

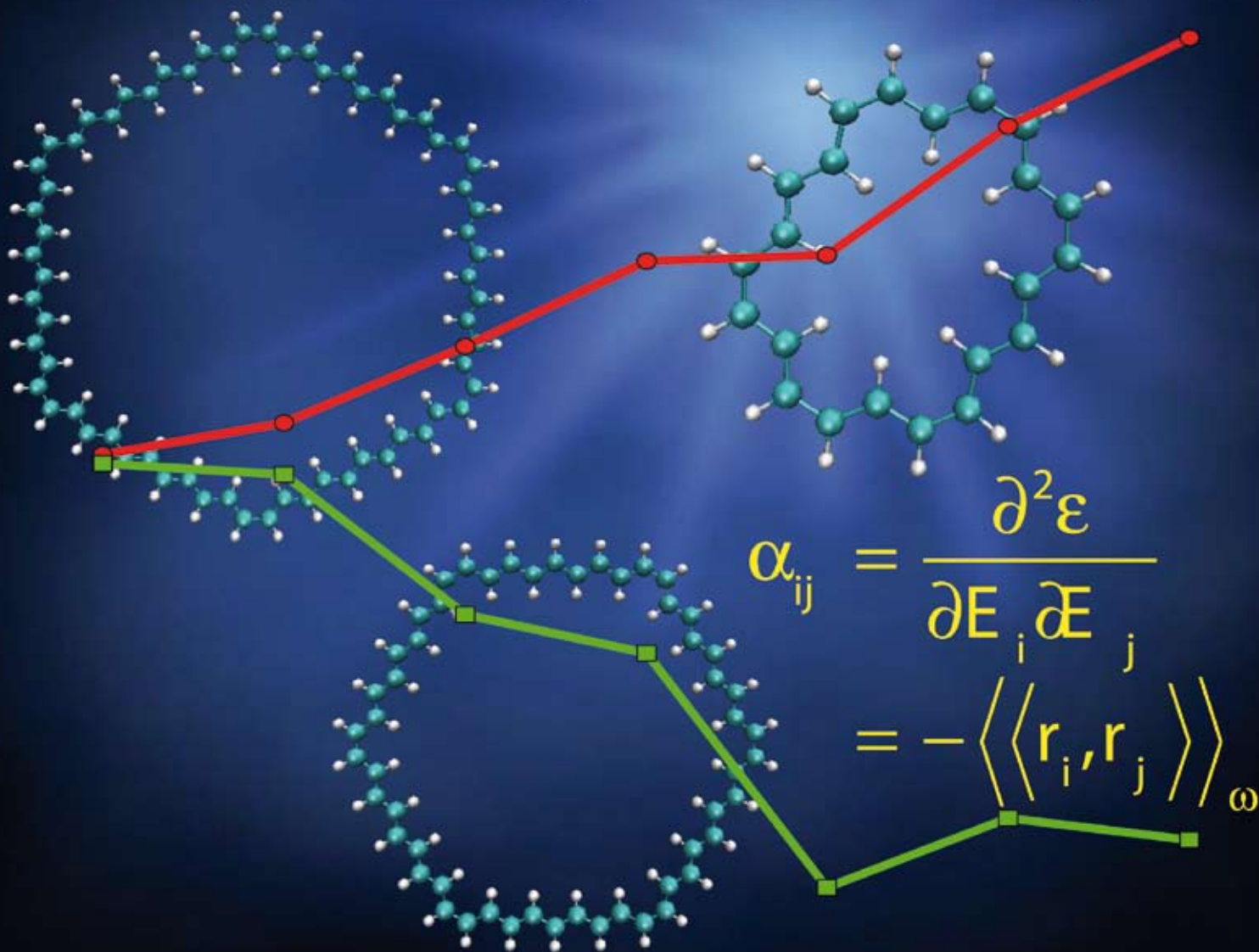
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Physical Chemistry Chemical Physics

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Volume 10 | Number 3 | 21 January 2008 | Pages 337–460

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ISSN 1463-9076

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1463-9076(2008)10:3;1-A

Variation of polarizability in the $[4n + 2]$ annulene series: from [22]- to [66]-annulene†

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Received 3rd September 2007, Accepted 18th October 2007

First published as an Advance Article on the web 7th November 2007

DOI: 10.1039/b713459b

Using correlated *ab initio* methods, the polarizability of large $[4n + 2]$ -annulenes is determined, showing that there exists an almost linear relation between the exaltation of magnetic susceptibility (a measure of aromaticity) and an equivalent enlargement of polarizability.

