

# Concurrence between Current Density, Nucleus-Independent Chemical Shifts, and Aromatic Stabilization Energy: The Case of Isomeric [4]- and [5]Phenylenes

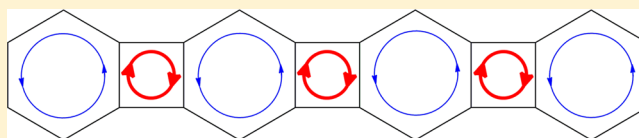
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## S Supporting Information

**ABSTRACT:** The 17 isomers of the [4]- and [5]phenylenes have been studied with three different computational levels of current-density analysis (CDA) and by calculation of the out-of-plane contribution to nucleus-independent chemical shifts (NICS<sub>πzz</sub>). Current-density maps for these isomeric phenylenes are typically dominated by strong paratropic ring currents in four-membered rings. The relative energies of the isomers, which differ only through the effects of differential strain and aromaticity, were computed at the B3LYP/6-311G\* computational level. It was found that the three levels of CDA correlate well among themselves and with NICS<sub>πzz</sub>. The latter correlation is improved when the ring sum  $\sum \text{NICS}_{\pi zz}$  for each isomer is correlated to the ring-current sum  $\sum I$  extracted from CDA. The strain-corrected relative energies of the isomers correlate linearly with  $\sum \text{NICS}_{\pi zz}$ . In particular, the compatibility of different summed quantities with easily computed Hückel–London ring currents suggests a simply calculated measure for dealing with global aromaticity of polycyclic systems.



## INTRODUCTION

Aromaticity is a prominent concept in the chemical literature,<sup>1</sup> and yet, its exact nature remains a point of debate. There are three criteria commonly used to identify and quantify the aromatic character of a given compound: energetic,<sup>2</sup> magnetic,<sup>3–5</sup> and structural.<sup>6</sup> Depending on the method of analysis chosen, even qualitative conclusions about the aromaticity of a given system may differ. It has also been suggested that aromaticity is a multidimensional phenomenon.<sup>7</sup>

The *energetic* criterion compares the stability of the compound to a nonaromatic reference system, which may be hypothetical. Usually, this comparison is made through homodesmotic and isodesmotic reactions, again real or hypothetical.<sup>1</sup> The *structural* criterion is based on the assumption that symmetry is driven by aromaticity, but it has been shown that this assumption is not always correct.<sup>8,9</sup> The *magnetic* criterion, which seems to be viewed in much of the literature as the most appropriate index of aromaticity, is defined in terms of the ring currents induced when an aromatic/antiaromatic compound is placed in an external magnetic field.<sup>10</sup> The induced ring currents may be evaluated directly with current-density analysis (CDA) methods.<sup>11</sup> They may also be probed indirectly with nucleus-independent chemical shifts (NICS),<sup>12</sup> which evaluates an average of the magnetic field induced at a point or set of points by the induced current density, according to the Biot–Savart law.<sup>13</sup> Experiment-based methods also exist, such as magnetic exaltation<sup>14</sup> and <sup>1</sup>H NMR measurements,<sup>15</sup> which give indirect information about ring current.

In this work, we examine whether there is a correlation between two different methods of calculation based on the magnetic criterion. The first is CDA, carried out at (all-electron) ab initio level and with pseudo- $\pi$ <sup>16</sup> and Hückel–London models (hence, CD-Full, CD-PP, and CD-HL). The second method uses NICS<sub>πzz</sub><sup>17</sup> obtained from a NICS-Scan.<sup>18</sup> In addition, we study the relationship between two separate criteria of aromaticity, the energetic and the magnetic.

