

FULL PAPER

Nucleus-Independent Chemical Shifts from Semiempirical Calculations

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Abstract A recently developed special MNDO parameterization for NMR chemical shifts is used to compute the nucleus-independent chemical shifts (NICS) for a wide range of organic molecules, including [n]annulenes, polycyclic hydrocarbons, heterocycles, cage molecules, fullerenes, and pericyclic transition states. The results are compared with published NICS data from *ab initio* and density functional calculations. In general, there is reasonable agreement. The semiempirical NICS values tend to be smaller in absolute value than their *ab initio* counterparts, but they often show similar trends. The aromatic or antiaromatic character of a given system can normally be assigned correctly on the basis of the MNDO NICS values.

Keywords MNDO-GIAO, NICS, Semiempirical, Large molecules

Introduction

Aromaticity and antiaromaticity are basic qualitative concepts that are widely used in chemistry [1,2]. There are three major criteria for classifying a given system as being aromatic or antiaromatic: energies (aromatic stabilization and antiaromatic destabilization), geometries (aromatic bond length equalization and antiaromatic bond length alternation), and magnetic effects such as ¹H-NMR chemical shifts or magnetic susceptibility exaltation and anisotropy (resulting from aromatic diatropic and antiaromatic paratropic ring currents). In 1996, Schleyer et al proposed an additional

magnetic criterion for aromaticity [3]: nucleus-independent chemical shifts (NICS), which are computed as the negative magnetic shielding at some selected point in space, e.g., at a ring center. This criterion has been applied in many *ab initio* and density functional studies since then (see refs. [4-30] for an incomplete list of such applications). These studies have demonstrated that NICS is a useful indicator of aromaticity that usually correlates well with the other energetic, geometric, and magnetic criteria for aromaticity. NICS has the advantage that it is a rather direct manifestation of cyclic electron delocalization (which is commonly connected with the notion of aromaticity). In addition, it is an effective probe for local aromaticity in the individual rings of polycyclic systems.

We have recently implemented [31] the evaluation of the NMR chemical shift tensor at the semiempirical MNDO level [32] using gauge-including atomic orbitals (GIAO) and analytic derivative theory. A special MNDO parameterization has been carried out for the elements H, C, N, and O [31] to

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

reproduce the experimental NMR chemical shifts for a large number of (mostly organic) molecules and ions. The final rms deviations from experiment are less than 5% of the total chemical shift range for each element [31]. In the present paper we apply this GIAO-MNDO approach to compute NICS values for a wide range of organic molecules, in order to assess its performance in this area through comparison with published *ab initio* and density functional NICS results.

Computational method

The original GIAO-MNDO paper provides two different parameterizations (methods A and B, respectively) and an analysis of the influence of the three-center terms on the computed shifts [31]. In accordance with the given recommendations [31] all present NICS results have been obtained with parameterization B and with inclusion of the three-center terms. The computational procedures have been fully documented [31] and used as implemented in the MNDO97 program [33].

It is well known that NMR chemical shifts depend on geometry, often in a fairly sensitive manner [34]. Generally, as recommended [31], the present study employs geometries obtained from standard MNDO [32] calculations, which have been optimized within the same point group as in the reference *ab initio* and density functional studies [3-12]. The differences between the MNDO and the reference geometries will cause some of the observed deviations between the corresponding NICS values. This seems acceptable in a survey study as long as the differences in geometry can be considered minor, which is usually true. In a few rare cases, however, these differences were large enough to necessitate the use of constrained geometries (details see below).

Results and discussion

Table 1 compares the NICS values from GIAO-MNDO with those from published *ab initio* and density functional studies [3-12]. Figure 1 shows a corresponding correlation plot, and Table 2 presents a statistical evaluation of the data.

Since GIAO-MNDO parameters are currently only available for the elements H, C, N, and O [31], our comparisons are essentially restricted to organic molecules. Within this limitation, we have attempted to cover a broad range of reference compounds, supplementing the molecules studied in the original NICS paper [3] with other classes of compounds [4-12] such that our chosen validation set includes [n]annulenes, polycyclic hydrocarbons, heterocycles, cage molecules, fullerenes, and pericyclic transition states.

The *ab initio* reference data in Table 1 have generally been computed at a reasonably high level [3-12], typically GIAO-RHF at B3LYP geometries using basis sets of at least 6-31G* or polarized double-zeta quality. However, it should be kept in mind that the reference NICS values are not yet converged

with regard to improvements in the theoretical level. For example, introduction of diffuse functions (6-31+G* vs 6-31G* basis, level B vs C, see Table 1) may cause NICS changes up to 2 ppm for neutral molecules or cations, and up to 6 ppm for anions [3]. Therefore, it seems best not to focus on small quantitative discrepancies in Table 1, but rather on larger effects and on qualitative trends.

