J. Phys. Chem. A **2007,** *111,* 1123−1132

A Quantitative Scale for the Degree of Aromaticity and Antiaromaticity: A Comparison of Theoretical and Experimental Enthalpies of Hydrogenation

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Received: September 5, 2006; In Final Form: November 7, 2006

Chemical structures and transition states are often influenced by aromatic stabilization or antiaromatic destabilizing effects, which are not easy to characterize theoretically. The exact description and precise quantification of the aromatic characteristics of ring structures is difficult and requires special theoretical investigation. The present paper suggests a novel, yet simple, method to quantify both aromatic and antiaromatic qualities on the same linear scale, by using the experimentally measured or theoretically computed enthalpy of hydrogenation reaction of the compound examined [ΔH_{H_2}(examined)]. A reference hydrogenation reaction is also considered on a corresponding nonaromatic reference compound [ΔH_{H_2}(reference)] to cancel all secondary structure destabilization factors, such as ring strain or double bond strain. From these data the relative enthalpy of hydrogenation may easily be calculated: $\Delta\Delta H_{H_2} = \Delta H_{H_2}(\text{examined}) - \Delta H_{H_2}(\text{reference})$. In the present work concept, the $\Delta\Delta H_{H_2}$ value of benzene defines the completely aromatic character (+100%), and the closed shell of the singlet cyclobutadiene represents maximum antiaromaticity (−100%). The component ΔH_{H_2} values were computed at different levels of theory offering a computational “method-independent” measure for aromaticity. A total of 28 well-known aromatic, antiaromatic and nonaromatic, neutral and charged compounds were examined to demonstrate the efficiency of this methodology. Finally, a correlation was made between the calculated aromaticity percentage of the compound examined and their popular Schleyers NICS values.

Introduction

Cyclobutadiene and therefore antiaromaticity has returned to the limelight. This revival is due to rapidly developing experimental techniques, which can provide data about very labile antiaromatic compounds that exist only for a few milliseconds.[1,2] In view of that, aromaticity must also be the center of attraction.[3−11] It is not surprising therefore that, despite more than a century of intense chemical research, aromaticity remains a unique and continuous source of research in chemistry.[3] The subject has been popular with many comprehensive reviews of the history of the field, beginning with the discovery of the π-aromaticity of benzene (**1**, 1920s)[3,4] and, subsequently, antiaromaticity of cyclobutadiene (**2**, 1965),[4−6] followed by the σ-aromaticity[7,8] (1979) and δ-aromaticity[9] (2004) of metal cages.[3−6] Moreover, aromaticity not only is limited to two dimensions but also can be extended into a third dimension, known as spherical aromaticity[10] (1978), which appears in the case of compounds like fullerene. Chemical structures and transition states are often influenced by aromatic stabilization or antiaromatic destabilizing effects, which are not easy to characterize theoretically. The exact description and precise quantification of the aromatic characteristics of ring structures is difficult and requires special theoretical investigation. The present paper suggests a novel, yet simple, and unique method to quantify both aromatic and antiaromatic qualities on the same scale. The term aromaticity had various connotations at different times in the past.[3] Well before the time of Kekule, in the 19th century, it was the odor or fragrance of certain benzene ring-containing compounds that resulted in the name “aromatic”. Subsequently, different methods were used to replace the initial qualitative description. For example, the harmonic oscillatory model of aromaticity (HOMA)[12,13] was based on geometric considerations, and the nucleus independent chemical shift (NICS)[11] with magnetic shielding background[14] and homodesmic reaction[11] focused on resonance enthalpy (H_{RE}) and aromatic stabilization enthalpy (H_{ASE})[15,16] or antiaromatic destabilization enthalpy[17,18] determination (Scheme 1). In fact, H_{ASE} may be considered as a good measure of aromaticity or antiaromaticity, where, by definition, H_{ASE} is positive for aromaticity and negative for antiaromaticity. One should mention another trial to describe the aromaticity based on the isomerization stabilization energy (H_{ISE}),[19] which can be defined by the energy difference between the methyl derivative of an aromatic compound and its nonaromatic exocyclic methylene isomer (Scheme 1).

By definition, the experimentally determined H_{RE} of benzene in kJ mol^{-1} units is based on the hydrogenation experiments[20−27] shown in Scheme 2.

The problem with this definition is that the aromaticity or the aromatic stabilization enthalpy (H_{ASE}), which is considered as a real measure of aromaticity, vanishes already when only one of the three double bonds is hydrogenated (Scheme 3).

The resultant cyclohexadiene exhibits conjugative stabilization, but not aromatic stabilization. Thus, the $\Delta\Delta H$ values listed

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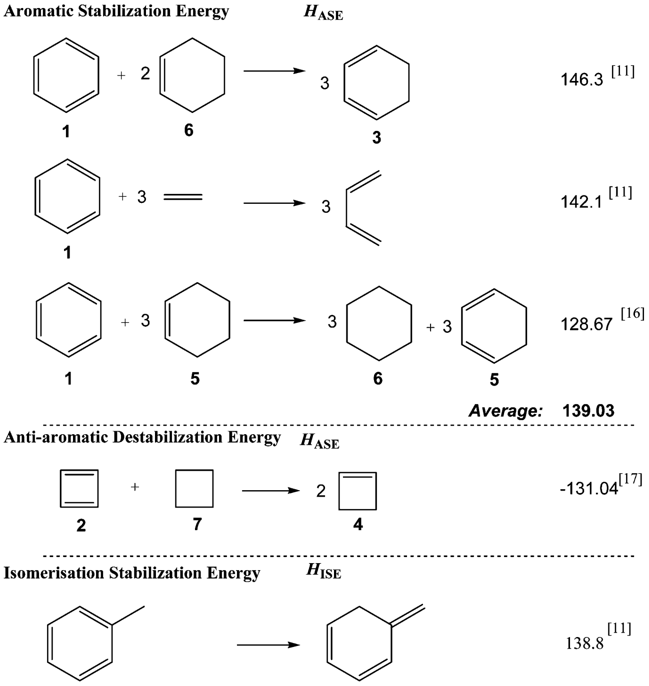
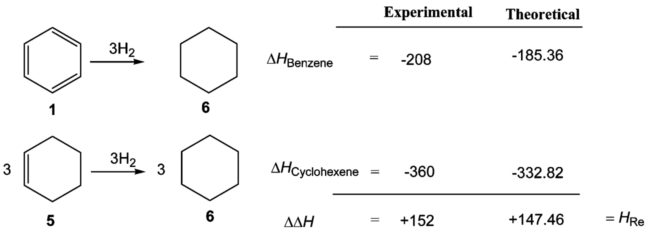
10.1021/jp0657686 CCC: $37.00

SCHEME 1: Different Approaches To Obtain H_{ASE} Values (in kJ mol^{-1})

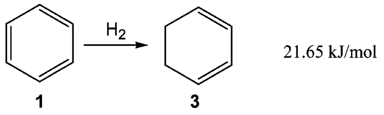


SCHEME 2: Determination of Aromaticity of Benzene via the Historically Developed Method by Dewar[a]



[a] The values computed at the G3MP3B3 level of theory are also shown for comparison.

SCHEME 3: Enthalpy of Partial Hydrogenation, Leading to Conjugatively Stabilized Cyclohexadiene



in Scheme 2 encompass both aromatic stabilization and diene conjugative stabilization. In this sense, the $\Delta\Delta H$ value (which are H_{RE}), given in Scheme 2, overestimates the extent of aromaticity for the benzene molecule.