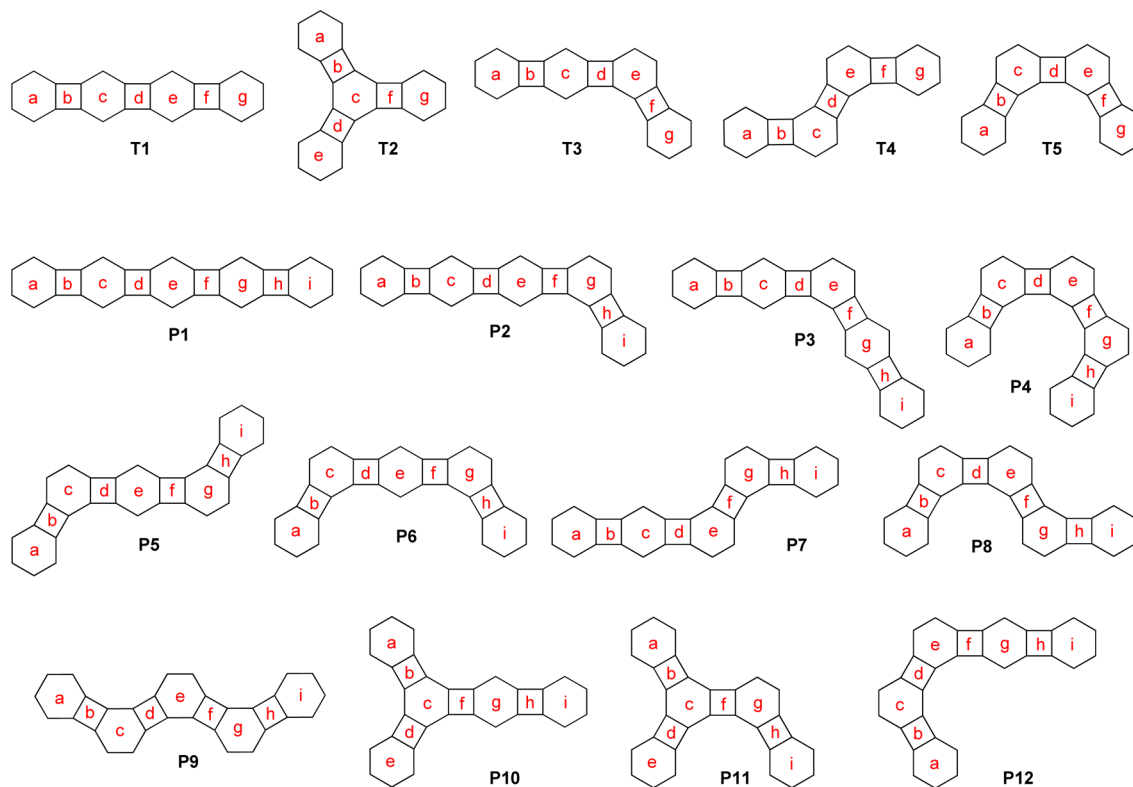
The species chosen for this study belong to the [N]-phenylene family, exemplified by the [4]phenylene and [5]phenylene subfamilies (see Scheme 1). An [N]phenylene consists of N unsaturated six-membered rings, separated by [N – 1] intervening unsaturated four-membered rings, and hence combines the quintessential aromatic and antiaromatic motifs of benzene and cyclobutadiene in a single molecule.

Comparison of CDA and NICS methods presents some challenges. Although in principle both methods examine the same underlying property, they evaluate different aspects of that property and give data in different forms. CDA provides the total induced current density, which is usually represented as a vector map that can be interpreted in terms of ring currents but by its very nature is not easily reduced to a single value for comparison. NICS is an integrative method that gives single numbers (which are actually integrals involving the current density) related to the induced magnetic field at any desired location, often chosen for simplicity to be the geometrical

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Scheme 1. Molecules Studied, with Ring Labeling



center of a ring. The fact that current-density maps for phenylenes typically show localized ring currents (see below) justifies this association with ring centers. However, the NICS integral may include many effects in addition to those of the local ring current,<sup>19</sup> such as local effects and induced magnetic fields from neighboring rings, which could give rise to double or triple counting. For the NICS<sub>πzz</sub> method, there are no local (sigma) effects, but induced fields from neighboring ring currents are still included. When this nonlocality is taken into account for benzenoid systems, improved correlations between NICS and other indices are obtained.<sup>20</sup> On the simplest conceptual picture, interactions between ring currents may be expected a priori to be strong in the [*N*]phenylene molecules, where six-membered rings characterized by local diatropic ring current are adjacent to one, two, or three four-membered rings, which typically support (strong) local paratropic ring currents. According to the Biot–Savart law,<sup>13</sup> the magnetic field of the paratropic current loops will act to enhance diatropic circulation in neighboring hexagons, and likewise, the hexagon ring currents will enhance the paratropic circulations in neighboring four-membered rings, leading to a tendency for all NICS values to increase (in absolute value) compared to the isolated rings. We reasoned that this tendency could be counteracted to some extent by taking a sum over rings, to benefit from partial double-counting cancellation within pairs of neighbors, and this was done, as discussed below, to provide comparisons with CDA results and with energetic properties of the molecule as a whole. The fundamental justification for comparing the sums lies in the fact that global aromaticity is a molecular property (as exemplified by aromatic stabilization energy), not a property of a single ring within a molecule. Potential overcounting in NICS calculations was considered previously in the work of Mills and Llagostera,<sup>21</sup> where ring-

summation was again used in making correlations, in this case with the magnetic measure of exaltation of magnetic susceptibility.

The challenge in using the energetic criterion for arbitrary molecules typically lies in the need for a nonaromatic reference system. Fortunately, the [4]phenylene subfamily contains 5 structural isomers and the [5]phenylene subfamily contains 12. By comparing relative energies within the isomer sets, the need for an external reference can therefore be circumvented.

## METHODS

**Treatment of NICS Values.** To obtain molecular geometries, energies, and NICS properties, Gaussian 03 and Gaussian 09 codes were used<sup>22</sup> and OriginLab software was used for the mathematical analysis.<sup>23</sup> The molecules underwent full geometry optimization at the B3LYP/6-311G\* level of theory, followed by analytical frequency calculations to ensure true local minima (i.e.,  $N_{\text{imag}} = 0$ ). All molecules are planar and have singlet ground states at this level of theory. All energies reported are the relative ZPE-corrected energies, in kilocalorie per mole. NICS probes (bq centers) were placed above the geometric center of each of the rings within the system, at distances ranging from 0 to 4.9 Å, at intervals of 0.1 Å along the normal to the (*xy*) molecular plane. NICS values were calculated at the GIAO-B3LYP/6-311+G\* level.