We shall now discuss the individual entries in Table 1. Aromatic and antiaromatic rings are associated with highly negative (i.e. shielded) and positive (i.e. deshielded) NICS values, respectively. In view of previous *ab initio* results [3-30], e.g. the NICS values [3] for benzene (-10 ppm) and cyclobutadiene (+28 ppm), we shall label a system as being aromatic (antiaromatic) if its *ab initio* NICS value is below -5 ppm (above +5 ppm).

MNDO confirms the five-membered heterocycles pyrrole and furan to be aromatic, with NICS values that are slightly too negative in MNDO. The NICS value of cyclopentadiene from MNDO is clearly too negative, but the differences between cyclopentadiene and its ions are well reproduced (MNDO/*ab initio*: anion -10/-11 ppm, cation +53/+57 ppm) indicating that MNDO properly differentiates between the aromatic cyclopentadienyl anion and the antiaromatic cyclopentadienyl cation. For indene (C₉H₈) and fluorene (C₁₃H₁₀) as well as the corresponding indenyl (C₉H₇) and fluorenyl (C₁₃H₉) cations and anions, MNDO gives the correct sequence of NICS values for the five- and six-membered rings in all cases, even though the differences between the rings are underestimated in four cases. The indenyl and fluorenyl anion are confirmed to be highly aromatic, while the indenyl cation is antiaromatic. As found previously [6] the pentagon in the fluorenyl cation is antiaromatic while the hexagon is nonaromatic.

Benzene is the prototypical aromatic molecule. The MNDO NICS value of -11.6 ppm is close to the *ab initio* reference value of -9.7 ppm. In several *ab initio* studies [3,7,8,13,14,18] it has been considered advantageous to discuss NICS values not only at the ring center, but also above the ring, e.g. at a distance of 0.5 Å or 1.0 Å from the center, in order to minimize the influence of the σ -electrons in the ring. Therefore, Table 1 also contains several other NICS data for benzene along the C₆ axis. At a distance of 0.5 Å, the MNDO and *ab initio* values almost coincide, and thereafter they fall off in a comparable manner with increasing distance (MNDO somewhat faster).

For the next four entries in Table 1, there is good agreement between the MNDO and *ab initio* NICS values: o-benzyne, tropylium cation, and cyclooctatetraenyl dication and dianion are all aromatic, as expected, and of the latter two systems, the aromatic character is more pronounced in the dianion. Concerning nine-membered rings, the *ab initio* NICS values indicate that both the Hückel-type cyclononatetraenyl anion (C₉H₉⁻, D_{9h}) with 10 π -electrons and the Möbius-type monocyclic cation (C₉H₉⁺, C₂) with 8 π -electrons are aromatic; this is confirmed by MNDO for the Hückel-type anion and, to some extent, also for the Möbius-type cation (NICS: MNDO/*ab initio* -5/-13 ppm). Furthermore, both approaches agree that two other C₉H₉⁺ cations

Table 1 (continues next page) Comparison of NICS values (ppm) from MNDO and ab initio calculations

