Can aromaticity be described with a single parameter? Benzene *vs.* cyclohexatriene

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The problem of magnetic *vs.* geometric criteria of aromaticity is approached using NICS/GIAO/B3LYP/6-31G* calculations on benzene and distorted benzenes, the conclusion being that a relationship exists between these criteria but only for specific subsets.

There is a long standing controversy about the minimum number of descriptors that are necessary to describe aromaticity. For the sake of simplicity, we will limit ourselves to Bird's (i), Katritzky's (ii) and Schleyer's (iii) contributions. Other criteria of aromaticity, as those based on energetics, are outside the frame of the present study (for pioneering contributions to this problem see Pauling[1] and Dunitz;[2] for comprehensive reviews on aromaticity, see Balaban's[3] and Minkin's[4] books). (i) Bird introduced and extensively used an aromaticity criterion V which is based on the variation of ring bond orders:[5–9]

$$V = 100/\bar{N}\sqrt{[\Sigma(N-\bar{N})^2/n]} \qquad (1)$$

where $\bar{N}$ is the arithmetic mean of various bond orders and n the number of bonds. The bond orders, N, were calculated from the bond length, R, using Gordy's relationship,[10] which for CC bonds is:

$$N = 6.80/R^2 - 1.71 \qquad (2)$$

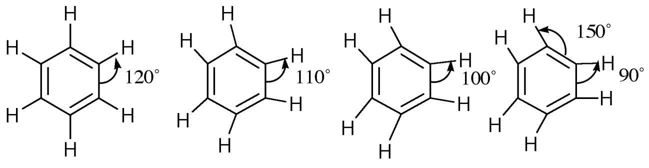
Using these definitions, the value of V for benzene is 0 and 33.3 for cyclohexatriene (CC bond 1.537 Å, C=C bond 1.333 Å). (ii) Schleyer has proposed that the most significant criterion for aromaticity is the magnetic one as exemplified by the NICS parameter (Nucleus Independent Chemical Shift).[11–13] (iii) Katritzky's contribution is of a more methodological nature:[14,15] from a statistical analysis of the different criteria, he concludes that two or three orthogonal factors are necessary to describe all aspects of aromaticity, in particular, the geometrical and magnetic criteria are orthogonal (*i.e.* unrelated).

Results and discussion

We have carried out GIAO/B3LYP/6-31G* calculations on two series of compounds: benzene *vs.* distorted benzenes and benzene *vs.* 'localized' benzenes.[16–19] Following our previous work where we described the effect of the benzene ring current on the ^{1}H shieldings of a methane molecule,[20] we first carried out the calculations using a methane molecule as a 'probe'. We then realized that these effects are dependent not only on the nucleus and its distance but also on (i) the molecule to which it is attached and (ii) its relative position. (i) The variations in the ^{1}H-NMR isotropic shielding of the hydrogens of different molecules located at 2.4 Å perpendicular from the center of the benzene ring are: 2.75 for H_2, 2.68 for HLi, 2.36 for HF, 2.45 for CH_4 and 2.88 ppm for C_2H_2. (ii) The variation in the ^{1}H-NMR isotropic shielding of hydrogen fluoride with the hydrogen at 3.0 Å from the center of the benzene ring with the H of HF pointing towards the aromatic ring is 1.42 and 3.4 ppm in the opposite disposition. Therefore, we decided to use NICS[13] at different distances including at the ring centers (Bader's ring critical points).[21] Howard and Krygowski have shown that NICS values are linearly correlated with one of the geometrical indexes of aromaticity (HOMA: harmonic oscillator model of aromaticity).[22,23] Using NICS from ref. 13 and HOMA values for 18 benzenoid hydrocarbons, they found a linear model with $r^2 = 0.80$.[23]

First approach using theoretically calculated distorted benzenes

This method is based on a proposal of Stanger,[24,25] which we have already used in the study of the Mills–Nixon effect in pyrazoles.[26] An artificially constrained benzene molecule with H–C–C angles bent to 90° leads, *via* optimization, to a central ring with a bond length alternate geometry (1.5298 and 1.3482 Å). A similar approach has been used by Kutzelnigg and coworkers in an IGLO study of benzene, but he used an assumed structure for cyclohexatriene.[27] Siegel *et al.* have demonstrated that ring currents are related to bond localization for [14]- and [18]-annulenes.[28,29]



In Table 1 are gathered the NICS for benzene and three distorted benzenes (angular deformation $\theta = 110$, 100 and 90°). Note that for the most distorted benzene, $\theta = 90°$, V is close to 33.3, that is, similar to cyclohexatriene. Although they have been calculated for all the distances d from the center of the ring between 0 and 4 Å at 0.2 Å intervals, we have reported in Table 1 only the values for $d = 0$, 1.4, 2.0 and 2.4 Å, the last distance corresponding to our calculations for the methane (H)/benzene complex[20] and to the classical distance for estimating "aromatic solvent-induced shifts", ASIS, using the Johnson–Bovey formula.[30]