Introduction

According to the pioneering definition by Sondheimer,¹ annulenes are fully conjugated hydrocarbon monocycles. Benzene, [6]-annulene, in addition to being the most prominent aromatic molecule, is the smallest representative of the neutral $[4n + 2]$ series, while cyclobutadiene represents the absolute smallest annulene. Like benzene, annulenes have been extensively used as model systems to study aromaticity. In fact, the last decades have seen a renewed interest in this kind of compounds, partly motivated by a number of synthetic findings. Moreover, $[4n + 2]$ -annulenes may serve as prototypes of one-dimensional metals² and some annulenes show very interesting properties from a nanotechnological perspective.³ For instance, Pak *et al.* have reported a series of site-specific electron-donor and/or acceptor-functionalized [18]-annulenes,⁴ some of them presenting nonlinear optical properties.⁵ In addition, dehydrobenzo[20]annulenes can form ordered onion- and tube-type nanostructures.⁶ For some recent review on the chemistry of annulenes, see the paper by Haley and coworkers.⁷ All these findings make research in this kind of systems very interesting. In this context, theoretical methods provide a cheap way of predicting such properties, including molecules of higher molecular weight. Among these properties, polarizability has an essential function in a variety of physical and chemical processes. In this work, we report an *ab initio* study of static and dynamic polarizabilities of $[4n + 2]$ -annulenes for $n = 5, 6, 7, 10, 13,$ and 16 computed using a CC2 linear response approach.

Calculation details

All the calculations presented here have been done using Dunning's aug-cc-pVDZ basis.⁸ This is a rather small basis consisting of a [10s5p2d/4s3p2d] contraction for carbon and a [5s2p/3s2p] contraction for hydrogen, but a larger basis would make it impossible to carry out the largest computations. Moreover, in a previous work⁹ we showed that the effect of basis set size is less important for the larger annulenes. Summarizing, the selected basis comprises 704, 832, 960, 1344, 1728 and 2112 basis functions for the annulenes with 22, 26, 30, 42, 54 and 66 carbons, respectively. The geometric parameters have been taken from the compilation by Wannere and Schleyer.¹⁰ Optimization was done by these authors using the 6-31G* basis set¹¹ at the B3LYP¹² DFT level for the symmetric aromatic structures but only at Hartree–Fock level for the non-aromatic conformations. In addition, they imposed symmetry restrictions to force planarity and delocalized or bond alternating structures for the forms aromatic or non-aromatic, respectively.‡

As mentioned in the Introduction, we have employed a linear response function approach using a CC2 reference wave function. The CC2 model was introduced by Christiansen *et al.*¹³ as an N^5 -scaling approximation to the complete CCSD model. The CC2 total energy is of second-order Møller–Plesset perturbation theory (MP2) quality, but unlike MP2, excitation energies and transition moments can be obtained in CC2 since a response formalism can be established. In the hierarchy of coupled cluster models, CC2 represents an improvement over the essentially non-correlated CCS, although CCSD is actually required to get significantly better results.¹⁴

We have calculated the Cartesian components of the polarizability and in addition present the average polarizability and the anisotropy, which are rotational invariant. All polarizabilities in this work are reported in atomic units (a.u.). The conversion factor from a.u. to S.I. for polarizabilities is $1.648778 \times 10^{-24} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$. The usual volume polarizability (in Å^3) can be obtained from the a.u. number by multiplying with a factor of 0.148185.

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† The HTML version of this article has been enhanced with colour images.

‡ See ref. 10 as well as its supporting information at <http://pubs.acs.org> for details.