Molecule	PG [a]	Ring [b]	MNDO [c]	ab initio reference data		
				value	level[d]	ref[e]
pyrrole	C _{2v}	5	-18.0	-15.1	A	3
furan	C _{2v}	5	-16.0	-12.3	A	3
cyclopentadiene	C _{2v}	5	-11.1	-3.2	A	3
cyclopentadienyl anion	D _{5h}	5	-21.5	-14.3	B	3
cyclopentadienyl cation	C _{2v}	5	41.5	54.1	C	6 (4)
indene	C _s	5	-7.8	-1.4	C	6 (8)
		6	-10.7	-11.3	C	6
indenyl anion	C _{2v}	5	-19.9	-19.5	C	6 (2)
		6	-11.0	-12.5	C	6
indenyl cation	C _{2v}	5	18.9	34.5	C	6 (5)
		6	5.4	8.6	C	6
fluorene	C _{2v}	5	-4.7	0.5	C	6 (9)
		6	-10.3	-10.7	C	6
fluorenyl anion	C _{2v}	5	-16.3	-16.4	C	6 (3)
		6	-10.9	-12.4	C	6
fluorenyl cation	C _{2v}	5	13.2	24.7	C	6 (6)
		6	0.6	1.9	C	6
benzene	D _{6h}	6	-11.6	-9.7	B	3
		6 +0.5	-11.2	-11.5	B	7
		6 +1.0	-8.8	-11.5	B	7
		6 +1.5	-5.9	-8.4	B	7
		6 +2.0	-3.8	-5.3	B	7
		6 +2.5	-2.5	-3.4	B	7
		6 +3.0	-1.7	-2.2	B	7
o-benzyne	C _{2v}	6	-19.4	-20.8	B	7 (1)
tropylium cation	D _{7h}	7	-7.3	-7.6	B	3
cyclooctatetraenyl dication	D _{8h}	8	-6.2	-6.4	B	3
cyclooctatetraenyl dianion	D _{8h}	8	-10.8	-13.9	B	3
cyclononatetraenyl anion	D _{9h}	9	-10.8	-15.1	B	3
monocyclic (CH) ₉ cation	C ₂	9	-4.5	-13.4	D	10 (4)
monocyclic (CH) ₉ cation [f]	C _s	9	6.6	8.6	D	10 (5)
monocyclic (CH) ₉ cation	C _{2v}	9	41.6	42.0	D	10 (6)
all-cis-[10]annulene	D _{10h}	10	-10.9	-14.9	B	3
1,6-didehydro[10]annulene [f]	D _{2h}	10	-12.4	-17.3	C	4 (2)
dodecahedrapentaene [f]	D _{5d}	10	-11.5	-16.5	J	9 (1)
all-trans-[10]trannulene [f]	D _{5d}	10	-14.2	-14.0	J	9 (2)
all-trans-[12]trannulene	D ₆	12	6.8	35.7	J	9
naphthalene	D _{2h}	6	-9.8	-9.9	B	3 (1)
phenanthrene	C _{2v}	6 inner	-5.8	-6.5	B	3 (2)
		6 outer	-10.4	-10.2	B	3
triphenylene	D _{3h}	6 inner	-1.7	-3.0	C	3 (3)
		6 outer	-10.1	-10.8	C	3
		6 inner	-10.9	-13.3	B	3 (4)
anthracene	D _{2h}	6 outer	-8.1	-8.2	B	3
		5	-20.7	-19.7	B	3 (5)
azulene [f]	C _{2v}	7	-6.7	-7.0	B	3
		4	-0.1	27.6	B	3
		4 +0.8	7.7			

Table 1 (continues next page) Comparison of NICS values (ppm) from MNDO and ab initio calculations

Molecule	PG [a]	Ring [b]	MNDO [c]	ab initio reference data		
				value	level[d]	ref[e]
pentalene	C _{2h}	5	5.4	18.1	B	8 (1)
		5 +0.5	7.8	18.2	B	8
pentalene dianion	D _{2h}	5	-20.1	-12.2	B	8
		5 +0.5	-15.9	-11.7	B	8
pentalene dication	D _{2h}	5	-10.2	-5.6	B	8
		5 +0.5	-11.6	-11.6	B	8
acepentalene [g]	C _s	5 s	11.1	19.9	B	8 (2)
		5 a	1.6	11.2	B	8
		5 s+0.5	6.5	13.0	B	8
		5 a+0.5	2.3	9.0	B	8
		5 s-0.5	14.9	22.0	B	8
		5 a-0.5	4.0	14.0	B	8
acepentalene dianion [g]	C _{3v}	5	-17.0	-10.9	B	8
		5 +0.5	-12.8	-9.3	B	8
		5 -0.5	-15.2	-14.1	B	8
acepentalene dication [f,g]	C _{3v}	5	-6.7	0.8	B	8
		5 +0.5	-5.1	3.4	B	8
		5 -0.5	-7.8	-8.3	B	8
heptalene [f]	C _{2h}	7	10.2	22.7	B	3
cyclooctatetraene, planar	D _{4h}	8	19.5	30.1	B	3
benzocyclobutadiene	C _{2v}	6	-5.4	-2.5	B	3 (6)
		4	-1.3	22.5	B	3
biphenylene	D _{2h}	6	-6.8	-5.1	B	3 (7)
		4	-1.6	19.0	B	3
acenaphthylene	C _{2v}	6	-8.5	-8.6	B	3 (8)
		5	-3.1	2.9	B	3
pyracyclene	D _{2h}	6	14.4	-0.1	B	3 (9)
		5	28.4	12.8	B	3
cyclohexane	D _{3d}	6	-6.3	-2.2	B	3
adamantane	T _d	center	-4.8	-1.1	B	3 (10)
1,3-dehydro-5,7- -adamantanediyl dication	T _d	center	-39.0	-50.1	A	3 (11)
1,4-furanofuran	C _{2h}	5	-15.0	-11.9	D	5 (1a)
1,6-furanofuran	C _{2v}	5	-15.2	-11.0	D	5 (1b)
1,5-furanofuran	C _s	5	-11.9	-6.7	D	5 (1c)
		5	-16.3	-14.9	D	5
2,5-furanofuran	D _{2h}	5	-16.7	-15.6	D	5 (1d)
1-benzofuran	C _s	5	-12.6	-9.8	D	5 (3a)
		6	-11.6	-11.6	D	5
2-benzofuran	C _{2v}	5	-16.3	-15.6	D	5 (3b)
		6	-6.0	-4.2	D	5
TS hydrogen exchange in H ₆	D _{6h}	6	-30.8	-24.0	H	11 (7)
TS Diels-Alder butadiene	C _s	[i]	-31.1	-23.5	D	11 (8)
		[i]	-23.4	-27.2	D	11
		[i]	-17.2	-21.4	D	11
TS Diels-Alder cyclopentadiene	C _s	[i]	-25.8	-22.4	D	11 (9)
		[i]	-22.9	-29.7	D	11
		[i]	-16.3	-23.0	D	11
TS 1,5-H-shift cyclopentadiene	C _s	[j]	-19.6	-14.8	D	11 (10)
TS 1,5-H-shift 1,3-pentadiene	C _s	[j]	-17.6	-16.6	D	11 (11)
TS Cope rearrangement, chair	C _{2h}	[k]	-21.2	-25.4	D	11 (12)