Antiaromaticity is a relatively new concept dating back to 1965;[25,26] therefore, the experimentally obtained thermochemical values (e.g., enthalpy of formation and ΔH_{H_2}) of **2** were measured only very recently.[1,27,28] Thus, H_{ASE} can in fact be used to quantify antiaromaticity.

Methods

Molecular Computations. The ΔH_{H_2} values were computed at different levels of theory: A, HF/3-21G; B, HF/6-31G(d); C, B3LYP/6-31G(d);[29] D, B3LYP/6-311++G(2d,2p); E, MP2-(FC)/6-31G(d);[30] F, G3MP2B3;[31] G, CCSD/6-31G(d);[32] H, CCSD(T)/6-311++G(2d,2p)//CCSD/6-31G(d)[33] (Table 2) by using the Gaussian03 program.[34] The basis sets were chosen to be reliable to study aromaticity in agreement with the recent assessment.[31] Except for methods G and H, vibrational frequencies were calculated at the same levels of theory as was used for geometric optimization. For the thermodynamic values for methods G and H, the thermodynamic correction values of method C were used. The thermodynamic functions (*U*, *H*, *S*, *G*, listed in the Supporting Information) were calculated at 298.15 K using the quantum chemical, rather than the conventional, thermodynamic scale. Except for compounds **14**, **15**, **16** and **17**, the NICS(0) and NICS(1) values were computed at the B3LYP/6-311++G(2d,2p) (D) level of theory using the geometry obtained by method D. The NICS(0) and NICS(1) values of compound **14**, **15**, **16** and **17** were computed by method C, using optimized geometries of method C.

TABLE 1: Collection of the Literature Enthalpies of Hydrogenations for 1, 2, 3, 4, 5, 10, 29, 11, 30, 12, 31, 52, 24, 43 and 64 in kJ mol^{-1}

	ΔH_f(**A**)	error	ΔH_f(**B**)	error	ΔH_{H2}(**A**→**B**)	error
1 → 3	82.93	±0.50	104.58	±0.63	21.65	±1.13
3 → 5	104.58	±0.63	−4.32	±0.98	−108.90	±1.61
5 → 6	−4.32	±0.98	−123.10	±0.79	−118.78	±1.61
2 → 4	428.00	±14.00	157.00	±2.00	−271.00	±16.00
4 → 7	157.00	±2.00	−28.40	±0.60	−128.60	±2.60
10 → 29	−34.70		−72.25	±0.41	−37.55	>±0.41
29 → 50	−72.25	±0.41	−184.20	±0.71	−111.95	±1.12
11 → 30	108.3	±0.50	103.40	±0.80	−4.90	±1.30
30 → 51	103.40	±0.80	−33.60	±0.96	−106.80	±1.76
12 → 31	115.00	±1.00	90.70	±1.30	−24.30	±2.30
31 → 52	90.70	±1.30	−33.60	±1.20	−124.30	±2.50
24 → 43	139.00		36.00		−103.00	
43 → 64	36.00		−76.40	±0.79	−112.40	>±0.79

Experimental Enthalpies of Hydrogenations. The enthalpies of hydrogenation are not available directly in the literature; therefore, they had to be calculated from the enthalpies of formation (ΔH_f) using eq 1, where $\Delta H_f(H_2) \equiv 0.00$.

$$\mathbf{A} + H_2 \rightarrow \mathbf{B} \tag{1a}$$

$$\Delta H_{H_2}(\mathbf{A}\rightarrow\mathbf{B}) = \Delta H_f(\mathbf{B}) - \Delta H_f(\mathbf{A}) \tag{1b}$$

A critical assessment had been made for the choice of the enthalpy of formation of **1** and the most reliable value had been chosen.[20−24] The enthalpy of formation of **2** was determined only recently,[1,27,28] which offers the possibility to calculate the ΔH_{H_2} value for **2**.

The enthalpies of formation and the resultant ΔH_{H_2} values for various compounds involved in the present work, obtained from the NIST database,[21] are listed in Table 1.

Results and Discussion

The Concept. In this paper, we present a new common linear scale for aromaticity and antiaromaticity based on modifications to Scheme 2. The modified scheme of the enthalpies of hydrogenation, in term of ΔH_{H_2}, is shown in Scheme 4, where the $\Delta\Delta H_{H_2}$ values are proportional to a compound's loss of aromaticity or antiaromaticity (H_{ASE}).

$$\Delta\Delta H_{H_2} = \Delta H_{H_2}(\text{examined}) - \Delta H_{H_2}(\text{reference}) \tag{2}$$

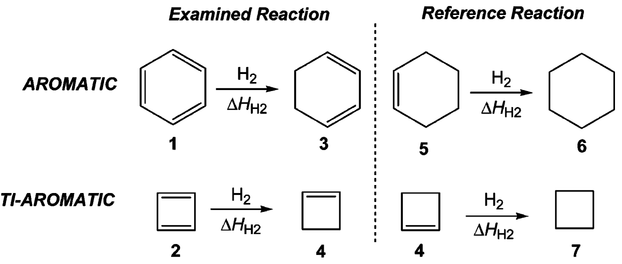
Our method is based on these two pairs of theoretical hydrogenation reactions, where the difference between the ΔH_{H_2} values of an examined and a carefully chosen reference reactions are considered ($\Delta\Delta H_{H_2}$, in eq 2, Scheme 5).

TABLE 2: Parameters for the Linear Fitting of a Quantitative Scale for Aromaticity Calculated from Experimental and Theoretical $\Delta\Delta H_{H_2}$ Values (kJ mol^{-1})[a]

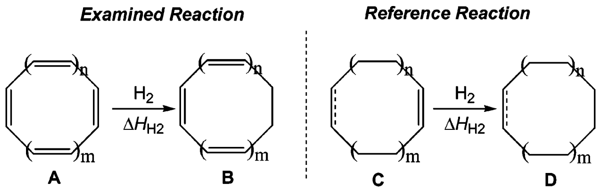
	benzene ($y = 100\%$)			cyclobutadiene ($y = -100\%$)			fitted parameter		
method	ΔH_{H_2} **1 → 3**	ΔH_{H_2} **5 → 6**	$\Delta\Delta H_{H_2}$ **1**	ΔH_{H_2} **2 → 4**	ΔH_{H_2} **4 → 7**	$\Delta\Delta H_{H_2}$ **2**	m	y_0	R^2
				Experimental Results[b]					
	21.65	−118.78	140.43	−271	−128.60	−142.40	0.7013	0.4644	0.9999
error	±1.13	±1.77	**±2.9**	±16	±2.60	**±18.60**	±0.051	±3.401	
				Theoretical Results					
A	24.55	−139.28	163.83	−324.08	−172.47	−151.61	0.6337	−2.5313	0.9995
B	23.40	−130.70	154.10	−311.01	−154.10	−156.91	0.6431	0.6023	0.9999
C	52.27	−106.07	158.34	−274.67	−125.23	−149.44	0.6496	−1.9273	0.9997
D	42.62	−107.55	150.17	−275.52	−128.43	−147.09	0.6844	−1.8637	0.9997
E	50.14	−118.69	168.83	−279.31	−134.95	−144.36	0.6373	−5.1982	0.9980
F	30.28	−110.96	141.24	−258.63	−127.60	−131.04	0.7342	−2.4962	0.9995
G[c]	33.43	−108.12	141.55	−273.35	−127.88	−145.47	0.6968	0.9105	0.9999
H[c]	30.11	−128.23	**158.34**	−267.71	−136.29	**−131.42**	0.6883	−6.1759	0.9971

[a] The fitting was carried out as a three point linear fit (−100 → 0 → 100) according to eq 17. A: HF/3-21G. B: HF/6-31G(d). C: B3LYP/6-31G(d). D: B3LYP/6-311++G(2d,2p). E: MP2/6-31G(d). F: G3MP2B3. G: CCSD/6-31G(d). H: CCSD(T)/6-311++G(2df,2dp)//CCSD/6-31G(d). [b] See refs 20−27. [c] With thermodynamic corrections; taken from method C.