For the examination of the separate rings within each compound, the NICS-Scan results were analyzed with NCS<sup>24</sup> within NBO 5.G.<sup>25</sup> The contribution of the  $\pi$  orbitals to the *zz* component of the chemical shift tensor was extracted for each bq and plotted against the distance from the molecular plane. For convenience, the NICS<sub>πzz</sub> at a distance of 1 Å, recalculated from a cubic polynomial regression, was chosen as the basis for a quantitative descriptor. The value  $\sum \text{NICS}_{\pi zz}$  for each molecule was calculated as follows: NICS<sub>πzz</sub> for the separate rings were summed at each distance to afford a plot of  $\sum \text{NICS}_{\pi zz}$  versus distance (see Figure S1 in the Supporting Information). This plot was then fitted with a third degree polynomial equation, from which the value at 1 Å was calculated. Herein, we present the results obtained from the

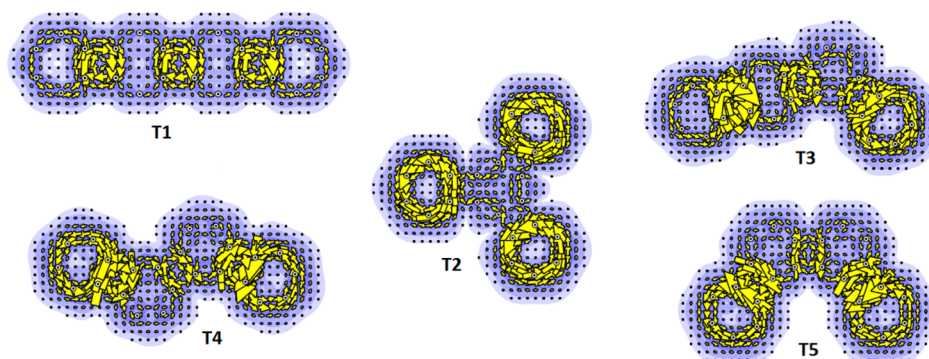


Figure 1. Current-density pseudo- $\pi$  (CD-PP) ring current maps for the [4]phenylene isomers (labeled as in Scheme 1).

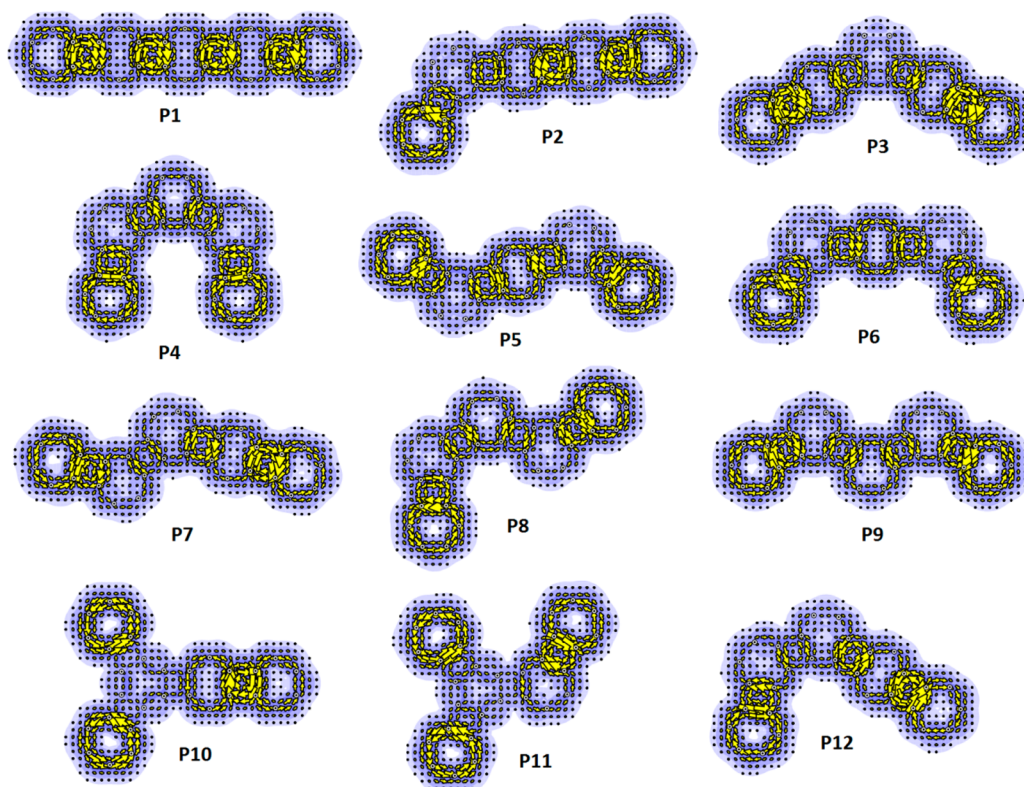


Figure 2. CD-PP ring current maps for the [5]phenylene isomers (labeled as in Scheme 1).

contribution of the  $\pi$  orbitals to the  $zz$  component of the chemical shift tensor (CMO-NICS), as obtained from the NCS analysis and calculated from the polynomial fit.