Table 1 (continued) Comparison of NICS values (ppm) from MNDO and ab initio calculations

Molecule	PG [a]	Ring [b]	MNDO [c]	ab initio reference data		
				value	level[d]	ref[e]
TS Cope rearrangement, boat	C _{2v}	[k]	-18.6	-22.7	D	11 (13)
TS Claisen rearrangement, chair	C ₁	[l]	-13.4	-21.2	E	11 (14)
TS Claisen rearrangement, boat	C ₁	[l]	-12.5	-18.5	E	11 (15)
TS hexatriene ring closure	C _s	[j]	-13.8	-25.4	E	11 (16)
TS 1,7-H-shift 1,3,5-heptatriene	C ₂	[j]	-10.4	-14.0	E	11 (17)
TS octatetraene ring closure	C ₂	[j]	-9.4	-13.2	E	11 (18)
TS cyclobutene ring opening	C ₂	[j]	-24.5	-12.3	E	11 (19)
TS trimerization of acetylene	D _{3h}	[h,m]	-4.0	-24.1	H	11 (2)
triquinacene	C _{3v}	[h]	-3.1	-2.3	G	11 (4)
diademane	C _{3v}	[h]	-6.5	-10.9	G	11 (6)
TS triquinacene-diademane	C _{3v}	[h]	-17.8	-26.8	G	11 (5)
C ₆₀ fullerene [n]	I _h	center	-5.5	-11.2	F	12
		5	3.2	7.0	F	12
		6	-3.1	-6.6	F	12
C ₇₀ fullerene [n]	D _{5h}	center	-9.7	-28.5	F	12
C ₈₄ isomer 23 [n]	D _{2d}	center	-5.2	-11.9	F	12
C ₆₀ hexaanion [n]	I _h	center	-26.6	-64.4	F	12
		5	-11.6	-28.8	F	12
		6	-7.8	-29.4	F	12

[a] Point group.

[b] By default, the NICS value is computed at the geometrical center of the ring indicated (i.e. the average of the Cartesian coordinates of the ring atoms). "+0.5" denotes a point which is 0.5Å above the center (likewise for other decimal numbers). "outer" and "inner" are used to distinguish between different rings in condensed hydrocarbons. In more complicated cases, the NICS point is specified explicitly in a footnote.

[c] MNDO-NMR parameterization B, see ref. [31]. Three-center terms are included. Unless noted otherwise, the geometries have been optimized by standard MNDO calculations, within the given point group.

