Although the HMO method has been long recognized to be of limited accuracy by itself to estimate Dewar-type resonance energies,[27] it is used here as a logical tool to bring out a measure of topological aromaticity. However, the validity of a Hückel treatment must be checked, and the β parameter then estimated for each molecule: a fit is first sought between a reliable *ab initio* orbital analysis and that provided by the Hückel method.

DFT MO analysis and σ/π separation. Although the utility of DFT orbitals have long been disregarded, Stowasser and Hoffmann recently shed new light on the relevance of (Kohn-Sham) DFT valence MOs (occupied or not) with respect to the corresponding HF or EH MOs.[28] One step beyond, DFT MOs are here correlated with the simple Hückel MOs. The DFT π MOs are first classified according to their orientation (out-of-plane π_z or in-plane π_{xy}), and to their symmetry properties. The π_z MO diagram is depicted in Fig. 2.

The symmetries of the lowest bonding π_z MO (without a nodal plane) and the highest antibonding π_z^* MO (with a maximum number of nodal planes) are identical in the

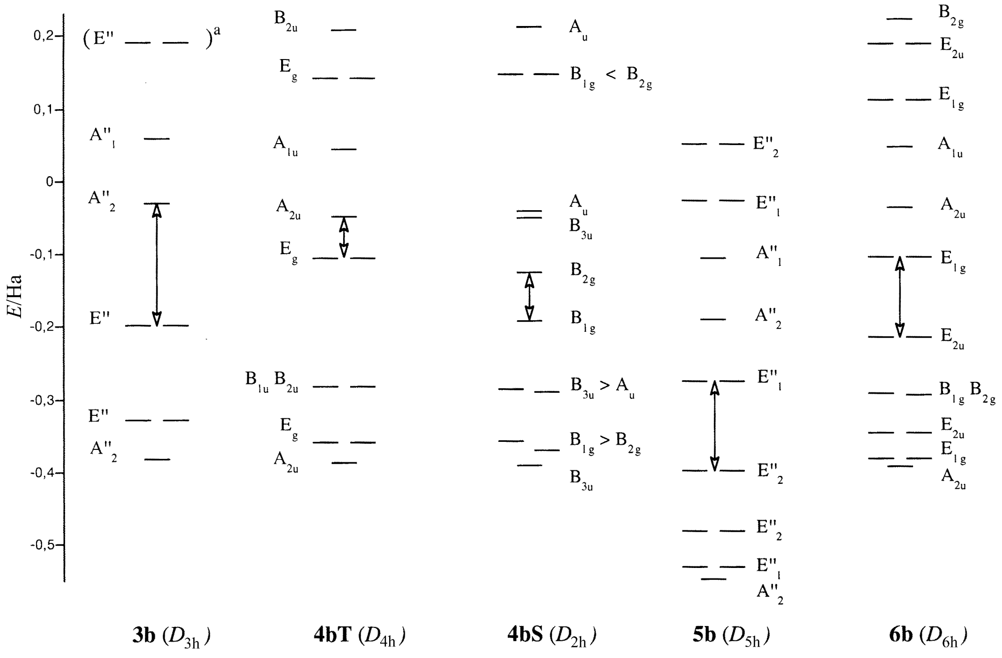


Fig. 2 DFT π_z orbital diagram for ring carbomers ***N*b** of [*N*]annulenes ***N*a**. Double arrows indicate the HOMO–LOMO gaps.[a] When the structure is calculated in the presence of a sodium counterion, this E″ type MO is not a pure annulene MO due to some mixing with sodium AOs.

[N]annulene derivatives and in the corresponding carbomers: the other π_z and π_z^* MOs appearing in the carbomer structure insert between these limits, while the HOMO–LUMO gap of ***N*b** is lowered with respect to that of ***N*a** (the frontier MOs of ***N*b** are always of π_z nature). Another salient feature of the π_z MO diagrams of ***N*b** is the large gap (*ca.* 0.1 Ha) between two successive non-degenerate low-lying unoccupied π_z MOs, which are derived from the same degenerate level in the Hückel diagram of the corresponding [$3N$]annulene (see below).

