ChemComm

Visualisation of counter-rotating ring currents in kekulene

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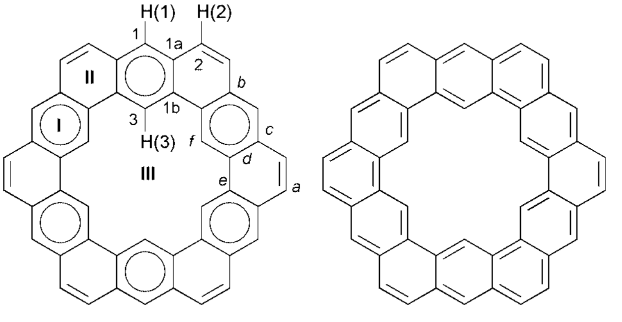
Received (in Cambridge, UK) 5th December 2000, Accepted 26th February 2001
First published as an Advance Article on the web 19th March 2001

Current-density maps for kekulene 1 computed using an *ab initio* all-electron distributed-origin method show global diamagnetic and paramagnetic circulations around outer and inner perimeters ('rim' and 'hub'), subsuming six local benzenoid diamagnetic π circulations, in qualitative agreement with the Hückel–London π model, but in contradiction of an [18]-in-[30] concentric-annulene description of 1.

Even before its synthesis in 1978 the cyclic polyacene kekulene (**1**, $C_{48}H_{24}$),[1] which consists of twelve annelated benzene rings, was already a subject of debate. Qualitative considerations suggest that **1** may be represented either as a D_{6h} Clar structure containing six benzenoid sextets[2] (**1a**) or an [18]annulene-within-a-[30]annulene corresponding to superposition of two D_{3h} Kekulé resonance structures (**1b**, Fig. 1). The proposal[3] that circularly conjugated **1** possesses superaromaticity, *i.e.* enhanced stabilisation energy, led to controversy[4] resolved by a recent *ab initio* study.[5] A comparison of the computed geometric, energetic and magnetic properties[6] of **1** with those of anthracene, phenanthrene, 1,2:7,8-dibenzanthracene and [18]annulene, showed no enhanced stabilisation energy, diamagnetic exaltation or magnetic anisotropy, all as would be expected from the qualitative graph theoretical analysis,[4] indicating that **1** is not superaromatic, and is realistically described by the D_{6h} structure **1a**.[5] These conclusions are compatible with the single-crystal X-ray structure of **1**. They also match the ^{1}H NMR data: the downfield-shifted $\delta(^1H)$ of the inner protons [H(3); 10.45/10.47][7] differs markedly from that of the corresponding protons in [18]annulene (-3.0[8]), as expected from the positive (paramagnetic; 5.0[5]) and negative (diamagnetic; -13.4[5]) NICS[6] values calculated for the geometric centres of **1** and [18]annulene, respectively (**III**, Fig. 1).

In a recent paper[9] the general picture of the 'annulene-within-an-annulene' model[10] for planar coronene (**2**, $C_{24}H_{12}$) and bowl-shaped corannulene (**3**, $C_{20}H_{10}$) was rejected on the basis of direct computation using *ab initio* all-electron distributed-origin methods and mapping of the current densities induced by a uniform magnetic field.† For **2** and **3**, two strong counter-rotating ring currents, a diamagnetic (anti-clockwise) and paramagnetic (clockwise) circulation around the rim and hub, respectively, were found.

To address the question of the electronic structure of kekulene **1**, *ab initio* all-electron current-density maps were calculated using the same distributed-origin methods.† Here we report the results, which support the Clar and Hückel pictures (*cf.* **1a**, Fig. 1).



1a **1b**

Fig. 1 Alternative Clar (**1a**) and Kekulé (**1b**) structures for **1**.