[d] Ab initio levels A-J are defined in the usual notation:

A=GIAO-RHF/6-31+G*/MP2/6-31G*,

B=GIAO-RHF/6-31+G*/B3LYP/6-31G*,

C=GIAO-RHF/6-31G*/B3LYP/6-31G*,

D=GIAO-RHF/6-31+G*/B3LYP/6-311+G**,

E=GIAO-RHF/6-31G*/B3LYP/6-311+G**,

F=GIAO-RHF/DZP//BP86/3-21G,

G=GIAO-RHF/6-31G*/MP2/6-31G*,

H=SOS-DFPT-PW91//RHF/6-31G*,

I=SOS-DFPT-PW91//B3LYP/6-311+G**,

J=CSGT-B3LYP/6-31G*/B3LYP/6-31G*.

[e] Numbers in parentheses refer to the label of the molecule used in the cited literature.

[f] Saddle point in MNDO which relaxes to a less symmetrical structure upon removing the point-group constraint. For

the sake of comparison, the NICS values are computed for the same point group as in the ab initio reference calculations.

[g] Acepentalene contains one symmetrical (s) and two asymmetrical (a) pentagons. For this bowl-shaped molecules and its ions, NICS values are given for the ring centers and for points above these centers inside (-0.5) and outside (+0.5) of the bowl.

[h] NICS at the geometric center of the six active carbon atoms (ref.[11]).

[i] For each Diels-Alder reaction, the three NICS entries correspond to the geometrical center of four carbon atoms (see ref.[11]), i.e. for the butadiene moiety, for ethylene plus the two closest carbon atoms of the diene, and for ethylene plus the two distant carbon atoms of the diene.

[j] NICS at the geometrical center of all carbon atoms.

[k] NICS at the geometrical center of the six carbon atoms. The lengths of the breaking/forming CC bonds were fixed at the B3LYP values (ref.[11]).

[l] NICS at the geometrical center of the six heavy atoms. The length of the breaking/forming CC bond was fixed at the B3LYP value (ref.[11]).

[m] CC distances in MNDO optimization constrained to B3LYP values (ref.[11]).

[n] The NICS values at the center of fullerene cages are very close to the corresponding endohedral ³He shifts which have been measured: C₆₀ -6.3, C₇₀ -28.8, C₈₄ -9.0, C₆₀ hexaanion -48.7 (refs.[37-39]).

considered [10] are antiaromatic, particularly the C_{2v} isomer (NICS: MNDO/*ab initio* +42/+42 ppm). In the case of the ten-membered rings, all four molecules studied are found to be aromatic at the MNDO and *ab initio* level, with NICS values in the range between -11 and -17 ppm: this applies not only to the planar all-cis-[10]annulene and 1,6-didehydro[10]annulene molecules with the usual π -conjugation, but also to dodecahedrapentaene and all-trans-[10]trannulene, which show an unusual in-plane conjugation involving p-orbitals pointing inside the ring [9]. The next member of the proposed [n]trannulene family [9], i.e. [12]trannulene, is antiaromatic according to the NICS values (strongly at the *ab initio* level, +36 ppm, and less pronounced in MNDO, +7 ppm).

The next five entries in Table 1 refer to polycyclic hydrocarbons. The MNDO and *ab initio* results for naphthalene, phenanthrene, triphenylene, anthracene, and azulene agree very well with each other. In particular, MNDO reproduces the relative magnitudes of the NICS values in different rings quite nicely (inner vs outer and five- vs seven-membered rings).

Cyclobutadiene is the prototypical antiaromatic molecule, as evidenced by an *ab initio* NICS value of +28 ppm. MNDO

fails for cyclobutadiene, predicting a NICS value around 0. Closer analysis shows that this is partly due to the influence of the σ -electrons in the ring: the MNDO NICS values in the C_2 axis perpendicular to the ring are above +6 ppm for distances of 0.5-1.0 Å, with a maximum of +8 ppm around 0.8 Å. Since the effects of the σ -electrons must fall off faster than those of the π -electrons, these data indicate that the intrinsic NICS contributions from the π -electrons are positive also in MNDO, as expected. We conclude that the MNDO NICS values in the center of four-membered rings are not useful, while those above the ring may reflect the aromaticity or antiaromaticity of the π -system to some extent.