The whole study has been carried out using a local version of the DALTON electronic structure program¹⁵ in which we have implemented the recently developed algorithms based on Cholesky decomposition of two-electron integrals.¹⁶ Based on former experience,¹⁷ we have used a Cholesky decomposition threshold of 1.0×10^{-8} , which is enough to warrant that errors with respect to the conventional CC2 values are below the reported accuracy of our results. Comparing to experiment, we showed in a preceding paper⁹ that for this kind of systems the CC2 values of polarizability computed using aug-cc-pVDZ basis⁸ are expected to have an error of around 5%.

Before discussing our results, a word of caution is needed with respect to the chosen geometries. A great controversy has existed about if $[4n + 2]$ -annulenes prefer to adopt either a delocalized (aromatic) structure or a less symmetric localized (π -conjugated bond-alternating) one. It is well known that the relative stabilization due to delocalization decreases with the size of the annulenes and that methods lacking electron correlation favor the less symmetric conformations while correlation effects tend to stabilize the delocalized structure. Thus, Choi and Kertesz¹⁸ determined at the MP2 and B3LYP levels of theory that delocalized symmetric forms should be more stable below $n = 30$, confirming the predictions done by Longuet-Higgins and Salem¹⁹ already at the end of the fifties. Conversely, the HF method predicts that the crossover should occur at $n = 10$. However, high level CCSD(T) calculations²⁰ conclude that [10]-annulene adopts a twist-shaped conformation of C_2 symmetry instead of the expected aromatic heart-shaped conformation of C_s symmetry. This issue was recently revisited by Schleyer and coworkers,²¹ who showed that also [14]-annulene prefers adopting a C_s structure despite [18]- and [22]-annulene being more stable in the geometries of C_2 symmetry according to their KMLYP, BHLYP and CCSD(T) results.

In spite of the discussion in the paragraph above, we have chosen to keep the planar symmetric structures determined by Wannere and Schleyer in ref. 10. In this way, the considered species can serve as a simplified model for assessing the aromatic properties of large planar π -systems. At the same time, we can easily make comparison with previous results found in the literature. A theoretical study of the electric and magnetic properties of the real C_2 and C_s isomers is left for a subsequent publication.

Results and discussion

Fig. 1 shows the variation of the difference in energy between the localized and delocalized planar structures with the number of carbons; the dashed lines represent the corresponding values per carbon atom (scaled by a factor of 10 for the sake of clarity). Similar to previous findings, we have established that from [10]-annulene the Hartree–Fock method determines the localized structure as the most stable. We have also found that the correlated CC2 method predicts that from [22]-annulene the delocalization stabilization energy per atom is decreasing (in absolute value). However, at the CC2/aug-cc-pVDZ level of theory, the changeover to localized structures is not yet observed for $n_C = 30$. In any case, the above-mentioned trend of the stabilization energy per atom to decrease makes us

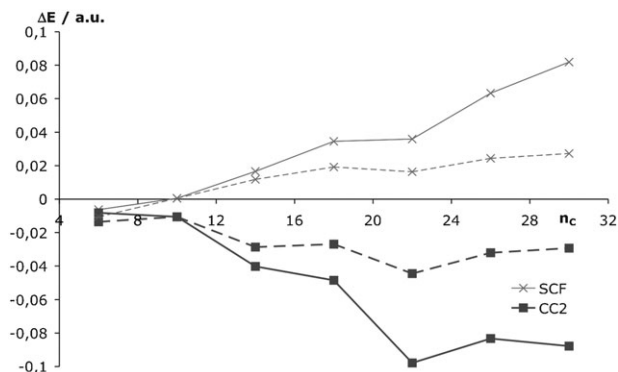


Fig. 1 Difference in absolute energies between the delocalized and localized conformers. The dashed lines represent the corresponding values per carbon atom (scaled by a factor of 10).