Only the DFT MOs can be directly significant for the DFT-optimized structure. Nevertheless, the HF MO diagrams of the DFT-optimized structures have also been determined and a Hoffmann-type HF-DFT correlation sought for all the π_z MOs:[29]

$$E_k(\text{DFT}) = cE_k(\text{HF}) + d \tag{4}$$

where k = rank of the π_z levels = 1, 2, ..., $3N$. A proportionality factor ($c \approx 0.61$) turns out to be applicable for all the π_z levels of all the DFT-optimized structures ***N*a** and ***N*b**:

$$E_{k,\,\pi_z}(\text{DFT}) \approx 0.61 E_{k,\,\pi_z}(\text{HF}) + d \tag{5}$$

The constant term d depends on the structure, but is quasi constant for neutral structures: $d \approx -0.067$ Ha. Therefore, provided that this correlation is taken into account, the DFT π_z MO diagram is relevant.

Quantitative Hückel analysis. Similarly to the linear fit between HF and DFT MOs, a linear fit is sought between the energies of the DFT MOs of a given ground state structure **3**–**6** and those of the associated Hückel MOs:

$$E_k(\text{DFT}) = aE_k(\text{Hückel}) + b \tag{6}$$

The Hückel analysis of a ring carbomer $(C_3H)_N$ of approximate $D_{N\text{h}}$ symmetry relies on the $\sigma + \pi_z + \pi_{xy}$ separation. Regarding the π_z system, one should *a priori* resort to four parameters: the Coulomb integrals α_1 and α_2 for the sp and sp^2 carbon atoms, respectively, and the resonance integrals β_1 and β_2 for the Csp–Csp and Csp–Csp^2 overlaps, respectively. The simplest analysis is undertaken under the assumptions: $\alpha = \alpha_1 = \alpha_2$ and $\beta = (\beta_1 + \beta_2)/2$. The latter approximation is justified by the similarity of the Csp–Csp and Csp–Csp^2 bond distances (1.3 ± 0.05 Å). This topological Hückel MO analysis is identical for the ring carbomer of a [N]annulene and for the [$3N$]annulene. Thus, the energy of the kth π_z MO of a conjugated structure through N_c carbon atoms is given by:

$$E_k(\text{Hückel}) = \alpha + \beta x(k) \tag{7}$$

The searched fit is thus linear:

$$\begin{aligned} E_k(\text{DFT}) &= aE_k(\text{Hückel}) + b \\ &= a[\alpha + \beta x(k)] + b = A + Bx(k) \end{aligned} \tag{8}$$

where $A = a\alpha + b$, $B = a\beta$, a and b depending *a priori* on the molecular structure.

For a cyclic conjugation path through N_c carbon atoms ($N_c = N > 2$ for [N]annulenes and $N_c = 3N$ for their ring carbomers):[30]

$$x(k) = x_c(k) = 2\cos\left(\frac{2k\pi}{N_c}\right) \tag{9}$$

with $k = 1, \ldots, N_c$. For neutral structures **4aS, 4aT, 6a, 4bS, 4bT** and **6b**, the fit over all π_z valence orbitals (occupied or not) affords B values with good to excellent correlation coefficients. The fitted constant coefficient is always very close to $A = -0.122$ Ha for the neutral structures **4aS, 4aT, 6a, 4bS, 4bT** and **6b**, greater than -0.122 Ha for anions **3b** and **5a**, and smaller than -0.122 Ha for cations **3a** and **5b**.

The B values are found to decrease smoothly with the number of carbon atoms in the ring (Fig. 3), according to the empirical equation:

$$B \approx B_c(N_c) = \frac{N_c}{N_c + 2} B_0 \tag{10}$$

for $B_0 = -0.1690$ Ha. In particular, this fit is of high accuracy for non-strained singlet [N]annulenes and their ring carbomers (Table 3).[31]

Since the Hückel method needs to be scaled (β is an empirical parameter) and since no experimental data are available for most ring carbomers, the Hückel levels are identified with the HF levels. Elimination of E_k(DFT) in eqn. 5 and eqn. 8 leads to:

$$\beta = B/0.61 \tag{11}$$

$$\alpha = (A - d)/0.61 \tag{12}$$

β is thus proportional to B, with $\beta = \beta_0 N_c/(N_c + 2)$ where $\beta_0 = B_0/0.61 = -0.277$ Ha $= -174$ kcal mol^{-1}.