SCHEME 4: Theoretical Hydrogenation Reactions 1, 2, 5 and 6



SCHEME 5: Hydrogenation Reactions of a General System for the New Definition of Aromaticity and Antiaromaticity



One may well recognize that the total enthalpy contents of aromatic and antiaromatic compounds are complex, consisting of several different quantities as outlined below.

1. The chemical structure has a basic enthalpy content, originated from the basic scaffold of the ring, which can be described as a H_0 value.

2. They may possess a certain ring strain enthalpy (H_{RS}).

3. An additional strain can be released from the hydrogenated C═C double bond (double bond strain enthalpy, H_{DBS}), because the optimal bond angle of an sp^3 C atom is nearly 109°, whereas an sp^2 C atom is 120°, meaning that during the hydrogenation a significant geometric relaxation may occur. In the case of saturated compounds the H_{DBS} value is evidently zero.

4. Finally, the third component is the H_{RE} due to the electronic structure of the ring.

Considering the general structures **A**, **B**, **C** and **D** in Scheme 5, one may write the following relationships.

$$H(\mathbf{A}) = H_0 + H_{RS}(\mathbf{A}) + nH_{DBS} + H_{RE}(\mathbf{A}) \quad (3)$$

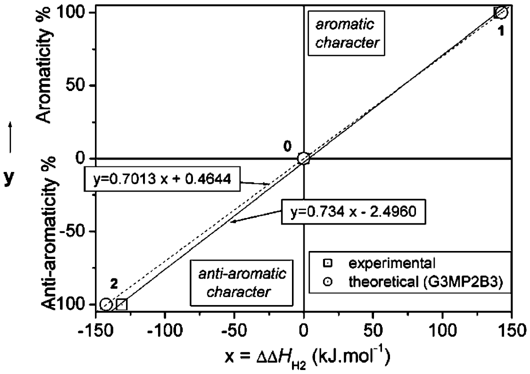


Figure 1. Experimental and theoretical (G3MP2B3) aromaticity and antiaromaticity scale. For both experimental and theoretical data the equations were fitted to three points: **0** (origin), **1** (benzene) and **2** (singlet cyclobutadiene). The theoretical $\Delta\Delta H_{H_2}$ values were computed at the G3MP2B3 level of theory.

$$H(\mathbf{B}) = H_0 + H_{RS}(\mathbf{B}) + (n-1)H_{DBS} + H(H_2) + H_{RE}(\mathbf{B}) \quad (4)$$

$$\Delta H_{H_2}(\mathbf{A}\rightarrow\mathbf{B}) = H(\mathbf{B}) - H(\mathbf{A}) = -[H_{DBS} + \Delta H_{RS}(\mathbf{A}\rightarrow\mathbf{B}) + H_{ASE} + H(H_2)] \quad (5)$$

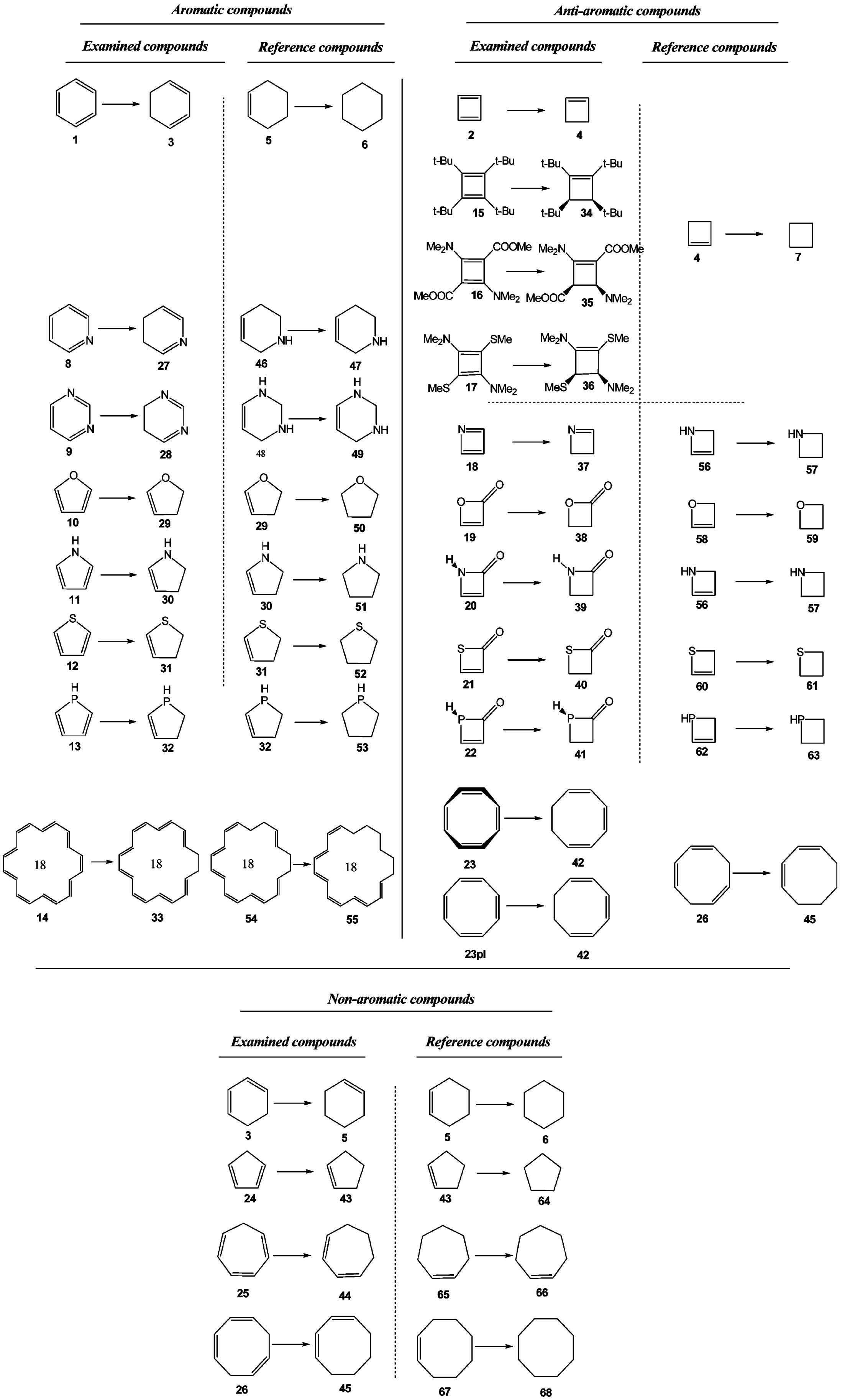
where

$$\Delta H_{RS}(\mathbf{A}\rightarrow\mathbf{B}) = H_{RS}(\mathbf{B}) - H_{RS}(\mathbf{A}) \quad (6)$$

$$H_{ASE} = \Delta H_{RE}(\mathbf{A}\rightarrow\mathbf{B}) = H_{RE}(\mathbf{B}) - H_{RE}(\mathbf{A}) \quad (7)$$