expect that the cross point should be near $n_C = 30$. Anyway, we again point out that the structures considered here are idealized planar forms and not the real ones, as discussed at the end of the previous section. Moreover, observe that the employed geometries were optimized with a different theoretical model and a different basis set and, therefore, they are not necessarily optimal for CC2/aug-cc-pVDZ. At this level of calculation, a geometry optimization is unfeasible because of the size of the considered species. We have restricted ourselves to check that for the smallest $[4n + 2]$ -annulene, *i.e.* benzene, the differences between the optimized geometries at the CC2/aug-cc-pVDZ and the B3LYP/6-31G* levels are negligible. The effect of such differences on the calculated polarizabilities is considerably less than the expected error and does not modify the conclusions of this study. As we anticipated, CC2 optimization of the corresponding localized partner, the hypothetical cyclohexatriene, converges to the stable aromatic benzene. We predict similar behavior for the annulenes with n_C less than 30.

In Table 1 we have collected the elements of the polarizability tensor as well as the average polarizability[§] and the anisotropy[¶] of the considered annulenes in their delocalized conformation. Similarly in Table 2 the corresponding results for the smallest localized partners are presented. The perpendicular component of polarizability (chosen as the z direction) is essentially the same independently of whether the π bonds are conjugated or delocalized along the whole ring. From the data in Table 1, the same behavior is encountered for the zz component of the dynamic polarizability at the frequency of the sodium D-line ($\lambda = 589$ nm). Nevertheless, the dynamic polarizability grows slightly faster than the static one in the delocalized annulenes series. Likewise, the static polarizability increases more rapidly in the delocalized set than in the localized one. In all the cases, there exists a perfect linear

$$^{\S} \quad \alpha_{\text{ave}} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}).$$

$$^{\P} \quad \Delta\alpha = \left\{ \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2] \right\}^{\frac{1}{2}}.$$

Table 1 Static (dynamic^a) polarizability components of delocalized annulenes in atomic units^b

n_c	Symmetry	α_{xx}	α_{yy}	α_{zz}	α_{ave}^{\S}	$\Delta\alpha^{\parallel}$
22	D_{2h}	850 (1350)	668 (1070)	156 (159)	558 (860)	623 (1078)
26	D_{2h}	1193 (2351)	981 (1981)	185 (189)	786 (1507)	921 (2002)
30	D_{6h}	1502 (4157)	1502 (4157)	214 (219)	1072 (2844)	1288 (3938)
42	D_{6h}	3326	3326	300	2318	3026
54	D_{6h}	6203	6203	387	4264	5816
66	D_{6h}	10 342	10 342	474	7052	9868

^a Frequency of the sodium D-line ($\lambda = 589$ nm). ^b Calculated at the CC2/aug-cc-pVDZ level.

Table 2 Static polarizability components of localized annulenes in atomic units^a

n_c	Symmetry	α_{xx}	α_{yy}	α_{zz}	α^{\S}	$\Delta\alpha^{\parallel}$
22	C_{2v}	596	485	152	411	400
26	D_{3h}	756	639	180	525	527
30	D_{3h}	868	868	209	648	659

^a Calculated at the CC2/aug-cc-pVDZ level.

fitting of the polarizability with respect to the number of carbons (or, equivalently, of double bonds) of the annulene.

The situation with respect to the in-plane polarizability (the average of the xx and yy components) is entirely different. An analysis of the variation of the polarizability with respect to the square of the number of carbons, which in turn is roughly proportional to the area delimited by the ring, reveals that while the static polarizability of the delocalized conformers grows almost linearly, it grows in a sub-linear manner in the case of the bond-alternating structures. In Table 3 we present the results of a least-square fitting of the data calculated in this paper. The set has been increased by including the values (n_c less than 22) reported in our previous work,⁹ which were computed at the same level of approximation.