The assumption of a universal β value for all the bonds of fully conjugated carbocycles corresponds to the "topological Hückel method". Cioslowski showed that the exact π electron energy depends on the topological π electron energy and on

Table 3 Parameters (A, B, R) and (A', B', R') of the fits of the DFT *vs.* HMO levels, for the π_z and π_{xy} levels using eqn. 8 and 20 respectively. All values are in Hartree units

	π_z system				π_{xy} system			
***N*b**	$B_c(\approx B)$[a]	R[b]	$\beta \approx B_c/0.61$[c]	RE	B'	R[b]	$\beta = B'/0.53$[c]	RE′
6b	−0.1521 (−0.1516)	0.990	−0.2493	−0.2034	−0.005 73	0.949	−0.010 81	+0.0002
5b	−0.1491 (−0.1512)	0.991	−0.2445	−0.2023	−0.010 63	0.989	−0.020 05	−0.0008
4bT	−0.1449 (−0.1456)	0.991	−0.2375	−0.1943	−0.018 72	0.995	−0.035 43	−0.0026
4bS	−0.1449 (−0.1445)	0.984	−0.2375	−0.0797	−0.018 78	0.986	−0.035 33	−0.0026
3b[d]	−0.1383 (−0.1326)	0.984	−0.2267	−0.2018	−0.028 27	1.00	−0.053 33	−0.0086

[a] B_c is calculated from eqn. 10. B is the fitted value. [b] Correlation coefficients of the fits giving the B values. [c] The DFT levels are scaled with respect to the HF levels by the proportionality factors 0.61 and 0.53 for the π_z levels and the π_{xy} levels, respectively. [d] The highest π_z^* (E″) level is not taken into account in the fits because of mixing with sodium AOs (see Fig. 2).

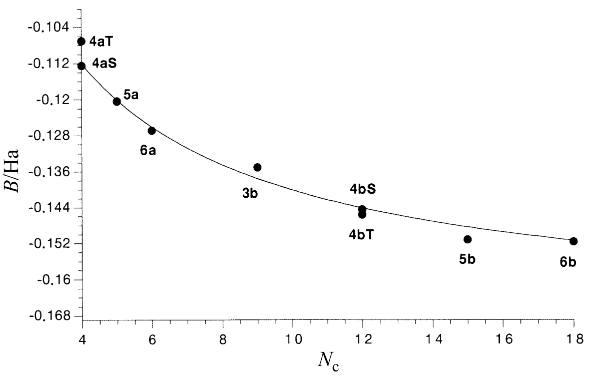


Fig. 3 Variation of B *vs.* N_c for [N]annulenes and their ring carbomers. The fitted curve is: $B_c(N_c) \approx B_0N_c/(N_c+2)$ with $R = 0.991$ for $B_0 = 0.1690$ Ha, eqn. 10.

the number of ring carbon atoms of the ring only.[32] This dependence is qualitatively reproduced by our empirical process. Cioslowski's exact π electron energy was derived by "the variable β Hückel method", asssuming that the resonance integrals β_{ij} vary as the order of the i–j bonds. The apparent average β value, obtained here from the exact π electron energy, is therefore a function of a mean bond order, or equivalently of the mean CC bond length in the ring (Table 1). This is illustrated in Fig. 4, showing that the average Hückel resonance integral β indeed regularly increases with the mean bond length d_{ccm} in structures **3**–**6**.

Breslow resonance energy. The Hückel treatment of the π_z MOs of the reference *acyclic* conjugated molecule with N_c atoms leads to an expression of $x(k)$ different from that of its cyclic congener:

$$x(k) = x_a(k) = 2\cos\left(\frac{k\pi}{N_c+1}\right) \tag{13}$$

with $k = 1, \ldots, N_c$. The acyclic reference structure is defined by Hückel parameters (α_a, β_a) identical to those of the studied cyclic structure, namely: $\alpha_a = \alpha$ and $\beta_a = \beta \approx B_c(N_c)/0.61$. The resonance energy is thus:

$$\mathrm{RE} = E_{\pi,\,\mathrm{cyclic}} - E_{\pi,\,\mathrm{acyclic}} \tag{14}$$

$$\begin{aligned}\mathrm{RE} &= [\Sigma\, n_k(\alpha + \beta x_c(k))] - \Sigma\, n'_k[\alpha + \beta_c(N_c)x_a(k)] \\ &= 2\beta\{\Sigma n_k \cos(2k\pi/N_c) - \Sigma n'_k \cos[k\pi/(N_c+1)]\}\end{aligned} \tag{15}$$

where n_k and n'_k (=0, 1 or 2) are the occupation numbers of the kth MOs in the cyclic and acyclic structures, respectively ($\Sigma n_k = \Sigma n'_k = m$).