Pentalene with 8 π -electrons is antiaromatic both at the MNDO and *ab initio* level, but MNDO underestimates its NICS value significantly (+5 vs +18 ppm). Both approaches agree that the pentalene dianion with 10 π -electrons and the pentalene dication with 6 π -electrons are aromatic. Similar results are found for the nonplanar bowl-shaped acepentalene: the neutral molecule is antiaromatic, the dianion is highly aromatic, and the dication shows a reduced aromaticity. MNDO reproduces the *ab initio* predictions that the symmetric pentagon in acepentalene has a much higher NICS value than the two unsymmetrical pentagons, and that the

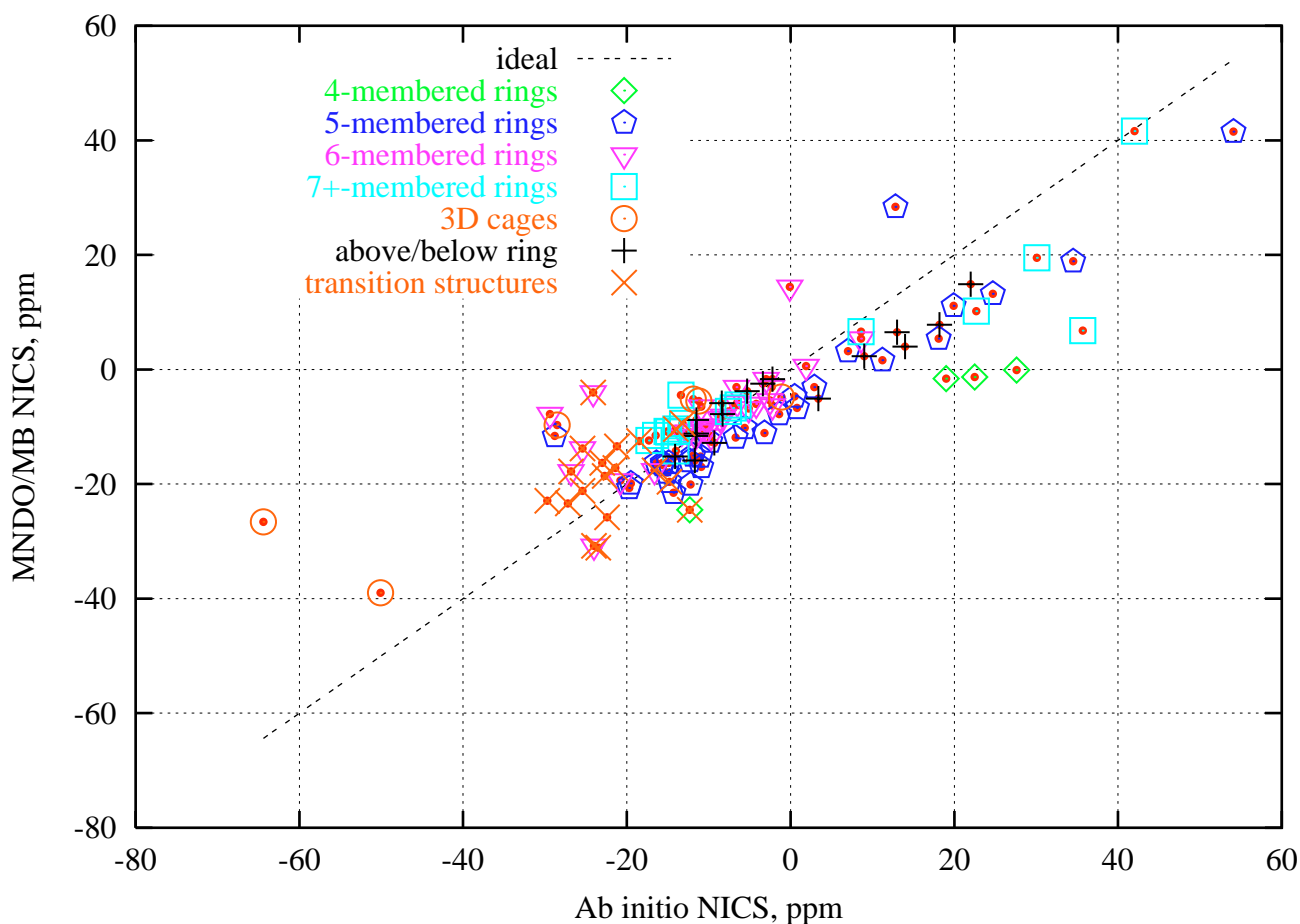


Figure 1 Correlation between MNDO and *ab initio* NICS values

Table 2 Statistical evaluation [a] of the MNDO NICS values (ppm)

	N [b]	mean error	mean abs. error	rms error
all	116	-0.9	6.1	9.0
4-membered rings [c]	3	-24.0	24.0	24.2
5-membered rings [c]	30	-4.2	6.4	8.0
6-membered rings [c]	26	1.4	2.8	5.4
7-membered or larger rings [c]	15	-1.6	5.7	9.2
above/below rings [d]	17	-2.9	3.9	5.2
center of cages [e,f]	6	12.7	14.0	18.2
transition states [g]	19	2.9	6.7	7.9
aromatic [h]	78	2.1	4.7	7.6
antiaromatic [h]	22	-10.4	11.9	14.1
non-aromatic [h]	16	-2.4	4.6	5.9