The variation with the distance can be represented by a polynomial equation for distances $d \geqslant 1$ Å, $\text{NICS} = a(1/d) + b(1/d^2) + c(1/d^3)$ (16 points, Table 2). The variation with θ, which is much more important for the present purpose, is related to Bird's V parameter. The best fits (four points) are obtained using V^2 and, in order to have coefficients around 1

Table 1 NICS (ppm) calculated along a line perpendicular to the middle of the ring

d/Å	0	1.4	2.0	2.4	V
Benzene	9.6527	8.5782	4.7472	3.1579	0.00
$\theta = 110$	9.6900	8.5217	4.7075	3.1279	5.91
$\theta = 100$	9.6198	8.2523	4.5399	3.0089	14.36
$\theta = 90$	8.8106	7.2992	3.9975	2.6448	29.16

(between 0.5 and 1.5), we have defined $V' = V^2/1000$. Eqns. (3)–(6) are represented graphically in Fig. 1:

$$d = 0\ \text{Å},\ \text{NICS} = (9.73 \pm 0.06) - (1.05 \pm 0.14)V',\ r^2 = 0.996 \quad (3)$$

$$d = 1.4\ \text{Å},\ \text{NICS} = (8.57 \pm 0.01) - (1.50 \pm 0.01)V',\ r^2 = 1.000 \quad (4)$$

$$d = 2.0\ \text{Å},\ \text{NICS} = (4.74 \pm 0.01) - (0.87 \pm 0.02)V',\ r^2 = 0.999 \quad (5)$$

$$d = 2.4\ \text{Å},\ \text{NICS} = (3.15 \pm 0.06) - (0.60 \pm 0.02)V',\ r^2 = 0.998 \quad (6)$$

Second approach using bridged benzenes

We have selected the five structures represented below, two of them, **1**,[25,31,32] and **3** {bis(bicyclo[2.1.1]hexano)benzene},[6] are usual compounds for localizing the π-system in benzene and for studying the so-called Mills–Nixon effect (Table 3). Siegel designed compound **3** for these purposes in 1992,[28,33] synthesized it in 1995,[34] determined its structure crystallographically and quantum mechanically,[35] and extended its properties to a series of bicyclic annelations.[36] Siegel is strongly opposed to the existence of the Mills–Nixon effect;[35] we[20] and others[32] are less peremptory. The use of annelation to modify the structure of benzene owes much to the work of Mitchell,[37] Kohnke[38] and Komatsu.[39]

The model (Fig. 2) NICS $= a + bV'$ (6 points) is not so good as the preceding case, which is probably related to two facts, the effect of the peripheral saturated rings and the relatively small range of V's (as was pointed out by several authors, **3** contains one of the most localized benzene rings).[6,35]

$$d = 0\ \text{Å},\ \text{NICS} = (10.2 \pm 0.3) - (15 \pm 3)V',\ r^2 = 0.82 \quad (7)$$

$$d = 1.4\ \text{Å},\ \text{NICS} = (8.5 \pm 0.3) - (13 \pm 3)V',\ r^2 = 0.79 \quad (8)$$

$$d = 2.0\ \text{Å},\ \text{NICS} = (4.6 \pm 0.2) - (8 \pm 3)V',\ r^2 = 0.67 \quad (9)$$

$$d = 2.4\ \text{Å},\ \text{NICS} = (3.0 \pm 0.2) - (6 \pm 2)V',\ r^2 = 0.57 \quad (10)$$

Both models contain benzene as a standard and both show linear relationships between the aromatic and geometrical cri-

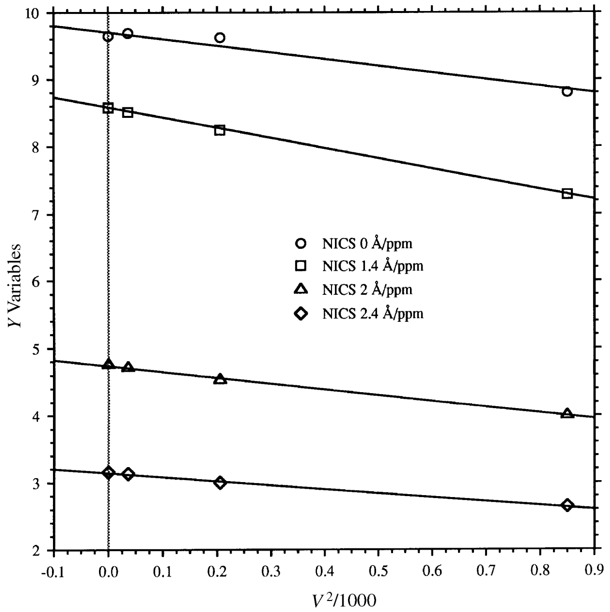


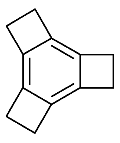
Fig. 1 Plot of NICS for different d values against $V' = V^2/1000$ (model 1).