As eq 7 shows, the enthalpy of hydrogenation contains H_{DBS}, ΔH_{RS}(**A**→**B**), H_{RE}(**A**) and H_{RE}(**B**) values, where ΔH_{RS}(**A**→**B**) represents the change in ring strain enthalpy during the hydrogenation process. To remove the disturbing H_{DBS} and ΔH_{RS}(**A**→**B**) values from the ΔH_{H_2} expression, and to obtain the pure H_{ASE}, it is practical to consider a nonaromatic, reference hydrogenation reaction (e.g., **5** → **6** in Scheme 4 or **C** and **D** in Scheme 5), where one can estimate both the H_{DBS} and ΔH_{RS}(**A**→**B**) values. For this reason, the reference reaction should exhibit a ΔH_{RS} value similar to that in the reaction (eq 11) examined. The H_{RE} values of the reference (**C**) and the hydrogenated reference (**D**) compounds must be equal (eq 12); therefore, they must be nonaromatic and the hydrogenated

SCHEME 6: Neutral Compounds Involved in the $\Delta\Delta H_{H_2}$ Calculations[a]



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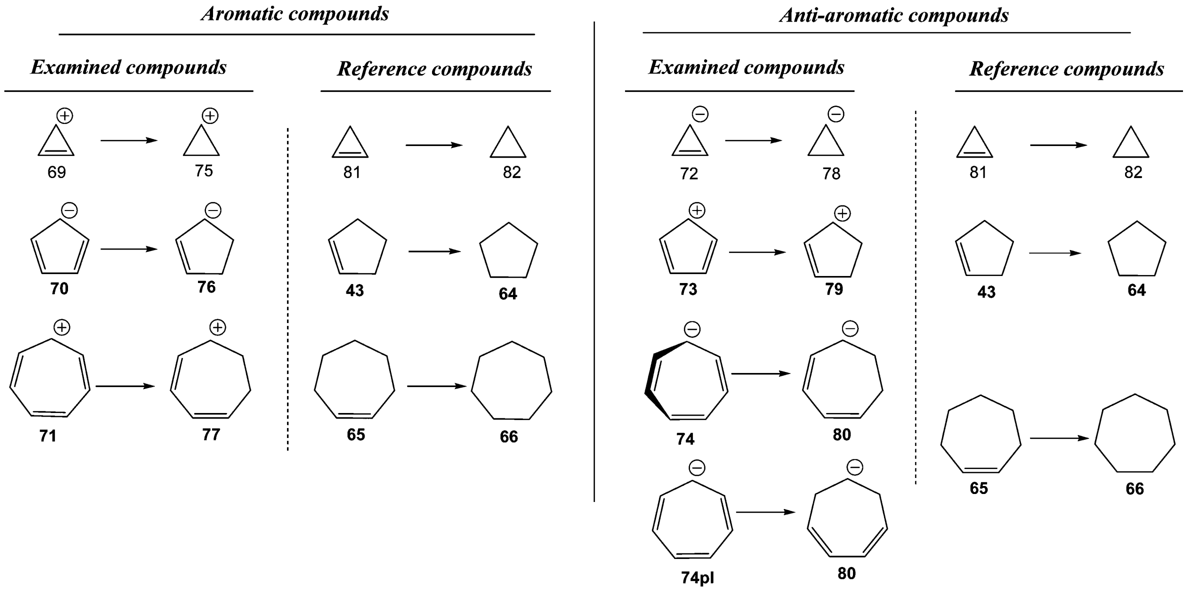
[a] The corresponding ΔH_{H_2} and $\Delta\Delta H_{H_2}$ values are listed in Table 4. The planar geometries of compounds **23** and **74** are indicated by **23pl** and **74pl**.

SCHEME 7: Charged Compounds (69−74) Involved in the $\Delta\Delta H_{H_2}$ Calculations[a]



[a] The corresponding ΔH_{H_2} and $\Delta\Delta H_{H_2}$ values are listed in Table 4. The planar geometries of compounds **23** and **74** are indicated by **23pl** and **74pl**.

TABLE 3: Comparison of Computed $\Delta\Delta H_{H_2}$ (kJ mol^{-1}) Percent Aromaticity for Selected Compounds Examined, Obtained at Different Level of Theory

	experimental		theoretical									
			B		C		D		E		F	
	$\Delta\Delta H_{H_2}$	%	$\Delta\Delta H_{H_2}$	%	$\Delta\Delta H_{H_2}$	%	$\Delta\Delta H_{H_2}$	%	$\Delta\Delta H_{H_2}$	%	$\Delta\Delta H_{H_2}$	%
1	140.43	100.00	154.10	100.00	158.34	100.00	150.17	100.00	168.83	100.00	141.24	100.00
2	−142.40	−100.00	−156.91	−100.00	−149.44	−100.00	−147.09	−100.00	−144.36	−100.00	−131.04	−100.00
8			150.30	97.26	154.11	98.18	144.82	97.25	164.64	99.72	137.04	98.12
9			130.02	84.22	123.72	78.44	114.43	76.45	134.68	80.62	110.35	78.52
10	74.40	52.64	59.80	39.06	66.74	41.43	86.62	57.42	82.88	47.62	62.94	43.71
11	101.90	71.92	82.83	53.87	128.21	81.36	97.01	64.53	106.15	62.45	86.46	60.98
12	100.00	70.59	70.29	45.81	40.88	24.63	78.61	51.94	93.99	54.70	82.34	57.95
13			12.66	8.74	31.29	18.40	23.74	14.38	39.55	20.01	35.50	23.57
18			−145.55	−93.00	−142.68	−95.61	−148.06	−103.20	−143.00	−96.33	−95.93	−74.21
19			−38.34	−24.06	−47.22	−32.60	−49.92	−36.03	−48.04	−35.81	−49.60	−38.91
20			−47.90	−30.20	−57.98	−39.59	−60.83	−43.49	−54.64	−40.02	−54.67	−42.64
21			−28.36	−17.64	−30.45	−21.70	−37.77	−27.71	−33.19	−26.35	−40.62	−32.32
22			−4.51	−2.30	−5.81	−5.70	−10.00	−9.39	−6.25	−9.18	−8.48	−8.72
3	9.88	7.40	1.95	1.85	7.58	3.00	6.15	2.35	9.27	0.71	6.28	2.12
26	9.40	7.06	5.34	4.04	13.17	6.63	13.36	7.28	17.35	5.86	14.09	7.85

double bond has to be isolated from the others.

$$H(\mathbf{C}) = H_0 + H_{RS}(\mathbf{C}) + (n-2)H_{DB} \qquad (8)$$

$$H(\mathbf{D}) = H_0 + H_{RS}(\mathbf{D}) + (n-3)H_{DBS} + H(H_2) \qquad (9)$$

$$\Delta H_{H_2}(\mathbf{C}\rightarrow\mathbf{D}) = H(\mathbf{D}) - H(\mathbf{C}) = -[H_{DBS} + \Delta H_{RS}(\mathbf{C}\rightarrow\mathbf{D}) + H(H_2)] \qquad (10)$$

where

$$\Delta H_{RS}(\mathbf{C}\rightarrow\mathbf{D}) = H_{RS}(\mathbf{D}) - H_{RS}(\mathbf{C}) \qquad (11)$$

$$\Delta H_{RE}(\mathbf{A}\rightarrow\mathbf{B}) = H_{RE}(\mathbf{D}) - H_{RE}(\mathbf{C}) = 0 \qquad (12)$$