Since β is a function of N_c only (eqn. 10) the RE is given by a very simple analytical function:

$$\mathrm{RE} \simeq \frac{N_c}{N_c+2}\, 2\beta_0\{\Sigma n_k \cos(2k\pi/N_c) - \Sigma n'_k \cos[k\pi/(N_c+1)]\} \tag{16}$$

Entering the n_k and n'_k values for either singlet or triplet ground states, this energetic aromaticity measure is qualitatively correlated with other aromaticity criteria: small algebraic values of RE are associated with $D_{N\mathrm{h}}$ structures and a $4n+2$ π_z electron count, large algebraic values of RE are associated with structures of low symmetry and a $4n$ π_z electron count.

The resonance energy of both the [N]annulenes and their carbomers is thus a nonparametric analytical function of: (i) the number of ring carbon atoms (N_c), (ii) the number of π_z electrons ($m = N_c - q$) and (iii) the spin state. Since N_c(***N*b**) = 3 N_c(***N*a**), the RE of ***N*a** and ***N*b** are analytically related. Fig. 5 shows that the relationship is quasi linear for aromatic $4n+2$ π_z electron structures (**4aS** and **4bS** thus excluded) and that the more energetically aromatic is the [N]annulene, the more the related carbomer is energetically aromatic too.

Energetic criterion of in-plane homoaromaticity

Ring carbomers possess a π_{xy} MO system, but [N]annulenes do not. In-plane homoaromaticity in ***N*b** would result from a cyclic overlap of $2p_{xy}$ AOs in the ring.[33] The effects of the in-plane homoaromaticity are anticipated to be much weaker than those of out-of-plane aromaticity. Nevertheless, its specific influence in ring carbomers must be appraised. Furthermore, it could be compared with the negligible (in-plane and out-of-plane) homoaromaticity of [N]pericyclynes:[22] for $N \leqslant 5$ their equilibrium geometry is almost planar and resembles that of the aromatic $D_{N\mathrm{h}}$ structures.

DFT MO diagram. The π_{xy} MOs are identified by the absence of contributions from the p_z AOs of sp carbon atoms and high contributions of the p_x, p_y AOs of sp carbon atoms. The diagram of the DFT π_{xy} MO system has been determined for the optimized structures **3b**, **4bS**, **4bT**, **5b** and **6b**. In the absence of any delocalization, two N-degenerated π_{xy} and π^*_{xy} levels would be expected. The non-degeneracy of the corresponding DFT levels indicates that in-plane delocalization can be invoked (Fig. 6). However, the bonding π_{xy} MOs are gathered in a narrow range of energy (*ca.* 0.05 Ha), while their antibonding π^*_{xy} counterparts are more widely scattered because of mixing with σ* ($\mathrm{Csp^2}$–H) MOs (involving $2p_z$ and 2s AOs).

The validity of the DFT diagram is established by a homogeneous correlation between the DFT π_{xy} levels and the corresponding HF π_{xy} levels. As observed for the π_z systems, the

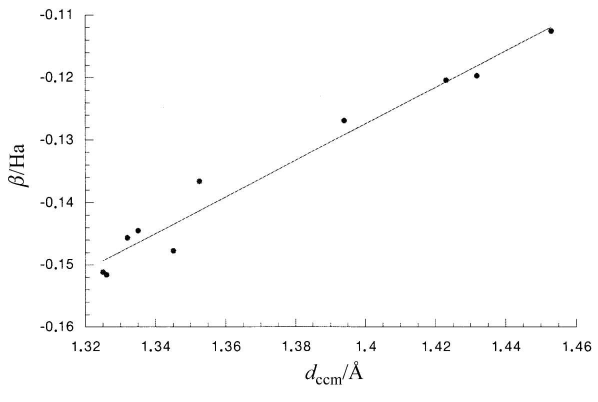


Fig. 4 Variation of $B = 0.61\beta$ *vs.* d_{cc}, the mean bond length of [N]annulenes ***N*a** and their ring carbomers ***N*b**.