[a] Based on the entries in Table 1, *ab initio* reference data

[b] Number of comparisons

[c] NICS values in ring centers, excluding transition states from ref.[11]

[d] NICS values above/below ring centers

[e] Adamantane and fullerene systems; when replacing the *ab initio* reference data for the fullerenes by the experimental ^3He shifts (see text) the errors drop to 8.9, 10.1, and 12.9 ppm, respectively

[f] For the set of 13 C_{84} isomers studied at the RHF/DZ//MNDO level [36] the mean absolute error of MNDO is 7.2 ppm relative to the *ab initio* endohedral shifts

[g] Transition states from ref.[11]

[h] See text. A system is considered to be aromatic or antiaromatic if the *ab initio* reference NICS value is less than -5 ppm or greater than +5 ppm, respectively; otherwise, it is non-aromatic

aromatic or antiaromatic ring current effects are higher inside the bowl than outside [8].

Heptalene and planar cyclooctatetraene, each with 8 π -electrons, are antiaromatic, as expected. MNDO again underestimates the *ab initio* NICS values (by 10-13 ppm). In benzocyclobutadiene and biphenylene, the MNDO NICS values are reasonable for the six-membered rings, and useless for the four-membered rings (see above). In acenaphthylene and pyracyclene, MNDO gives the correct sequence of NICS values for the five- and six-membered rings, but overemphasizes the antiaromatic character of pyracyclene.

Cyclohexane and adamantane should have NICS values close to zero since they are nonaromatic. This expectation is better fulfilled at the *ab initio* level (-2/-1 ppm) than at the MNDO level (-6/-5 ppm). In MNDO, there are apparently some residual local shieldings from the σ -electrons even in six-membered rings. On the other hand, the considerable aromaticity of the 1,3-dehydro-5,7-adamantanediyl dication is confirmed by the MNDO NICS value of -39 ppm (*ab initio* -50 ppm).

The next six entries in Table 1 concern fused heterobicycles, which were originally studied to analyze conflicting conclusions from different aromaticity criteria [5]. In the present context, we only note that the MNDO and *ab initio* results for these compounds agree quite well. For 2-benzofuran, in particular, both approaches agree that the pentagon is significantly more aromatic than the hexagon.

It has long been recognized that the transition states of thermally allowed pericyclic reactions are aromatic. The NICS criterion has confirmed this notion: the corresponding *ab initio*

NICS values are highly negative and thus indicate diatropic ring currents in these transition states, with cyclic electron delocalization [11]. The transition structures from standard MNDO calculations are known to be deficient for some of these pericyclic reactions. For example, MNDO predicts an unsymmetrical transition structure for the parent Diels-Alder reaction, whereas an MNDO optimization with C_s symmetry yields a second-order saddle point whose geometry is actually quite close to that of the first-order saddle point found in *ab initio* or density functional work. We have used this C_s structure in our comparisons to avoid geometry-related artifacts. Likewise, the lengths of the breaking/forming bonds in the Cope and Claisen rearrangements and in the acetylene trimerization are unrealistic in standard MNDO calculations, and we have therefore employed partially constrained geometries in these cases (see footnotes of Table 1 for details).

With these caveats in mind, we note that the transition states (TS) for the representative set of pericyclic reactions studied previously [11] are found to be aromatic also at the MNDO level, in agreement with the *ab initio* results. Most of the MNDO and *ab initio* NICS values are less than -10 ppm. Considering individual cases, MNDO overestimates the aromaticity of the hydrogen exchange TS in H_6 . In the case of the Diels-Alder reaction between ethylene and butadiene or cyclopentadiene and the sigmatropic 1,5-hydrogen shifts in cyclopentadiene or 1,3-pentadiene, the MNDO NICS values for the TS are of reasonable magnitude. This is also true for the Cope rearrangement where the difference between NICS values for the chair and boat TS is reproduced (3 ppm). In the case of the Claisen rearrangement, the electrocyclic

ring closure of hexatriene, the sigmatropic 1,7-hydrogen shift in 1,3,5-heptatriene, and the electrocyclic ring closure of octatetraene, the MNDO NICS values are generally somewhat less negative (less aromatic) than their *ab initio* counterparts. For the electrocyclic ring opening of cyclobutene, MNDO predicts a too negative NICS value, consistent with the problems generally encountered with four-membered rings (see above). The TS for the acetylene trimerization is not described well by MNDO. On the other hand, both the MNDO and *ab initio* NICS values characterize the TS for the triquinacene-diademane rearrangement as being highly aromatic. In an overall judgement, the aromaticity of the pericyclic transition states is generally reproduced well by the MNDO NICS values, despite some discrepancies with individual *ab initio* reference data [11].