**Treatment of Current Densities and Ring Currents.** Current maps and ring-current values were calculated using several different models. Calculations on the [4]phenylene series were carried out at the full ab initio level: ipsocentric<sup>26</sup> HF/6-31G\*\* calculations were performed on the B3LYP/6-311G\* optimized structures using the SYSMO package<sup>27</sup> and the currents mapped using our usual conventions: current is plotted at a height of  $1 a_0$  above the molecular plane, with contours representing the total magnitude, and arrows representing the magnitude and direction of the in-plane component, of the induced current density per unit external field; paratropic/diatropic circulations run clockwise/counter-clockwise.

For both [4]- and [5]phenylene series, current maps were also calculated in the pseudo- $\pi$  model, using the B3LYP/6-311G\* optimized structures. In this model,<sup>16</sup> the carbon framework is simulated by a set of pseudo-H atoms, each carrying a hydrogenic STO-3G  $s$  basis function, and the current is calculated with the full ipsocentric method, taking the electron count from the  $\pi$  system. In-

plane ( $\sigma$ ) currents for this pseudo-system have been shown to mimic, both qualitatively and quantitatively, the  $\pi$  currents of full ab initio maps. It will be seen that this close similarity is maintained for phenylene systems. Pseudo- $\pi$  calculations have been shown to mimic more sophisticated calculations in other contexts, for example, the calculation of multicenter delocalization and aromaticity indices.<sup>28</sup>

Pseudo- $\pi$  maps give spatial distributions of current rather than single values per ring. One way to reduce the two-dimensional information in the map to a set of single-number bond currents has been described:<sup>29</sup> the component of the current-density vector along the bond direction is calculated at the geometric midpoint of the line between the bonded nuclei. These values are taken as bond currents, and a “ring current” can be estimated in cata-fused systems from the average taken over external bonds of each ring (i.e., disregarding values on bonds common to fused rings). The individual bond current values assigned by this algorithm to the edges of the molecular graph do not obey Kirchhoff’s First Law. Nevertheless, they can give a qualitative picture of the strength and direction of ring current.

A third type of calculation used the empirical Hückel–London (HL) model to estimate ring currents. In this theory,<sup>30</sup> the effects of an

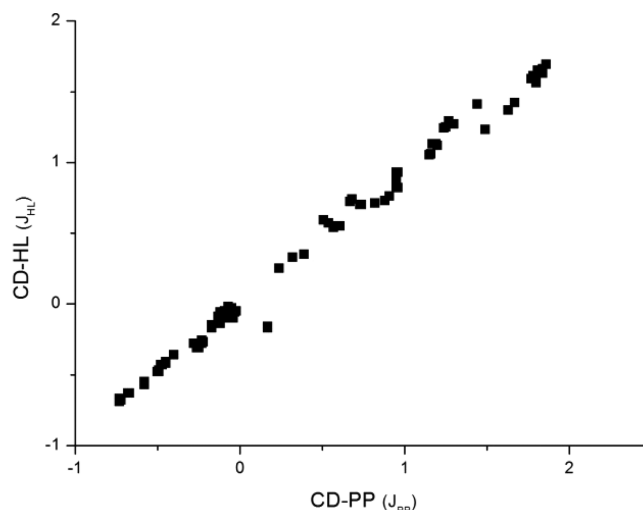
applied external magnetic field are simulated by modifying elements of the adjacency matrix of the molecular graph with weights that depend on ring area through the Cartesian coordinates of the carbon nuclei. Currents derived in this model flow along graph-edges and by construction obey Kirchhoff's First Law. The currents in perimeter bonds correspond exactly to ring currents. HL currents can be normalized with respect to a benzene standard with 1.4 Å bond lengths. As HL is essentially graph theoretical in nature, idealized geometries (all bonds 1.4 Å, and all 4- and 6-cycles taken to be regular polygons) were used. As will be seen below, the relative currents calculated in this way are remarkably similar to those extracted from the pseudo- $\pi$  maps, which themselves mirror the full ab initio maps.

## RESULTS AND DISCUSSION

**Comparisons between Methods of CDA.** Before using current-density maps to extract qualitative and quantitative information on the distribution of ring currents within the molecules, it is important to establish the reliability of the pseudo- $\pi$  model for systems with mixed diatropic and paratropic character. Maps were computed at both ab initio and pseudo- $\pi$  levels for the five [4]phenylene isomers. (The pseudo- $\pi$  maps are displayed in Figure 1, and the ab initio maps are shown in Figure S2 of the Supporting Information). The maps are typically in accordance with the intuition that, where there are strong local diatropic currents, these appear on the hexagonal rings and that any strong local paratropic currents are associated with four-membered rings. The patterns for [4]phenylene isomers are essentially identical, whether computed fully ab initio or at the pseudo- $\pi$  level. The details of which specific rings show strong currents in each isomer will be discussed below, but it is already clear that pseudo- $\pi$  maps give a good account of these details. The corresponding pseudo- $\pi$  maps are shown for the 12 [5]phenylene isomers in Figure 2.