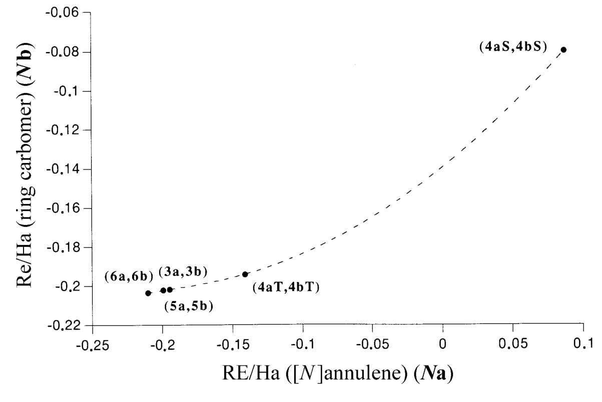


Fig. 5 Resonance energy of the ring carbomers of [N]annulenes (***N*b**) *vs.* that of the [N]annulenes (***N*a**), for N = 3, 4, 5, 6.

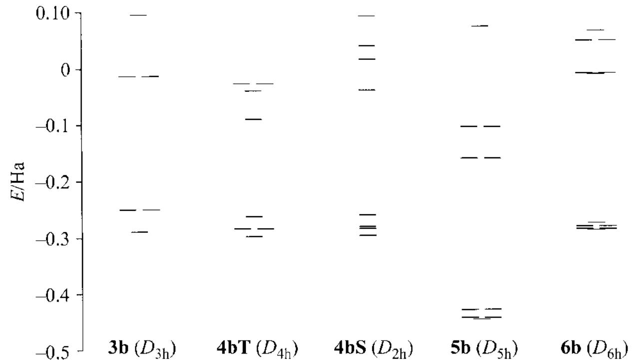


Fig. 6 DFT π_{xy} levels of the ground state structures of ring carbomers N**b** ($N = 3, 4, 5, 6$) obtained at the B3PW91/6-31G** level.

proportionality factor is identical for all the π_{xy} levels of all the N**b** structures but is slightly smaller than the proportionality factor found for the π_z levels ($c' = 0.53$ instead of $c = 0.61$):

$$E_{k,\,\pi_{xy}}(\text{DFT}) \approx 0.53 E_{k,\,\pi_{xy}}(\text{HF}) + d' \qquad (17)$$

The energetic effect of the cyclic component of the delocalization of the π_{xy} electrons can be quantified by an "in-plane Breslow resonance energy":

$$\text{RE}' = E_{\pi_{xy},\,\text{cyclic}} - E_{\pi_{xy},\,\text{acyclic}}(\alpha, \beta, \beta') \qquad (18)$$

In order to calculate RE′, a Hückel analysis of the π_{xy} MO system has been undertaken.

Quantitative Hückel analysis of the π_{xy} system. The energy of the kth π_{xy} Hückel MO level of the cyclic N**b** structures is:[34]

$$E_{k\pi_{xy}}(\text{Hückel}, N\mathbf{b}) = \alpha \pm \sqrt{\beta^2 + \beta'^2 + 2\beta\beta' \cos(2k\pi/N)} \quad (19)$$

with $k = 1, \ldots, N$; $N = 3, 4, 5, 6$. The α and β integrals are assumed to be equal in the π_z and π_{xy} systems. The resonance integral β' between p_{xy} AOs of non-bonded consecutive sp carbon atoms, separated by a sp^2 carbon vertex, is anticipated to be small, and the borderline assumption $\beta' = 0$, would lead to neglecting the π_{xy} delocalization.

Scaling $E_{k\pi_{xy}}(\text{Hückel}) = E_{k\pi_{xy}}(\text{HF})$, eqn. 17 and 19 lead to:

$$E_{k\pi_{xy}}(\text{DFT}) = A' \pm \sqrt{B''^2 + B'^2 + 2B''B' \cos(2k\pi/N)} \quad (20)$$

with $A' = 0.53\alpha + d'$, $B'' = 0.53\beta$ and $B' = 0.53\beta'$. β has been determined from the π_z MOs (eqn. 10, 11) and thus $B'' \approx (0.53/0.61)B_c$. Therefore, using the non-linear eqn. 9, a two-parameter fit (over A' and B') of the occupied π_{xy} DFT levels *vs.* the Hückel MO variable $\cos(2k\pi/N)$ has been performed, allowing for the determination of $\beta' = B'/0.53$ with reliable correlation coefficients (Table 3).

It is remarkable that the optimized B' (or β') parameters linearly vary with N (Fig. 7). The decrease of $|\beta'|$ with N actually reflects the increase of the vertex angles from *ca.* 30° ($N = 3$) to *ca.* 120° ($N = 6$). The outward bending of the sp carbon atoms at low N values does not make up for the increase of the p_{xy} AOs overlap.