In fullerenes, NICS may be evaluated at the center of the individual pentagons and hexagons, or at the center of the whole cage. The latter NICS values are usually termed endohedral chemical shifts. According to a simple classical model [12] the endohedral shifts can to a large extent be attributed to the ring currents in the individual pentagons and hexagons, as assessed by their NICS values. For C_{60} , it is generally accepted that there is a balance between paratropic (antiaromatic) currents in the pentagons and diatropic (aromatic) currents in the hexagons [35]. This is consistent with the positive and negative NICS values, respectively, that are found for the pentagons and hexagons of C_{60} both at the MNDO and *ab initio* level; the MNDO values are about half the *ab initio* values, which translates [12] into a correspondingly smaller endohedral shift (MNDO/*ab initio* -5/-11 ppm). In the C_{60} hexaanion, by contrast, both the pentagons and hexagons show strong diatropic (aromatic) currents, which combine to yield a much larger endohedral shift (MNDO/*ab initio* -27/-64 ppm). Hence, both approaches confirm that the C_{60} hexaanion is much more aromatic than C_{60} itself.

It has been demonstrated computationally [36] that the endohedral chemical shifts are very close to the measurable ^3He NMR chemical shifts in the endohedral compounds $\text{He}@C_n$. These are experimentally available for a large number of fullerenes, e.g., -6.3 ppm for C_{60} [37], -28.8 ppm for C_{70} [37], -9.0 ppm as dominant peak for C_{84} [38], and -48.7 ppm for the C_{60} hexaanion [39], and may thus serve to judge the accuracy of theoretical calculations. In the case of C_{60} , the theoretical endohedral ^3He shifts are very sensitive to the chosen geometry [40] and the chosen computational method [41]: for example, the normally reliable B3LYP hybrid functional gives an endohedral shift of +1.0 ppm (wrong sign) for C_{60} [41]. These difficulties are related to the subtle balance between paratropic and diatropic ring currents in C_{60} (see above). In view of these problems, the MNDO endohedral shift of -5 ppm for C_{60} is acceptable. For the other three fullerenes included in Table 1, MNDO underestimates the endohedral shifts as judged from the experimental ^3He shifts, particularly for C_{70} and for the C_{60} hexaanion. The *ab initio* results are much superior for C_{70} , but overestimate the endohedral shift for the C_{60} hexaanion significantly.

This completes our discussion of Table 1. A statistical evaluation of the results is provided in Table 2. The mean

absolute deviation between the MNDO and *ab initio* NICS values for the entire validation set of 116 points amounts to 6 ppm. Systematic errors occur for four-membered rings (mean error of -24 ppm) and, to a much smaller extent, also for five-membered rings (mean error of -4 ppm), which is probably due to an overestimate of the local shielding caused by the σ -electrons in the ring. Such effects are less important in six-membered and larger rings (small mean errors). The systematic deviations for the cage compounds arise mainly from the fact that MNDO underestimates the endohedral shifts of the fullerenes (see above); in this case, the statistical data in Table 2 are not representative because they refer to a small set of fullerenes including those with the highest shifts. There are no obvious systematic errors of MNDO for aromatic transition states or for aromatic systems in general (see Table 2). On the other hand, the NICS values of antiaromatic systems tend to be underestimated by MNDO (mean error of -10 ppm). Figure 1 gives a visual impression of the correlation between the MNDO and *ab initio* NICS values from Table 1. The correlation coefficient is 0.8671.

Conclusions

The GIAO-MNDO approach has been validated for NICS. In general, the *ab initio* reference data for a wide range of compounds are reproduced reasonably well, even though there are some problem cases such as four-membered rings. The aromaticity and antiaromaticity of a system with cyclic electron delocalization is normally reflected in the computed MNDO NICS values. This holds not only for planar conjugated Hückel-type hydrocarbons, but also for more unusual systems including Möbius-type rings, [n]trannulenes, three-dimensional cage compounds, and pericyclic transition states. Since many of the NICS trends at the *ab initio* level are also found at the semiempirical level, the GIAO-MNDO approach may be a useful tool for assessing aromaticity in large molecules.

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