**Comparison between CDAs and NICS<sub>zzz</sub>.** Current-density maps provide a very useful tool for obtaining qualitative insight and the underlying induced current density can be integrated to give various molecular magnetic response properties. It is also of interest to attempt to extract quantitative conclusions from such maps about comparisons of ring currents, for rings within given molecules and for rings in similar situations in different molecules. To this end, ring-current values were calculated using both pseudo- $\pi$  (CD-PP) and Hückel–London (CD-HL) models, as indicated above. Specifically: regular, planar, 1.4 Å structures were assumed for all isomers, and ring currents were calculated for each ring in each isomer from the *mean bond current*<sup>29</sup> taken over all bonds of the given ring that also lie in the molecular perimeter. This quantity will be denoted  $J$ , hence J-PP or J-HL according to the model, and is given relative to the  $-J$  value of benzene (defined as +1) at the respective level of theory. The excellent agreement between both methods is apparent from Figure 3. For comparison, NICS<sub>zzz</sub> was also computed for every ring in every isomer (using the B3LYP/6-311G\* optimized geometries), and the correlation between NICS<sub>zzz</sub> and  $J$  in each of the two CD models is shown in Figure 4.

The plots show that there is a clear relationship between CD results and the NICS method. Agreement is good for large absolute values (positive and negative) of NICS and  $J$ , while it is poor for the small values. This is in accordance with the rationalization proposed earlier: when the ring current is strong, the resulting induced magnetic field is strong, and the residual field from neighboring rings is relatively small. However, when the ring current is weak, the residual induced fields from the



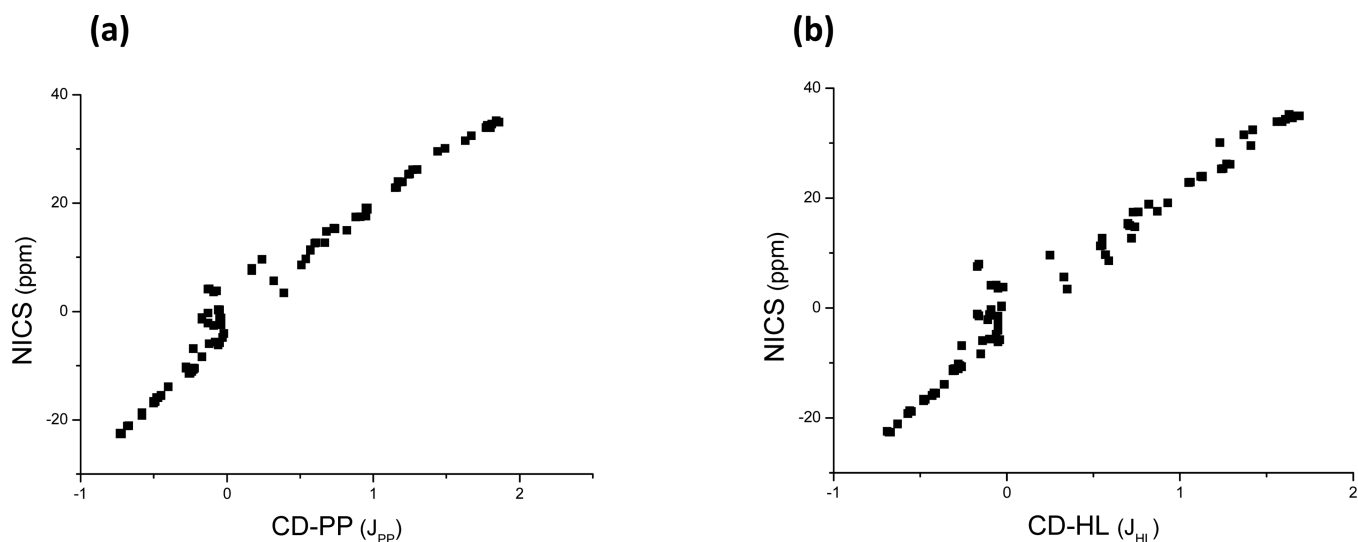
**Figure 3.** Correlation of the ring-current parameter  $J$  computed with CD-HL and CD-PP methods for all rings of all [4]- and [5]phenylene isomers.  $R^2 = 0.9905$ . Currents are reported as dimensionless quantities scaled to the standard benzene value for the method, as noted in the text.

neighboring rings are of the same order, causing NICS<sub>zzz</sub> (which is intended to reflect the strength of the total induced magnetic field) to deviate considerably from the correlation with  $J$ .

**Trends in Ring Properties.** Table 1 displays the values of ring currents J-HL and J-PP and the NICS<sub>zzz</sub> index obtained for each ring (labeled according to Scheme 1) in the three methods.