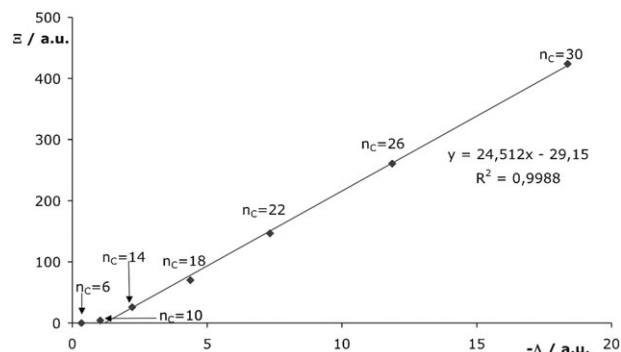
On the other hand, the dynamic parallel polarizability increases very quickly. Since at the same time the HOMO–LUMO gap decreases with the size of the annulene, already for the [42]-annulene the dynamic polarizability at $\lambda = 589$ nm cannot be computed in our approach, because this frequency is too close to the first excitation energy. The decrease of the HOMO–LUMO gap has been proposed¹⁸ as the leading factor for the tendency of larger annulenes to localization, as it favors the appearance of pseudo-Jahn–Teller effects, also known as Peierl's transition.

A closer inspection of the in-plane component of the aromatic structures' polarizability behavior reveals that it is not exactly linear but rather quadratic, although the linear term gives the dominant contribution even for the largest consid-

Table 3 Fittings of the static polarizability of delocalized annulenes ($6 \leq n_c \leq 30$) and exaltation of static polarizability^a

y	x	a_0	a_1	a_2	r^2
α_{\perp}	n_c	3.2857	6.9721	—	0.9997
α_{\parallel}	n_c^2	45.337	1.3214	0.0003	0.9999
Ξ^{**}	$-A_{\parallel}$	-15.264	20.41	0.1987	0.9986

^a $y = a_0 + a_1x + a_2x^2$.

**Fig. 2** Relationship between the exaltations of static electric polarizability^{**} (Ξ , computed in this work) and magnetic susceptibility \parallel (A , taken from ref. 10) of annulenes. Benzene data have not been included in the linear fit.

ered annulene. We must mention that a quadratic extrapolation of the values corresponding to the smallest annulenes ($n_c \leq 30$) gives a prediction for α_{\parallel} of [66]-annulene that is 10% in error with respect to the computed value. This error can be related to the above-mentioned decrease of the HOMO–LUMO gap with the size of the annulene ring, since it produces some multireference character in the wave function of the largest annulenes and consequently reduces the reliability of the CC2 approximation. However, the perpendicular polarizability predicted by the linear fitting differs only by 2% from the calculated estimation.

The exaltation of the magnetic susceptibility \parallel (*i.e.* the difference between the isotropic susceptibilities of the delocalized and the localized isomers) is a classical measure of the aromatic character of organic molecules. An equivalent exaltation of the electric dipole polarizability^{**} can be defined.

Although magnetic criteria are definitely preferable, it has been pointed out that polarizability could serve as a measure of relative aromaticity in similar compounds.²² However, as highlighted by Fowler and Soncini,²³ the use of polarizability as an aromaticity index is limited to non-clamped systems that fulfil Hückel's rule. Interestingly enough, excluding [6]-annulene, there is a nearly linear relation between the exaltations of polarizability computed in this work and the exaltations of susceptibility reported in ref. 10, as can be seen in Fig. 2. Furthermore, even including the benzene values in a quadratic

$$\parallel A = \chi_{ave}^{del} - \chi_{ave}^{loc}$$

$$** \Xi = \alpha_{ave}^{del} - \alpha_{ave}^{loc}$$

fitting, the coefficient of the linear term is two orders of magnitude larger than that of the quadratic one. From a computational point of view, this is a rather significant observation, since the calculation of electric polarizability is less demanding than that of magnetic susceptibility, as only one-half of the first order response equations need to be solved. In addition, complications arising from gauge invariance are obviously eliminated. Nevertheless it must be recalled that while the exaltation of polarizability is caused by the in-plane components of the tensor, the exaltation of susceptibility is fundamentally due to the component in the direction of the external magnetic field, which is perpendicular to the mean plane of the molecule. Indeed, the anisotropy of the magnetic susceptibility itself²⁴ has been proposed as a quantitative index to measure aromaticity.²⁵ According to Bilde and Hansen,²⁶ the observed increment of the perpendicular component of the magnetic susceptibility in aromatic compounds has to be attributed to the absence of paramagnetic currents and it is then governed by the diamagnetic contribution. Since such diamagnetic contribution depends on the electric second moment of charge, the relationship between the exaltations of polarizability and susceptibility might be understood by taking into account that both the electric polarizability and the second moment of charge are related to the molecular size. Moreover, this also makes us expect that a parallel behavior should be encountered in other compounds as long as these properties can be directly connected to the molecular size, as it happens in families of related species. Conversely, if the induced currents are of paramagnetic type or if diatropic currents are quenched by interaction with π systems such correlation should not be expected.²³ That is the case of antiaromatic $[4n]$ annulenes.