Table 2 Results of the polynomial regressions

	a	b	c	r^2
Benzene	-7.0 ± 0.3	47.5 ± 1.0	-29.4 ± 0.7	0.999 56
$\theta = 110$	-7.0 ± 0.3	47.2 ± 1.0	-29.2 ± 0.7	0.999 56
$\theta = 100$	-6.8 ± 0.3	45.8 ± 0.9	-28.2 ± 0.7	0.999 57
$\theta = 90$	-6.1 ± 0.2	40.5 ± 0.8	-24.8 ± 0.6	0.999 58

Table 3 NICS (ppm) calculated along a line perpendicular to the middle of the ring

d/Å	0	1.4	2.0	2.4	V'
Benzene	9.65	8.58	4.75	3.16	0.0000
1	10.13	7.64	4.04	2.61	0.0183
2	10.35	7.87	4.03	2.52	0.0220
3	7.34	6.15	3.28	2.15	0.1797
4	9.43	8.75	4.91	3.31	0.0099
5	10.24	8.86	4.84	3.18	0.0226



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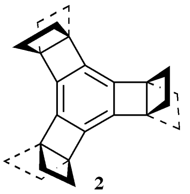

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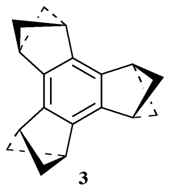

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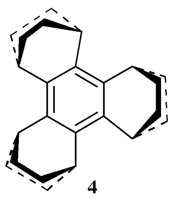

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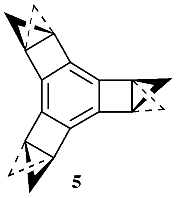

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teria of aromaticity. However, the slopes are very different, between 1.5 and 0.6 for model 1 and between 15 and 6 for model 2 due to the fact that the NICS for the same values of V' are very different (see Fig. 3 for $d = 2.0$ Å). This may explain why in some cases linear relationships are found[9,14] while in others multi-dimensional treatments are necessary,[8,15] and so both criteria are only related for specific subsets.

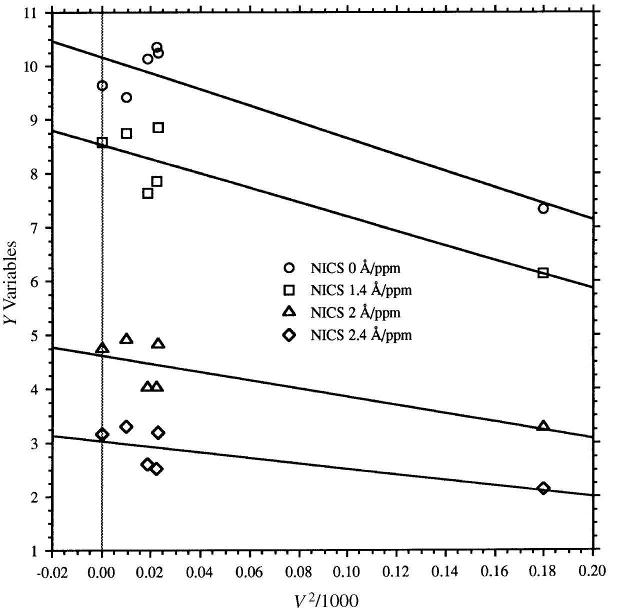

Fig. 2 Plot of NICS for different d values against $V' = V^2/1000$ (model 2).

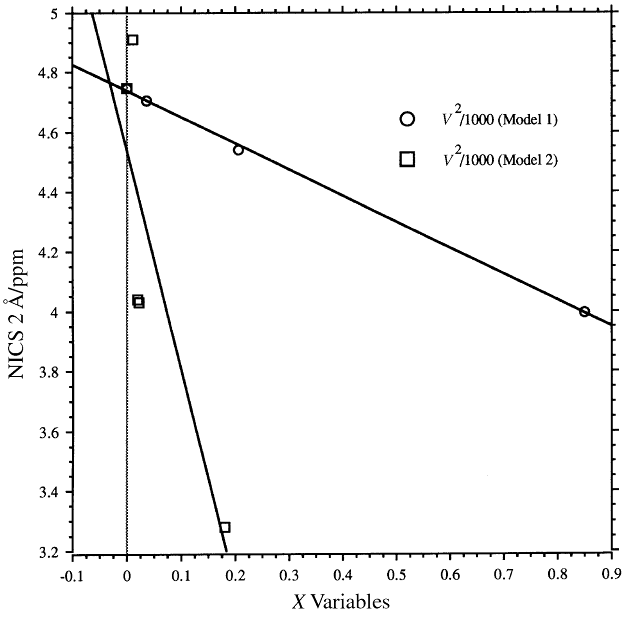

Fig. 3 Plot of NICS for $d = 2$ Å against $V' = V^2/1000$ (for models 1 and 2).

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