The data in Table 1 and the sets of maps in Figures 1 and 2 provide a wealth of detail. It is convenient to discuss the chainlike and triangular isomers separately. First, for the chainlike structures, one can see that, although all molecules are formally fully conjugated systems, ring currents are mainly localized in four- and six-membered rings, with no strong currents associated with larger circuits. Second, ring currents in four-membered rings ( $J_{HL} = 0.33$  to 1.69,  $J_{PP} = 0.32$  to 1.86, NICS = 3.43 to 53.22) are typically significantly larger in absolute value than those in the six-membered rings ( $J_{HL} = -0.03$  to  $-0.67$ ,  $J_{PP} = -0.02$  to  $-0.73$ , NICS =  $-0.25$  to  $-22.64$ ). The orbital interpretation arising from the ipsocentric approach offers a simple rationalization of this trend in terms of the energy denominators associated with paratropic (node-preserving) and diatropic (node-increasing)  $\pi$ - $\pi^*$  virtual excitations,<sup>26c,d</sup> which is borne out by calculations showing that paratropic ring currents in antiaromatic molecules are generally greater in absolute value than diatropic ring currents in aromatic compounds.<sup>30–34</sup> This is also consistent with the observation for single rings the negative (diatropic) values for aromatic systems are typically smaller in absolute value than the positive (paratropic) NICS values computed for antiaromatic systems.<sup>35</sup>

The chainlike isomers contain examples of both linearly and angularly annulated [3]phenylene subunits. Central six-membered rings of a linear subunits typically display appreciable ring currents ( $|J_{HL}| = 0.17$  to 0.28,  $|J_{PP}| = 0.16$  to 0.28, NICS =  $-1.11$  to  $-10.52$ ), whereas central rings of angular subunits show generally weaker ring currents ( $|J_{HL}| = 0.03$  to 0.26,  $|J_{PP}| = 0.06$  to 0.23, NICS =  $-0.29$  to  $-6.91$ ). End rings of angular subunits show larger currents ( $|J_{HL}| = 0.36$  to



**Figure 4.** Correlation of ring values for  $\text{NICS}_{zz}$  with the ring current parameter  $J$ . (a) CD-PP.  $R^2 = 0.9643$ . (b) CD-HL.  $R^2 = 0.9592$ . Scaled dimensionless currents are used as in Figure 3.

0.57,  $|J_{pp}| = 0.4$  to 0.58,  $\text{NICS} = -13.90$  to  $-19.22$ ), and in linear subunits show intermediate values ( $|J_{HL}| = 0.28$  to 0.31,  $|J_{pp}| = 0.23$  to 0.26,  $\text{NICS} = -10.45$  to  $-11.43$ ). The four-membered rings exhibit stronger currents in a linear subunit ( $|J_{HL}| = 0.76$  to 1.66,  $|J_{pp}| = 0.91$  to 1.84,  $\text{NICS} = 17.49$  to 34.98) than in an angular subunit ( $|J_{HL}| = 0.70$  to 1.27,  $|J_{pp}| = 0.83$  to 1.30,  $\text{NICS} = 14.98$  to 26.19), and four-membered rings with larger currents are always adjacent to six-membered rings that themselves have larger currents.

In the triangular isomers (**T2**, **P10**, and **P11**), a different pattern is seen. The central tricyclobutadieno-benzene cores display a ring current over the whole unit, namely, around the triply bridged [12]-annulene perimeter.<sup>36</sup> Ring currents in the central ring of the triangular subunit are small and paratropic ( $|J_{HL}| = 0.1$  to 0.25,  $|J_{pp}| = 0.04$  to 0.24,  $\text{NICS} = 7.54$  to 9.60). The four-membered rings annulated to the central core display the lowest values for four-membered rings across all isomers ( $|J_{HL}| = 0.33$  to 0.74,  $|J_{pp}| = 0.32$  to 0.68,  $\text{NICS} = 3.43$  to 12.68). The six-membered rings surrounding the trigonal core display the largest values found for six-membered rings ( $|J_{HL}| = 0.63$  to 0.69,  $|J_{pp}| = 0.68$  to 0.73,  $\text{NICS} = -21.12$  to  $-22.64$ ).

The decomposition of the various structures into [3]-phenylene subunits is not unique, and most rings can be assigned to more than one. For example, in **P3**, ring e is both the central ring of one angular unit and a terminal ring in two linear units. In such cases, it appears that effects on current are cumulative, with the dominating factor being the subunit in which the ring is in the middle. In the two examples mentioned above, ring e in **P3** shows almost no ring current, as would be expected from the middle ring in an angular unit.

These patterns can be rationalized in a resonance picture as a result of avoidance of antiaromatic cyclobutadiene rings in the resonance structures. For a structure in which cyclobutadiene is absent, delocalization of the  $\pi$  electrons is limited as a consequence of this preferred bond configuration, and such bond localization adversely affects the stabilizing effect of benzene rings. In other words, there is a trade-off: the delocalization in each compound is a balance of the negative influence of the cyclobutadiene rings and the positive influence of the benzene rings.

How are these considerations manifested in the different types of subunits? In a linear arrangement, the central six-membered ring cannot avoid sharing a double bond with one of its annulated four-membered rings, and there is nothing to be gained from localizing the bonds within this ring. However, the end hexagons in these subunits can rearrange in such a way as to avoid generating two double bonds within the same four-membered ring. This is compatible with the observation of currents in all these rings, with smaller currents in the central ring, where the delocalization is dictated by the interactions on two sides. Of course, it is also possible to draw a diradical resonance structure, in which the central ring shares no double bonds with the neighboring four-membered rings, but this is a very high-energy structure and a minor contributor to the closed-shell ground state. Interestingly, when the side rings are absent (i.e., in [1,2][4,5]-bicyclobutadienobenzene) the molecule adopts a doubly bridged 10-annulene form,<sup>18,33</sup> losing the aromaticity of the central ring but thereby avoiding the antiaromaticity of two cyclobutadienes. In the linear subunits seen in the [N]phenylenes, this does not occur, presumably because the aromaticity of the additional benzene rings balances out the antiaromaticity of the cyclobutadiene units.