The geometry of **1** was optimised using the 6-31G** basis set;[11] the planar, structure of **1** [D_{6h} symmetry (**1a**)] agrees with single-crystal X-ray data (Table 1).[3,5,7]

Fig. 2 shows the computed current-density maps† of **1a** for (a) the σ, (b) π and (c) total (σ + π) electrons at $1a_0$ above the molecular plane. The σ map demonstrates the characteristic superposition of diamagnetic circulations centred on σ bonds, giving rise to a cumulative net central paramagnetic circulation within each hexagonal ring. The π map shows a pattern of current density dominated by intense diamagnetic and paramagnetic circulations around outer and inner perimeters ('rim' and 'hub'), respectively. Residual benzenoid diamagnetic circulations within the central hexagons of the anthracene-like sub-units, are also visible (**1a**; rings **I**, Fig. 1). No diamagnetic circulations are observed in the hexagons at the six corner positions (**1a**; rings **II**, Fig. 1). This pattern is reminiscent of the computed *ab initio* current-density maps for anthracene and phenanthrene.[12] Thus, when placed in a perpendicular magnetic field, **1** has induced counter-rotating ring currents with a diamagnetic rim and a paramagnetic hub, in flat contradiction of the prediction of the [18]annulene-within-a-[30]annulene model, which would give diamagnetic rim and hub ring currents.[4]

The quality of the current-density maps is established by the calculated CTOCD-PZ2 integrated magnetic properties,† which are consistent with available experimental[7] and previous *ab initio* data acquired using different methods.[5]

The computed magnetic anisotropy $\Delta\xi$ (-153.9 a.u.) of **1a**, which tends to correlate[9] with the conventional exaltation of *isotropic* magnetic susceptibility Λ,[13] is *ca.* 10 times that of benzene. Thus, the CTOCD results support the conclusion that **1a** is not superaromatic.[3–5] The calculated $\Delta\xi$ is in qualitative agreement with an estimate of Λ (178×10^{-6} cm^3 mol^{-1} [14]).

The mean absolute shielding (σ) at the geometric centres of the distinct rings (**1a**; **I** 14.6, **II** 8.0 and **III** -3.2, Fig. 1), which with the required sign change are NICS[6] values (**I** -10.8, **II** -4.3 and **III** 5.0[5]), are consistent with the sense and strength of the calculated current densities (Fig. 2).

The computed mean absolute shieldings of the protons positioned on rim [H(1)/H(2)] and hub [H(3)] show good agreement with experiment (Table 1). The substantial downfield shift of H(3) with respect to H(1) [$\Delta\delta$ 1.62 (2.08/2.02[7])]

Table 1 Computed bond lengths (in Å) and shifts $\delta(^1H)$ and $\delta(^{13}C)$ for **1**

Bond[a]	6-31G**[b,c]	Atom[a]	$\delta(^1H)_{calc}$[b]	$\delta(^{13}C)_{calc}$
a	1.339 [1.347–1.351]	1	8.07 [8.37/8.45]	127.6
b	1.453 [1.438–1.449]	1a	—	131.5
c	1.394 [1.391–1.397]	1b	—	130.1
d	1.410 [1.415–1.421]	2	7.58 [7.95/8.01]	127.4
e	1.466 [1.453–1.461]	3	9.69 [10.45/10.47]	117.6
f	1.383 [1.381–1.390]			

[a] See **1a**, Fig. 1. [b] $\delta(^1H)_{calc} = 30.8 - 10^{-6}\sigma(^1H)$ and $\delta(^{13}C)_{calc} = 185.6 - 10^{-6}\sigma(^{13}C)$.† Experimental values in square brackets.[7] [c] See ref. 3.