Taking the difference between eq 5 and eq 10, we obtain eq 13, because the double bond strains (H_{DBS}) are expected to cancel.

$$\Delta\Delta H_{H_2} = \Delta H_{H_2}(\mathbf{A}\rightarrow\mathbf{B}) - \Delta H_{H_2}(\mathbf{C}\rightarrow\mathbf{D}) = H_{ASE} + \Delta H_{RS}(\mathbf{C}\rightarrow\mathbf{D}) - \Delta H_{RS}(\mathbf{A}\rightarrow\mathbf{B}) \qquad (13)$$

Supposing that $\Delta H_{RS}(\mathbf{A}\rightarrow\mathbf{B})$ and $\Delta H_{RS}(\mathbf{C}\rightarrow\mathbf{D})$ values may be almost equal in both the examined and the reference reactions (eq 14),

$$\Delta H_{RS}(\mathbf{C}\rightarrow\mathbf{D}) - \Delta H_{RS}(\mathbf{A}\rightarrow\mathbf{B}) \cong 0 \qquad (14)$$

Thus $\Delta\Delta H_{H_2}$ is expected to be equal to the aromatic stabilization enthalpy (H_{ASE}):

$$\Delta\Delta H_{H_2} = \Delta H_{H_2}(\mathbf{A}\rightarrow\mathbf{B}) - \Delta H_{H_2}(\mathbf{C}\rightarrow\mathbf{D}) = H_{ASE} \qquad (15)$$

The calculated values for eq 14 are usually less than 2−3 kJ mol^{-1} for common compounds; therefore, the error may not be more than a couple of percent for a total of 100 kJ mol^{-1} associated with H_{ASE}.

Hence, it is clear that H_{ASE}, which may be a good measure of the aromatic or antiaromatic character, is roughly equal to our $\Delta\Delta H_{H_2}$ value. If one compares the $\Delta\Delta H_{H_2}$ value of **1** with previously theoretically determined H_{ASE} values,[11,16] obtained by different theoretical methods (Scheme 1), it can be concluded that these are very close to each other. In the case of **2** the

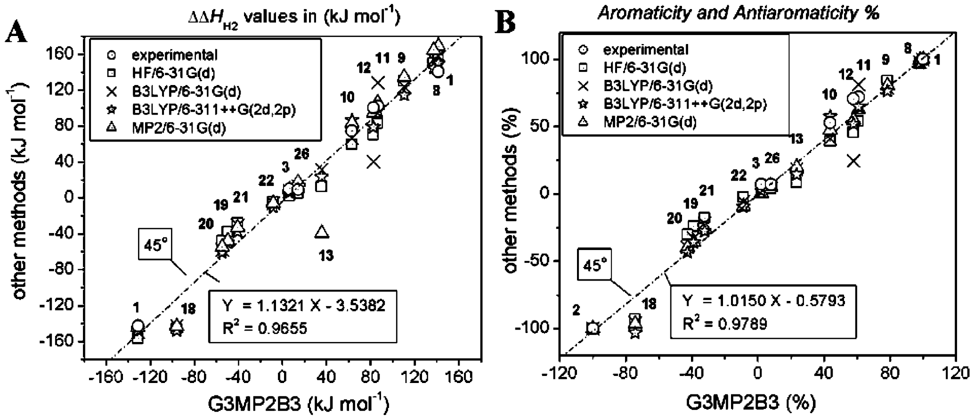


Figure 2. Correlation of $\Delta\Delta H_{H_2}$ (A) in kJ mol^{-1} and percent aromaticity (B) values obtained by G3MP2B3 (○) and those of obtained other methods: □, HF/6-31G(d); ×, B3LYP/6-31G(d); ☆, B3LYP/6-311++G(2d,2p); △, MP2/6-31G(d).

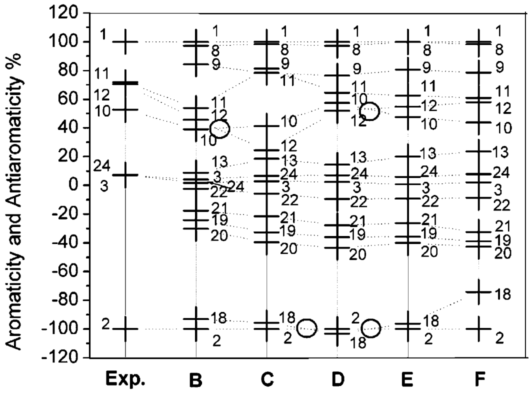


Figure 3. "Comb-diagram" for percent aromaticity obtained at different levels of theory [B, HF/6-31G(d); C, B3LYP/6-31G(d); D, B3LYP/6-311++G(2d,2p); E, MP2/6-31G(d); F, G3MP2B3] as denoted on the horizontal axis. Circles indicate the crossing points.

calculated $\Delta\Delta H_{H_2}$ value is exactly the same as was proposed earlier by isodesmic reaction as a H_{ASE} value,[17,18] because the two approaches (in Scheme 1 and Scheme 4) are identical from the thermodynamic point of view.

Using these values, one may define a continuous linear scale (Figure 1) for aromatic and antiaromatic properties, where the $\Delta\Delta H_{H_2}$ value of benzene (**1**) defines the completely aromatic character, which is taken arbitrarily as +100%, whereas the closed shell of singlet cyclobutadiene (**2**)[35] represents maximum antiaromaticity, which is arbitrarily taken as −100%. The ΔH_{H_2} values were also calculated from experimental enthalpies of formation of theory as summarized in Table 1. The background of this method may be related to a Dewar prediction,[36] where the H_{ASE} quantities for **1** and **2** were predicted as equal with opposite signs (eq 16). Consequently, the success of the linear approach to determine the percentage of aromaticity and antiaromaticity is not surprising.

$$H_{ASE}(\mathbf{1}) = -H_{ASE}(\mathbf{2}) \tag{16}$$

When choosing a hydrogenation reaction for a compound to determine its place in the scale, one must consider the following points.

(*i*) *Considerations for the Hydrogenation of the Compounds Examined:*

1. Only one of the double bonds in the compounds examined should be hydrogenated by cis addition.
2. Hydrogen addition should disrupt the continuous conjugation in the ring, leading exclusively to a nonaromatic compound.
3. It is necessary to place the two hydrogen atoms in adjacent (i.e., 1,2) rather than 1,4 positions.
4. If possible, the ring-heteroatom should not be hydrogenated.

(*ii*) *Considerations for the Hydrogenation of the Reference Compound:*

1. It should possess the same number of ring-carbon and heteroatoms and similar scaffolding as the examined compound, but without substituents and charges.
2. It should contain at least one double bond in the ring, which is separated from the others, but it should be a nonaromatic compound.
3. For more reliable results it has to contain as many double bonds as possible.
4. If possible, the same double bond in the reference compound should be saturated as in the examined compound.

If the rules are kept, all other secondary structure destabilization factors such as ring strain or double bond strain will be approximately cancelled, and the $\Delta\Delta H_{H_2}$ values obtained will represent the difference of two types of resonance energies which, in the present case, will become H_{ASE}.