In an angular subunit, the central six-membered ring can undergo bond localization in such a way that both of the annulated four-membered rings will contain only single bonds. By doing so, the end rings become able to delocalize freely, since no bond configuration they adopt results in a cyclobutadiene ring. This is consistent with the observation of small ring currents for the central ring and more substantial ring currents in the end rings.

In the trigonal molecules (**T2**, **P10**, and **P11**), the central six-membered ring displays small, paratropic ring currents. Inspection of the CD maps shows that the ring currents in the trigonal core do not reside within the four- and six-membered rings but rather in a 12-annulene moiety. Previous work has already shown that this core structure is highly localized and, in fact, nonaromatic.<sup>34,37</sup> In resonance terms, owing to the annulene character of the central core, the three four-membered rings cannot become cyclobutadiene moieties, regardless of the bond configuration of the outer six-membered rings. Therefore, those outer rings can freely delocalize, and

Table 1. Results of CD-PP and CD-HL CDAs and NICS<sub>zz</sub> Computations for Each of the Rings in the [4]- and [5]Phenylene Isomers<sup>a</sup>

ring	isomer																
	T1	T2	T3	T4	T5	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
a	CD-PP	-0.22	-0.73	-0.24	-0.47	-0.48	-0.23	-0.25	-0.50	-0.58	-0.58	-0.26	-0.50	-0.49	-0.72	-0.68	-0.45
	CD-HL	-0.27	-0.69	-0.28	-0.43	-0.43	-0.28	-0.30	-0.48	-0.56	-0.56	-0.31	-0.48	-0.48	-0.68	-0.63	-0.42
	NICS <sub>zz</sub>	-10.51	-22.48	-11.07	-15.96	-15.93	-10.45	-11.06	-16.59	-18.68	-18.85	-11.43	-16.91	-16.66	-22.64	-21.15	-15.49
b	CD-PP	1.86	0.54	1.81	1.25	1.24	1.84	1.78	1.17	0.95	0.96	1.77	1.17	1.19	0.51	0.67	1.27
	CD-HL	1.69	0.57	1.65	1.25	1.24	1.66	1.61	1.13	0.93	0.93	1.59	1.13	1.13	0.59	0.72	1.29
	NICS <sub>zz</sub>	34.98	9.69	34.59	25.37	25.29	34.98	34.36	23.97	19.13	19.10	33.93	23.87	23.92	8.57	12.68	26.15
c	CD-PP	-0.13	0.24	-0.05	-0.04	-0.04	-0.17	-0.06	-0.06	-0.13	-0.13	-0.03	-0.05	-0.06	0.17	0.17	-0.04
	CD-HL	-0.11	0.25	-0.04	-0.05	-0.05	-0.16	-0.05	-0.03	-0.09	-0.09	-0.06	-0.03	-0.03	0.16	-0.17	-0.05
	NICS <sub>zz</sub>	-2.14	9.60	-5.78	-1.56	-1.49	-1.46	-6.20	0.36	-0.29	4.12	-4.80	0.33	0.25	7.97	7.54	-2.36
d	CD-PP	1.49	0.54	0.88	0.60	0.61	1.63	0.82	0.73	0.95	0.96	1.16	0.74	0.74	0.51	0.68	0.57
	CD-HL	1.23	0.57	0.73	0.55	0.55	1.37	0.71	0.70	0.82	0.82	1.06	0.70	0.70	0.59	0.74	0.55
	NICS <sub>zz</sub>	30.10	9.69	17.42	12.61	12.67	31.52	14.98	15.38	18.92	18.87	22.87	15.35	15.31	8.57	14.77	11.39
e	CD-PP	-0.13	-0.73	-0.09	-0.04	-0.04	-0.09	-0.08	-0.23	-0.28	-0.28	-0.05	-0.23	-0.23	-0.73	-0.67	-0.04
	CD-HL	-0.11	-0.69	-0.05	-0.04	-0.04	-0.05	-0.02	-0.26	-0.28	-0.28	-0.10	-0.26	-0.26	-0.67	-0.63	-0.10
	NICS <sub>zz</sub>	-2.14	-22.48	3.57	-1.56	-1.49	-2.58	3.80	-6.91	-10.23	-10.52	-1.37	-6.91	-6.85	-22.64	-21.12	-1.19
f	CD-PP	1.86	0.54	0.97	1.25	1.24	1.63	0.91	0.83	0.74	0.95	0.57	0.74	0.73	0.39	0.32	1.15
	CD-HL	1.69	0.57	0.92	1.25	1.24	1.37	0.76	0.70	0.69	0.82	0.54	0.70	0.70	0.35	0.33	1.05
	NICS <sub>zz</sub>	34.98	9.69	18.61	25.37	25.29	31.52	17.49	14.98	18.92	18.87	11.30	15.28	15.31	3.43	5.63	22.84
g	CD-PP	-0.22	-0.73	-0.58	-0.47	-0.48	-0.17	-0.12	-0.06	-0.13	-0.13	-0.04	-0.06	-0.06	-0.17	-0.12	-0.02
	CD-HL	-0.27	-0.69	-0.55	-0.47	-0.48	-0.16	-0.06	-0.03	-0.09	-0.09	-0.05	-0.03	-0.03	-0.15	-0.14	-0.05
	NICS <sub>zz</sub>	-10.51	-22.48	-18.85	-15.96	-15.93	-1.46	4.16	0.36	-0.29	4.12	-2.46	0.30	0.25	-8.36	-5.95	-4.09
h	CD-PP	1.84	0.95	1.82	1.18	1.18	1.84	0.95	1.82	0.99	0.97	1.30	1.20	1.21	1.84	1.44	1.80
	CD-HL	1.66	0.87	1.57	1.12	1.12	1.66	0.87	1.12	0.92	0.92	1.27	1.12	1.12	1.63	1.41	1.56
	NICS <sub>zz</sub>	34.98	17.60	34.36	23.97	23.97	34.98	17.60	23.97	19.13	19.10	26.19	23.95	23.92	35.22	29.55	33.89
i	CD-PP	-0.23	-0.58	-0.24	-0.50	-0.58	-0.23	-0.58	-0.50	-0.57	-0.58	-0.45	-0.49	-0.49	-0.23	-0.40	-0.25
	CD-HL	-0.28	-0.57	-0.28	-0.48	-0.48	-0.28	-0.48	-0.48	-0.55	-0.55	-0.41	-0.47	-0.47	-0.26	-0.36	-0.30
	NICS <sub>zz</sub>	-10.45	-19.22	-11.06	-16.59	-16.59	-10.45	-19.22	-11.06	-18.68	-18.85	-15.56	-16.63	-16.66	-10.72	-13.90	-11.41