DOI: 10.1039/b009763m

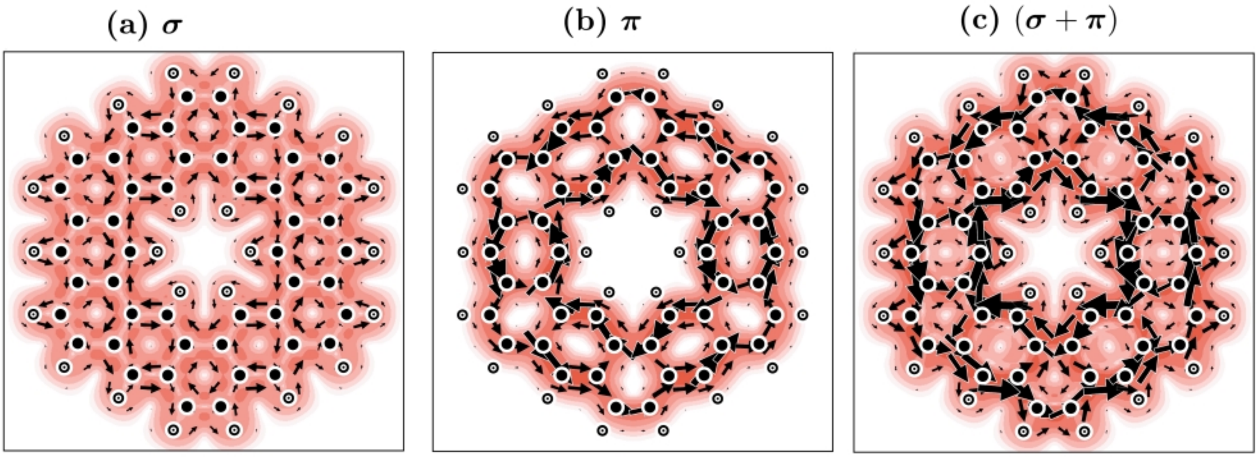


Fig. 2 Computed current-density maps of **1** [(a) σ, (b) π and (c) σ + π electrons].

and H(2) [$\Delta\delta$ 2.11 (2.50/2.46[7])] is in line with the strong paramagnetic hub ring current along the hub. Unfortunately, the extreme insolubility of **1** thwarted acquisition of its ^{13}C NMR spectrum. The δ(^{13}C) values of **1** compare with those of the corresponding position in anthracene and phenanthrene. We note that for C(3) an upfield shift of *ca.* 5 ppm is predicted (Table 1).

It is interesting to compare the results with the predictions of two simple models for the response of **1** to a uniform magnetic field. The annulene-within-an-annulene[10] picture of **1** (*cf.* **1b**, Fig. 1) considers the 48π-electron system as two separate $4n + 2$ circuits, an outer 30π and an inner 18π cycle. As *disjoint* aromatic monocycles, each would therefore carry a uniform induced diamagnetic ring current, and hence **1** would have *co-rotating* currents. In contrast, when the Hückel–London model[15] is applied of **1**, a more complex pattern of induced currents in all 60 bonds is predicted. Application of symmetry constraints and current conservation at each vertex of the graph (as in electrical circuits[16]) shows that in fact all bond currents are functions of just three independent parameters, which govern the inner, outer and radial current flow. In the simplest version, where all bonds have equal resonance integrals, counter-rotating circulations on rim and hub are predicted,[4] in qualitative agreement with the *ab initio* π map, though with much weaker currents in the radial bonds connecting inner and outer perimeters (Fig. 3). If the resonance integral of the radial bonds is reduced to zero, the interior current slows down and reverses recovering the (physically incorrect) annulene-within-an-annulene model.‡

We gratefully acknowledge travel grants from the Council for Chemical Sciences of the Netherlands Organisation for Scientific Research and the British Council and thank the European Union TMR Network scheme, contract FMRX-CT097-0126 (support for A. A., University of Bologna).