Method Independence. The *y*-intercept of both the experimental and theoretical lines are near 0% specifically (+0.46%, −2.40%, respectively). These intercept values are relatively close to 0 on the total of 100% − (−100%) = 200% range, which indicates an excellent fit. The nearly zero *y*-intercept is significant because all points around $x = 0$ kJ mol^{-1} represent nonaromatic characteristics (Figure 1, Table 2). The aromatic or antiaromatic percentage values of the compounds examined (Schemes 6 and 7) may be quantified by a new linear ($y = mx + b$) aromatic and antiaromatic scale (eq 17). All R^2 values (Table 2) are larger than 0.99. Interestingly enough, the worst results can be obtained by methods E and H, i.e., by MP2/6-31G(d) and CCSD(T)/6-311++G(2d,2p)//CCSD/6-31G(d) levels of theory (R^2 = 0.9981 and 0.9972). All other methods yielded R^2 values larger than 0.999. In contrast to the above, the linear fit to the experimental enthalpies of hydrogenation produce as good a fit as the best theoretical result with R^2 = 0.9999. Note that both *y* and y_0 are in percent in eq 16.

$$y = m\Delta\Delta H_{H_2} + y_0 \tag{17}$$

A representative sets of well-known aromatic (**1**, **8**−**14**), antiaromatic (**2**, **15**−**23**) and nonaromatic (**3**, **24**−**26**) compounds and charged species (**69**−**74**) were tested with this methodology (Schemes 6 and 7). First of all, the method dependence of this methodology is examined by calculating the

TABLE 4: Computed ΔH_{H_2} and $\Delta\Delta H_{H_2}$ Values, in kJ mol^{-1} and Percent Aromaticity for the Compounds (1−26, 69−74) Examined, Obtained at the G3MP2B3 Level of Theory[a]

	examined reaction			reference reaction				
	substrate	product	ΔH_{H_2}	substrate	product	ΔH_{H_2}	$\Delta\Delta H_{H_2}$	y (%)
aromatic	**1**	**3**	30.28	**5**	**6**	−110.96	141.24	100.00[b]
	8	**27**	21.48	**46**	**47**	−115.56	137.04	98.12
	9	**28**	12.01	**48**	**49**	−98.34	110.35	78.52
	10	**29**	−35.83	**29**	**50**	−98.77	62.94	43.71
	11	**30**	−6.28	**30**	**51**	−92.74	86.46	60.98
	12	**31**	−24.53	**31**	**52**	−106.87	82.34	57.95
	13	**32**	−87.16	**32**	**53**	−101.92	35.50	23.57
	14[c]	**33**	−108.08	**54**[c]	**55**	−132.78	24.69	11.78
	69	**75**	−133.19	**81**	**82**	−235.94	102.75	72.94
	70	**76**	60.60	**43**	**64**	−105.62	166.22	119.54
	71	**77**	3.46	**65**	**66**	−100.88	104.34	74.11
antiaromatic	**2**	**4**	−258.63	**4**	**7**	−127.60	−131.04	−100.00[d]
	15[c]	**34**	−178.94	**4**[c]	**7**	−139.16	−39.78	−28.74
	16[c]	**35**	−80.16	**4**[c]	**7**	−139.16	61.47	37.05
	17[c]	**36**	−124.63	**4**[c]	**7**	−139.16	14.53	6.55
	18	**37**	−257.05	**56**	**58**	−95.93	−95.93	−74.21
	19	**38**	−189.51	**58**	**59**	−139.91	−49.60	−38.91
	20	**39**	−192.66	**56**	**58**	−137.99	−54.67	−42.64
	21	**40**	−169.90	**60**	**61**	−129.28	−40.62	−32.32
	22	**41**	−133.21	**62**	**63**	−124.73	−8.48	−8.72
	23	**42**	−98.39	**26**	**45**	−92.67	−5.72	−7.95
	23pl	**42**	−152.11	**26**	**45**	−92.67	−59.44	−47.41
	72	**78**	−261.40	**81**	**82**	−235.94	−25.46	−21.19
	73	**79**	−265.12	**43**	**64**	−105.62	−159.50	−119.60
	74	**80**	−118.37	**65**	**66**	−100.88	−17.48	−15.33
	74pl	**80**	−121.10	**65**	**66**	−100.88	−20.22	−17.34
nonaromatic	**3**	**5**	−104.68	**5**	**6**	−110.96	6.28	2.12
	24	**43**	−91.54	**43**	**64**	−105.62	14.09	7.85
	25	**44**	−96.45	**65**	**66**	−100.88	4.43	0.76
	26	**45**	−92.67	**67**	**68**	−92.67	3.21	−1.39

[a] The planar geometries of compounds **23** and **74** are indicated by **23pl** and **74pl**. [b] The fitted value is 101.20%. [c] Computed at B3LYP/6-31G(d) level of theory. [d] The fitted value is −98.71%.

ΔH_{H_2} and $\Delta\Delta H_{H_2}$ values as well as aromaticity percentages for some selected compounds (**8**−**13** and **18**−**24**) from experimental enthalpies of hydrogenation (Table 1) and at different levels of theory (Table 3). The correlations between the $\Delta\Delta H_{H_2}$ values and aromaticity percentages are good, according to their R^2 values (Figure 2), but it does not mean that the orders of aromaticity are always the same at all levels of theory. The fit of the aromaticity percentage is better than in the case of $\Delta\Delta H_{H_2}$ values, meaning that the aromaticity percentage is less method dependent. Figure 3 collects all the data represented by the various levels of theory applied. All aromaticity percentages of a given compound computed at different levels of theory are linked together by dotted lines. The crossing points of the dotted lines indicate where two levels of theory predict a different order of aromaticity for antiaromaticity of a pair of compounds. Only four crossing points can be identified, two of them can be attributed to the values of compounds **10** and **12**, and the other two are the changes of the order between **2** and **18**. The first two of these crossings happened between methods B and C as well as D and E. The last two crossings occurred between C and D as well as between D and E. Otherwise, except for these four mentioned cases, the calculated aromaticity percentages for the same compound are in the same range, irrespective of the theoretical method applied. One may conclude, finally, that the results are as accurate as the theoretical method applied, meaning that a theoretical method, which does not give good electronic structure for the aromatic or for the corresponding hydrogenated molecule, predicts the aromaticity percentage inaccurately. In all these cases, the crossover occurred at various aromaticity values and the discrepancies fell within the range of approximately ±5%. Because these small deviations occur in methods C and D, they therefore may be regarded as the limitation of the DFT method of B3LYP in reproducing the correct electronic structure. The correct structure agrees with the experimental order of aromaticity pyrrole (**11**) > thiophene (**12**) > furan (**10**), whereas pyrrole (**11**) > furan (**10**) > thiophene (**12**). This methodology, therefore, can be considered as a quasi-rigorously method-independent technique. It has to be emphasized, however, that there is not any limitation in the theoretical method used, meaning that one may use as high-level or as low-level computational method as desirable.

Application. To test this novel aromaticity measure, the aromaticity percentage for 28 compounds was computed at G3MP2B3 and B3LYP/6-31G(d) levels of theory (Table 4 and Figure 4). Our results relate well with expected values for aromatic and antiaromatic systems. The only exceptions are some of the stable tetrasubstituted cyclobutadienes (**16**, **17**),[37,38] which had positive $\Delta\Delta H_{H_2}$ values, indicating that they are more aromatic than antiaromatic. This is due to the contribution of other important resonance structures shown in Scheme 8. In contrast to the above, compound **15** is slightly antiaromatic.