Resonance energy for the π_{xy} system. A topological Breslow π_{xy} resonance energy, RE′, is calculated with respect to a reference acyclic polyyne. The reference structure corresponds to the homoconjugated ring opened at a weak edge, namely with a β' resonance integral ($\beta \gg \beta'$).

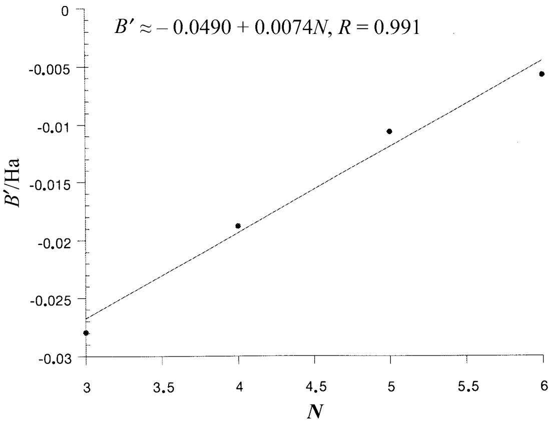


Fig. 7 Fit of $B' = 0.53\beta'$ values (optimized over occupied π_{xy} DFT MOs) *vs.* N.

$$\text{RE}' = E_{\pi_{xy}}(N\mathbf{b}) - E_{\pi_{xy}}[\text{H(C≡C–CH}_2)_N\text{H}] \qquad (21)$$

The resolution of the secular determinant of such linear structures with alternating resonance integrals is not straightforward. However, since $\beta' \ll \beta$, a Taylor expansion to the second order with respect to β'/β is appropriate. Resolution of the characteristic equation has been carried out for acyclic references. Whether $N = 3$, 4, 5 or 6, six different levels are obtained:

$$E_1 \approx \alpha - \sqrt{(u + v)/2} \quad \text{degeneracy} = 1 \qquad (22)$$

$$E_2 \approx \alpha + \beta \quad \text{degeneracy} = N - 2 \qquad (23)$$

$$E_3 \approx \alpha - \sqrt{u - v)/2} \quad \text{degeneracy} = 1 \qquad (24)$$

$$E_4 \approx \alpha + \sqrt{(u - v)/2} \quad \text{degeneracy} = 1 \qquad (25)$$

$$E_5 \approx \alpha - \beta \quad \text{degeneracy} = N - 2 \qquad (26)$$

$$E_6 \approx \alpha + \sqrt{(u + v)/2} \quad \text{degeneracy} = 1 \qquad (27)$$

where

$$u = 2\beta^2 + (N - 1)\beta'^2,$$
$$v = \sqrt{(N - 1)^2\beta'^4 + 4(N - 1)\beta'^2\beta^2}$$

and

$$E_1 < E_2 < E_3 < E_4 < E_5 < E_6.$$

Therefore, for a closed π_{xy} shell with $2N$ π_{xy} electrons (eqn. 28) is derived:

$$E_{\pi_{xy}}[(\text{C≡C–CH}_2)_N] = 2E_1 + 2(N - 2)E_2 + 2E_3 \qquad (28)$$

The resonance energy is:

$$\begin{aligned}\text{RE}' &= E_{\pi_{xy}}(N\mathbf{b}) - E_{\pi_{xy}}[(\text{C≡C–CH}_2)_N] \\ &= -2\sum_{k=1}^{N}\sqrt{\beta^2 + \beta'^2 + 2\beta\beta' \cos(2k\pi/N)} \\ &\quad - 2[E_1 + (N - 2)E_2 + E_3] \\ &= -2\sum_{k=1}^{N}\sqrt{\beta^2 + \beta'^2 + 2\beta\beta' \cos(2k\pi/N)} \\ &\quad + 2\sqrt{(u + v)/2} - 2(N - 2)\beta + 2\sqrt{(u - v)/2} \qquad (29)\end{aligned}$$

The RE′ values are more than 20 times smaller than the RE values, confirming the minor influence of the π_{xy} levels in the stabilization of ring carbomers (Table 3) with respect to open-chain references. Therefore, the π electron stabilization of the ring carbomers mainly occurs in the π_z levels, just as for the [N]annulenes. Nevertheless, the RE′ values are negative (except for the negligible value for **6b**) and thus represent a stabilization effect of the cyclic π_{xy} homoconjugation: rather surprisingly, whereas [N]pericyclyne **7** is not homoaromatic,[22] homoaromaticity occurs in its dehydro derivative

5b and in all ring carbomers of [*N*]annulenes, whatever the spin state and the number of π_{xy} electrons involved.