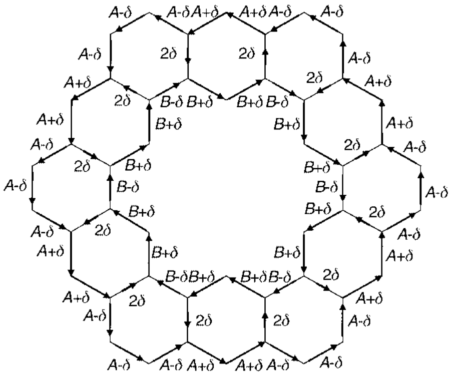


Fig. 3 Induced bond currents in the Hückel–London π model of **1**.‡

Notes and references

† For procedures see ref. 9.

‡ With all bond lengths set to 1.4 Å, perimeter resonance integrals set to the benzene β, and integrals for radial bonds to β', the variation $1 \geqslant \beta'/\beta \geqslant 0$ covers the range from **1** to a fully decoupled [18]-in-[30] annulene. All current strength parameters (Fig. 3) are monotonic: $1.18 \leqslant A \leqslant 3.64$, $0.18 \leqslant \delta \leqslant 0$, $0.99 \geqslant B \geqslant -2.24$, in units of the benzene ring current. The hub has a paramagnetic current for $0.424 < \beta'/\beta$, a diamagnetic current for $\beta'/\beta < 0.407$.

1 H. A. Staab and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 372; H. A. Staab and F. Diederich, *Chem. Ber.*, 1983, **116**, 3487.
2 E. Clar, *Polycyclic Hydrocarbons*, Academic Press Inc., London, 1964.
3 J. Cioslowski, P. B. O'Connor and E. D. Fleischmann, *J. Am. Chem. Soc.*, 1991, **113**, 1086; Z. Zhou, *J. Phys. Org. Chem.*, 1995, **8**, 103.
4 For an opposing view: J.-I. Aihara, *J. Am. Chem. Soc.*, 1992, **114**, 865. J.-I. Aihara, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 237.
5 H. Jiao and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2383.
6 P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6137; see also: U. Fleischer, W. Kutzelnigg, P. Lazzeretti and V. Mühlenkamp, *J. Am. Chem. Soc.*, 1994, **116**, 5298.
7 H. A. Staab, F. Diederich, C. Krieger and D. Schweitzer, *Chem. Ber.*, 1983, **116**, 3504.
8 F. Sondheimer, *Acc. Chem. Res.*, 1972, **5**, 81.
9 E. Steiner, P. W. Fowler and L. W. Jenneskens, *Angew. Chem., Int. Ed.*, 2001, **40**, 362.
10 For a review: R. Benshafrut, E. Shabtai, M. Rabinovitz and L. T. Scott, *Eur. J. Org. Chem.*, 2000, 1091 and references therein.
11 CADPAC: R. D. Amos and J. E. Rice, *The Cambridge Analytical Derivatives Package*, Issue 4.0, 1987.
12 E. Steiner and P. W. Fowler, *Int. J. Quantum Chem.*, 1996, **60**, 609; A. Ligabue, U. Pincelli, P. Lazzeretti and R. Zanasi, *J. Am. Chem. Soc.*, 1999, **121**, 5513.
13 H. J. Dauben, J. D. Wilson and J. L. Laity, *Diamagnetic Susceptibility Exaltations as a Criterion of Aromaticity*, in *Nonbenzenoid Aromatics*, ed. J. P. Snyder, Academic Press, New York, vol. 2, 1971.
14 G. Ege and H. Volger, *Z. Naturforsch., Teil B*, 1972, **27**, 918.
15 A. Pasquarello, M. Schluter and R. C. Haddon, *Phys. Rev. A.*, 1993, **47**, 1783; A. Ceulemans, L. F. Chibotaru and P. W. Fowler, *Phys. Rev. Lett.*, 1998, **80**, 1861.
16 G. Kirchoff, *Ann. Phys. Chem.*, 1847, 497–508; N. L. Biggs, E. K. Lloyd and R. J. Wilson, *Graph Theory 1736–1936*, Clarendon Press, Oxford, 1998, ch. 8.