As expected, each of the nonisolable compounds **19** and **20** possess a strong antiaromatic character (50%).[39] It should perhaps to be reemphasized that our methodology shows that the order of aromaticity is the following for the five-membered heterocycles: pyrrole (**11**) > thiophene (**12**) > furan (**10**) > phosphole (**13**), which is in agreement with the experimental findings. It is worthwhile to discuss the case of [18]annulene (**14**). In spite of 18 π electrons, which are fulfilling the $4n + 2$ rule,[11,40−42] **14** is significantly less aromatic than benzene. This result has been confirmed by other nonqualitative experimental and theoretical investigations,[11,43−45] but, in those days the degree of its aromaticity was questionable. Finally, in agreement

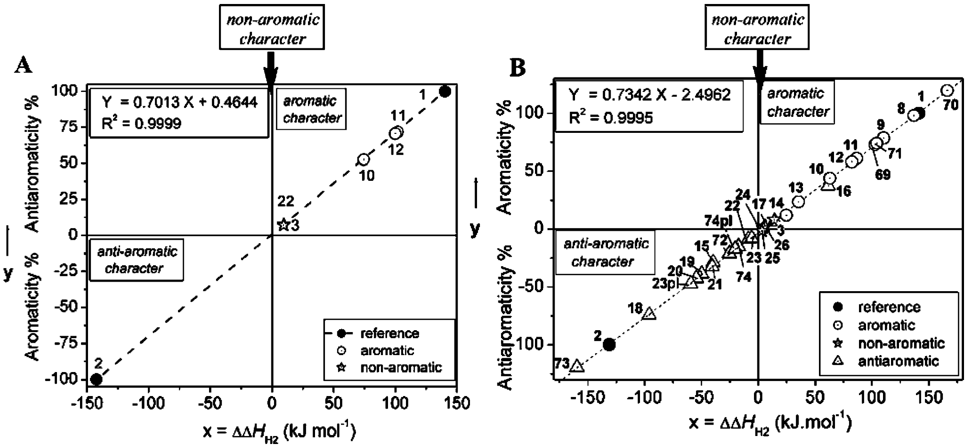
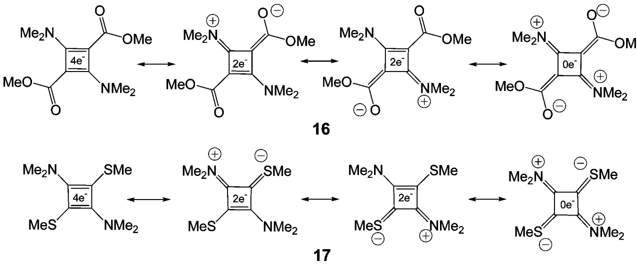


Figure 4. Experimental and theoretical (G3MP2B3) scale for aromaticity and antiaromaticity. (A) Percentage value of aromaticity or antiaromaticity based on the experimental $\Delta\Delta H_{H_2}$ value of a selected few compounds. (B) Percentage value of aromaticity or antiaromaticity based on the $\Delta\Delta H_{H_2}$ value of a given compound computed at the G3MP2B3 level of theory. For the description of each compound, see Tables 2 and 3 as well as Schemes 6 and 7. Compounds **14**, **15**, **16** and **17** were computed at B3LYP/6-31G(d) level of theory. The planar geometries of compounds **23** and **74** are indicated by **23pl** and **74pl**.

SCHEME 8: Contributing Resonance Structures to 16 and 17



with an earlier prediction,[46] compound **18** proved to be antiaromatic as −74.21% by the present methodology.

The charged compounds (**69**−**74**) examined (Scheme 7) also agree with the earlier results. Compound **69**−**71** proved to be aromatic and **72**−**74** turned out to be antiaromatic. Compound **70** exhibits, however, a large aromaticity percentage (119.54%), predicting it to be more aromatic than benzene (**1**). Analogously to that, the five-membered **73** also shows a larger antiaromatic value (−119.60%). It is noteworthy that the two values for **70** and **73** are practically equal, but with opposite signs.

The fitted lines in Figure 4 already indicate that the percent aromatic and percent antiaromatic characters, calculated from experimental and theoretical values, must be very similar. However, the explicit correlation of the experimental and theoretical enthalpy values of hydrogenation ($\Delta\Delta H_{H_2}$) indicate (Figure 5) that the theoretical $\Delta\Delta H_{H_2}$ values obtained at the G3MP2B3 level of theory are practically as accurate as the experimental values.

Correlation between Aromaticity Percentage and NICS Values. The determination of Schleyers nuclear independent chemical shift (NICS)[11,47] values is one of the most popular methods to examine aromaticity. During the past decade, this concept has undergone a noticeable evolution, whereby different types of NICS values were defined. One of these methods involves the calculation of the NICS values at different distances above the ring center (d_z) [NICS(d_z), where d_z may assume values in between 0 and 3 Å].[11] The two most favored values are NICS(0) and NICS(1).

Consequently, we attempted to correlate the calculated percentage values of aromaticity or antiaromaticity obtained from the $\Delta\Delta H_{H_2}$ data of the neutral compounds examined with the computed NICS(0) and NICS(1) values (Table 5 and Figure

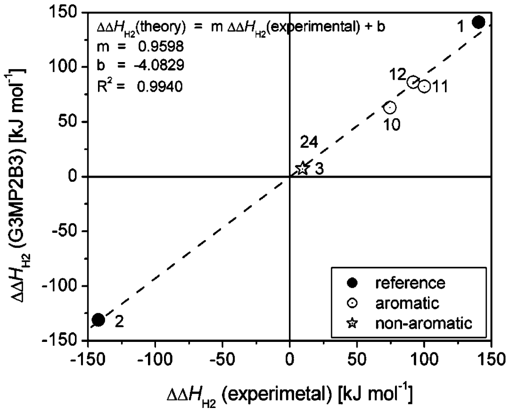


Figure 5. Correlation between the experimentally determined and theoretically computed $\Delta\Delta H_{H_2}$ values obtained at G3MP2B3 level of theory.

6). The trend follows an exponential decay function, but the fit is affected noticeably by cyclic compounds that contain a heteroatom. Nevertheless, the trend is clear, with only one outlier (**23pl**). Earlier studies found a linear relationship between NICS(0) and NICS(1) and H_{ASE} for five-membered ring compounds C_4H_4X (for example X = CH_2, NH, PH, O, S).[48] The straight line fitted to these five points (**10**, **11**, **12**, **13** and **24**) is shown, in Figure 6, as a solid line below the fitted exponential function. By analogy, we fitted the straight line of the family of the six-membered ring studied (**1**, **3**, **8**, **9**). This straight line is above the fitted exponential function. However, when the comparison is extended beyond the small families, the good linear correlation has disappeared, and an exponentional functional relationship has appeared. This suggests that the energetic and magnetic description of aromaticity and antiaromaticity are not completely equivalent.[49]

There are two important points to note:

1. NICS(0) and NICS(1) correlate exponentially with the percentage of aromaticity and antiaromaticity if all the compounds considered, throughout the whole range from +100% to −100%, indicating a somewhat different nature of the energetic and magnetic definition of aromaticity and antiaromaticity.

2. As a result of the exponential trend, a relatively large percentage of aromaticity creates a small change in both NICS(0) and NICS(1). In contrast to that, a relatively small

TABLE 5: Computed NICS(0) and NICS(1) Values of the Compounds Examined [B3LYP/6-311++G(2d,2p)]

aromatic			nonaromatic			antiaromatic		
compound	NICS(0)	NICS(1)	compound	NICS(0)	NICS(1)	compound	NICS(0)	NICS(1)
1	−7.59	−9.93	**3**	2.81	0.01	**2**	27.10	17.89
8	−6.36	−9.81	**24**	−2.92	−4.66	**15**[a]	16.55	14.56
9	−5.06	−9.53	**25**	−4.14	−6.78	**16**[a]	−1.47	0.84
10	−11.52	−9.14	**26**	−1.05	−2.32	**17**[a]	0.34	2.35
11	−13.30	−9.99				**18**	27.63	14.56
12	−12.74	−9.96				**19**	1.74	1.81
13	−7.28	−6.28				**20**	4.24	−0.08
14[a]	−14.68	−13.62				**21**	5.54	3.95
69	−22.82	−14.79				**22**	5.10	−0.57
70	−11.91	−9.42				**23**	4.88	1.08
71	−6.01	−9.36				**23pl**	41.01	32.42
						72	−11.39	5.92
						73	85.82	32.42
						74	52.18	41.02
						74pl	159.14	129.15

[a] **14**, **15**, **16** and **17** computed at B3LYP/6-31G(d) level of theory.