Conclusion

This theoretical exploration leads to the general statement that aromaticity and antiaromaticity are preserved by the carbomerization process. The Hückel rules, which have been formulated for [*N*]annulenes with a single cyclic conjugated π MO system, can be straightforwardly applied to the π_z system of their ring carbomers: though a weak energetic homoaromaticity is evidenced, the in-plane π_{xy} system is qualitatively bystanding. The HMO method is shown to be accurately valid for [*N*]annulene ring carbomers. This invaluable tool has been used to quantify topological aromaticity and homoaromaticity as Breslow-type resonance energies, which measure the energetic effect of the "ring-closing π overlaps", and which is conceptually related to the electrical "shortcut" giving rise to the ring currents in conjugated and homoconjugated cyclic systems. Beyond their academic and pedagogical value, these results prompted us to tackle the synthesis of aromatic ring carbomers of new [*N*]annulenic species from ring carbomers of cycloalkanes.[35]

Computational details

Full geometry optimization and vibrational analysis of [*N*]annulenes and their carbomers were performed at the B3PW91/6-31G** level using GAUSSIAN94.[12] Using these geometries single-point energy calculations were performed at the HF/6-31G** level for comparative orbital analysis. The magnetic shielding tensor and the corresponding NICS were calculated for a ghost atom located at the center of the ring of [*N*]annulenes and their carbomers within the framework of the GIAO (gauge including atomic orbital)[36] formalism at the HF/6-31+G* or B3LYP/6-31+G* levels. The B3LYP functional has been adopted in order to compare our results with other DFT-computed NICS values.[13b] In practice, B3PW91 and B3LYP are both hybrid functionals and are expected to yield very similar results.

For each optimized structure, a linear correlation between DFT (B3PW91) and HF π_z (respectively π_{xy}) levels was carried out using Kaleidagraph-3™ software, and the slopes were averaged as $c = 0.61$ (respectively $c' = 0.53$). Likewise, a linear correlation assumed between DFT (B3PW91) and Hückel π_z levels led to the determination of parameters *A* and *B* by a linear fit (eqn. 8) for each structure ***N*a** and ***N*b**. Finally, a linear correlation assumed between DFT (B3PW91) and Hückel π_{xy} levels led to the determination of parameters *A'* and *B'* by a non-linear fit (eqn. 2) for each structure ***N*b**.

For the calculation of the Breslow resonance energy (RE') of the π_{xy} levels, the approximate expression of the components E_i in $E_{\pi_{xy}}[(\mathrm{C{\equiv}C{-}CH_2})_N]$ was obtained by algebraic derivation of the secular determinant $\Delta_{2N}(E, \beta')$, which is equal to zero for the E_i solutions. A Taylor expansion in small β' values is:

$$\Delta_{2N}(E,\beta') = \begin{vmatrix} \alpha - E & \beta & 0 & . & . & 0 \\ \beta & \alpha - E & \beta' & 0 & . & . \\ 0 & \beta' & \alpha - E & \beta & . & . \\ . & . & \beta & . & . & . \\ . & . & . & . & . & \beta \\ 0 & . & . & . & \beta & \alpha - E \end{vmatrix}$$

$$\begin{aligned} &= \Delta_{2N}(E,0) + [\partial\Delta_{2N}/\partial\beta']_{E,0}\,\beta' \\ &\quad + 1/2[\partial^2\Delta_{2N}/\partial\beta'^2]_{E,0}\,\beta'^2 + \cdots \\ &\approx \Delta_{2N}(E,0) + 1/2[\partial^2\Delta_{2N}/\partial\beta'^2]_{E,0}\,\beta'^2 \end{aligned} \qquad (30)$$

Tedious, but not difficult, differentiation and expansion processes of Δ_{2N} afford:

$$\Delta_{2N}(E,\beta') \approx [(\alpha - E)^2 - \beta^2]^N - (N-1)(\alpha - E)^2[(\alpha - E)^2 - \beta^2]^{N-2}\beta'^2$$

Finally, the equation $\Delta_{2N}(E, ') = 0$ leads to the six solutions $E = E_1, \ldots, E_6$ for (eqn. 28).

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