The same argument is also enough to justify why the obtained relationship between the exaltations of electric polarizability and magnetic susceptibility should not depend on the theoretical method used to compute such quantities because although the numerical values could be different, in fact the same physical situation is described. In Table 4, we present the magnetic susceptibilities of $[4n + 2]$ -annulenes—with n from 1 to 6—as well as the corresponding exaltations computed with several theoretical procedures. In particular, using the CTOCD (continuous translation of the origin of the current density) method²⁵ to keep gauge origin independence,^{††} we have used CC2 (as we did for the reported polarizabilities) and B3LYP reference wave functions. It is easy to check that the linear relationship found earlier in Fig. 2 is still maintained. Nevertheless, for $n = 7$ the linearity is broken due to a huge increment of the perpendicular component of the susceptibility of localized $C_{30}H_{30}$. Similarly, for n_C larger than 30 Schleyer and coworkers¹⁰ detected an analogous effect when studying the ring currents contribution to total magnetic susceptibility.

†† Strictly speaking, the CTOCD method provides gauge-independent magnetic susceptibilities only when the dipole moment is zero. For annulenes, this is the case of the perpendicular component of χ , which determines the exaltation of magnetic susceptibility.

Table 4 Magnetic susceptibility and exaltation of susceptibility in cgs units at different levels of calculation

n_C (sym)	CC2		B3LYP	
	χ_{ave}^a	$-A_{ }$	χ_{ave}^a	$-A_{ }$
6 (D_{6h})	-54.32	1.18	-53.52	0.47
6 (D_{3h})	-53.14		-53.05	
10 (C_{2v})	-82.76	4.02	-116.66	2.89
10 (C_i)	-78.74		-113.77	
14 (D_{2h})	-216.44	77.16	-204.98	47.60
14 (C_{2v})	-139.28		-157.38	
18 (D_{6h})	-368.39	207.82	-350.75	136.90
18 (D_{3h})	-160.57		-213.85	
22 (D_{2h})	-564.77	400.66	-540.71	284.09
22 (C_{2v})	-164.11		-256.62	
26 (D_{2h})	-840.86	685.53	-813.08	520.89
26 (C_{2v})	-155.33		-292.19	

^a Defined similarly to α_{ave} .[§]

Conclusions

We have reported the polarizabilities of large $[4n + 2]$ -annulenes in both localized and delocalized structures computed at the CC2/aug-cc-pVDZ level of theory. As in the case of small annulenes, we have found a linear behavior of the perpendicular component of the polarizability with respect to the number of double bonds. Moreover, an almost linear relationship between the exaltations of magnetic susceptibility and electric polarizability has been determined.

Acknowledgements

This work was supported by European Network NANO-QUANT (MRTN-CT-2003-506842), Spanish MCT (Project CTQ2004-07768-C02-01/BQU of Plan Nacional I + D + I and European FEDER funds), by Generalitat Valenciana (GVA-COM06-147, ACOMP07/163 and GV/2007/093) and by Norwegian Research Council through the Strategic University Program in Quantum Chemistry (Grant no. 154011/420).

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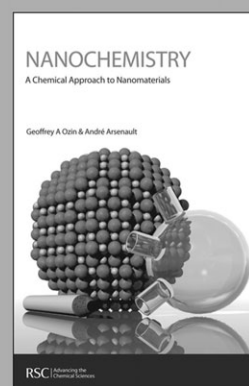
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