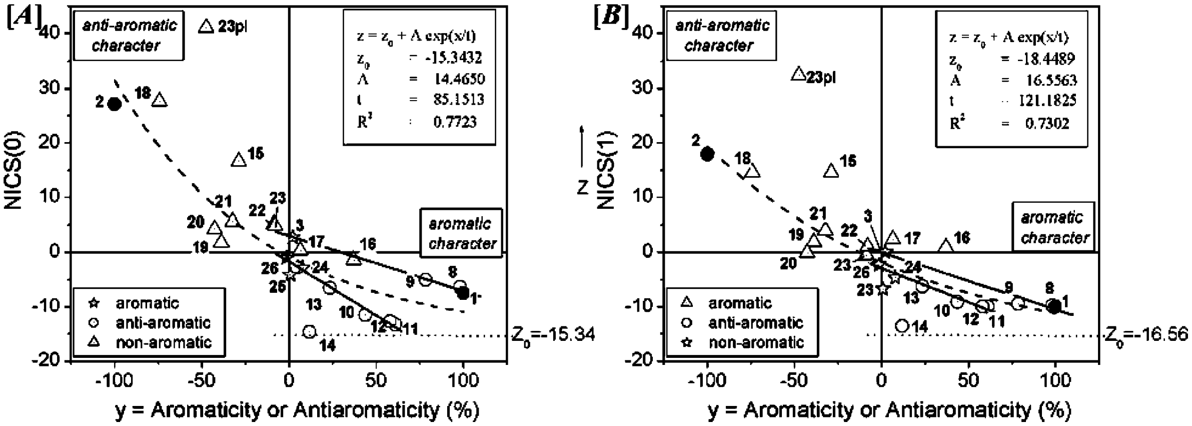


Figure 6. Correlation between NICS(0) (A) and NICS(1) (B) values (optimized and computed at B3LYP/6-311++G(2d,2p) level of theory) and the percentage of aromaticity or antiaromaticity for the neutral compounds. The point associated with the planar geometry of compound **23** (**23pl**) is omitted from the fitting. Compounds are identified by numerals according to Schemes 6 and 7. Molecules **14**, **15**, **16** and **17** were optimized and computed at B3LYP/6-31G(d) level of theory. The fitted exponential function is converging to z_0 with increasing aromaticity. The intercept of the vertical z-axis is equal to $z_0 + A$, which has turned out to be almost zero. The solid line below the exponential is for the five-membered ring system (the fitted equation for (A) $z = -0.10y - 3.01$, for (B) $z = -0.10y - 0.04$) and that above the exponential is for the six-membered ring system (the fitted equation for (A) $z = -0.20y - 1.73$, for (B) $z = -0.12y - 2.94$). For details see text.

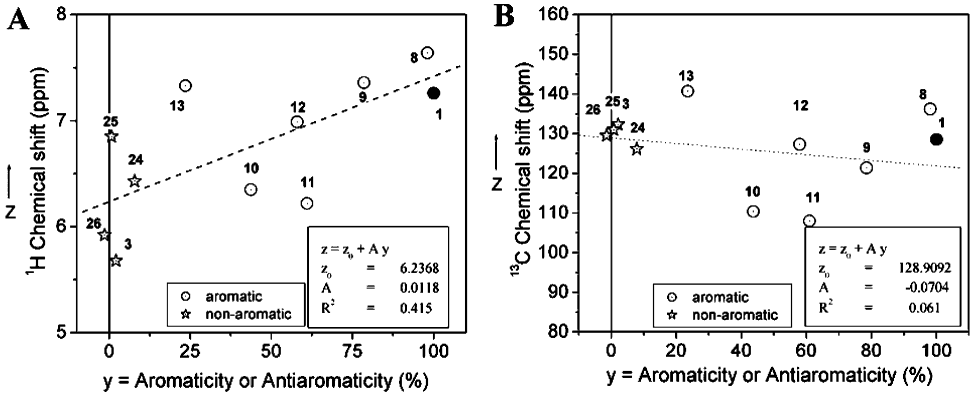


Figure 7. Correlation between experimental ^{1}H and (A) and ^{13}C NMR (B) values and the percentage of aromaticity or antiaromaticity for neutral compounds.

percentage of antiaromaticity causes a large change in the NICS values. Thus, both NICS(0) and NICS(1) are more sensitive to the measurement of the degree of antiaromatic character than to the degree of aromaticity.

Correlation between Aromaticity Percentage and Experimental ^{1}H and ^{13}C NMR Values. The experimental NMR values of the farthest ^{1}H and ^{13}C atoms of aromatic (**1**, **8**−**13**) and one unsaturated H and C atoms of nonaromatic compound examined (**3**, **24**, **25** and **26**) are considered and compared with the aromaticity percentage. Both of the plots of Figure 7 show a noticeable trend, but the available experimental points are considerably scattered. The ^{1}H chemical shifts exhibit a small positive and the ^{13}C chemical shifts have a small negative slope. The fitted ^{13}C line is somewhat reminiscent to the NICS lines of Figure 6 but the correlation is better for the NICS values.

Conclusion

A new aromaticity and antiaromaticity linear scale has been developed. The scale is based on the relative enthalpy values of hydrogenation reactions ($\Delta\Delta H_{H_2}$), with respect to the selected standard hydrogenation reactions, choosing, arbitrarily, benzene as +100% and cyclobutadiene as −100%. It has been demonstrated that the $\Delta\Delta H_{H_2}$ value is practically equal to the aromatic stabilization enthalpy (H_{ASE}) value, to a good degree of approximation. Analyzing several ring systems, the H_{ASE} value is considered to be a good measure of aromaticity and antiromaticity. The aromaticity percentage was also determined by experimental enthalpies of hydrogenation as well as at eight different levels of theory. From these results it has been concluded that this methodology is quasi-method independent. The possibility of the direct comparison of the computed and the experimentally determined values may be the main advantage of this method. A representative set of aromatic, antiaromatic and nonaromatic compounds were included in the present study. A comparison has been made between the novel aromaticity percentage of the compounds examined and their NICS(0) as well as NICS(1) values, where exponential relationships have been obtained for all the ring structures considered.

Acknowledgment. We thank Máté Labadi for technical support in the high Performance Computing Center at the University of Szeged. V.B. thanks the National Office for Research and Technology for the Öveges Research Program (HEF_06_1-PESINF06).

Supporting Information Available: The full author list for references 18. Table S1−S3 containing the computed energies (E), zero-point energies (E_{ZPE}), internal energies (E_{ZPE}), enthalpies (H) and Gibbs free energies (G) in hartrees and entropies (S) in cal mol^{-1} K^{-1} at various levels of theories for compounds **1−66pl**. Table S4 showing the fitting parameters for the linear quantitative scale for aromaticity computed for different theoretical level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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