<sup>a</sup>Currents are reported as dimensionless quantities scaled to the standard benzene value for the method, as noted in the text, and NICS values are in ppm.

indeed, they exhibit the most intense diatropic ring currents of all the isomers. The small paratropic ring current and the positive NICS value in the central ring of the trigonal core are consistent with the induced field generated by the three surrounding “Clar-sextet” six-membered rings. Lack of a central diatropic current is also compatible with the rules developed for  $\pi$ -clamped benzenes using ipsocentric molecular-orbital considerations.<sup>37c</sup>

Resonance considerations also rationalize the behavior of rings present in overlapping subunit motifs if the gain of antiaromaticity in creating cyclobutadiene rings is taken to be more costly than the loss of aromaticity in localizing benzene rings.

**Molecular Indices of Relative Overall Aromaticity.** It is clear from the foregoing that CD maps and NICS can be used to compare rings within one system, as well as rings within similar compounds. Is it also possible to identify the most aromatic (or least antiaromatic) and least aromatic (or most antiaromatic) compound in the set? In other words: to create a relative scale of aromaticity? To this end, the values of the calculated quantities for all rings in each compound were summed to afford a molecular value (Table 2). Figure 5 shows the plots of  $\sum J$  in the two CDA methods against  $\sum \text{NICS}_{\pi_{ZZ}}$ .

**Table 2. Ring-Summed Currents  $\sum J$  (CD-PP),  $\sum J$  (CD-HL), and Summed NICS Values  $\sum \text{NICS}_{\pi_{ZZ}}$  for the Studied Systems<sup>a</sup>**

compd	$\sum J$ (CD-PP)	$\sum J$ (CD-HL)	$\sum \text{NICS}_{\pi_{ZZ}}$
T1	4.51	3.85	74.76
T2	-0.33	-0.11	-28.79
T3	2.7	2.38	38.50
T4	2.08	2.06	28.29
T5	2.05	2.03	28.41
P1	6.05	5.13	106.59
P2	4.11	3.43	68.30
P3	4.57	3.89	67.97
P4	2.47	2.36	39.33
P5	2.15	1.92	38.68
P6	2.16	1.92	37.09
P7	3.97	3.53	59.80
P8	2.52	2.38	38.63
P9	2.54	2.38	40.38
P10	1.57	1.24	1.40
P11	1.41	1.27	8.05
P12	3.99	3.53	59.94

<sup>a</sup>Units are the same as in Table 1.

Given the fundamental differences between the various methods, the agreement shown in Figure 5 may be considered excellent. The fact of the agreement supports our prediction that double- and triple-counting in the NICS calculations essentially cancels out in the [N]phenylenes.

On an optimistic view, these plots could be taken to indicate the existence of a relative scale of (magnetic) aromaticity, as manifested by magnetic properties. The categorization suggested by the correlations in Figure 5 is simple: as positive  $\sum \text{NICS}$  and negative  $\sum J$  values correspond to paratropic currents (and antiaromaticity), and negative values correspond to diatropic currents (and aromaticity), it can be observed that the *most aromatic* (or least antiaromatic) compounds are those with the *trigonal* subunits, and the *least aromatic* (or most antiaromatic) isomers are those with long *linear* sequences. As

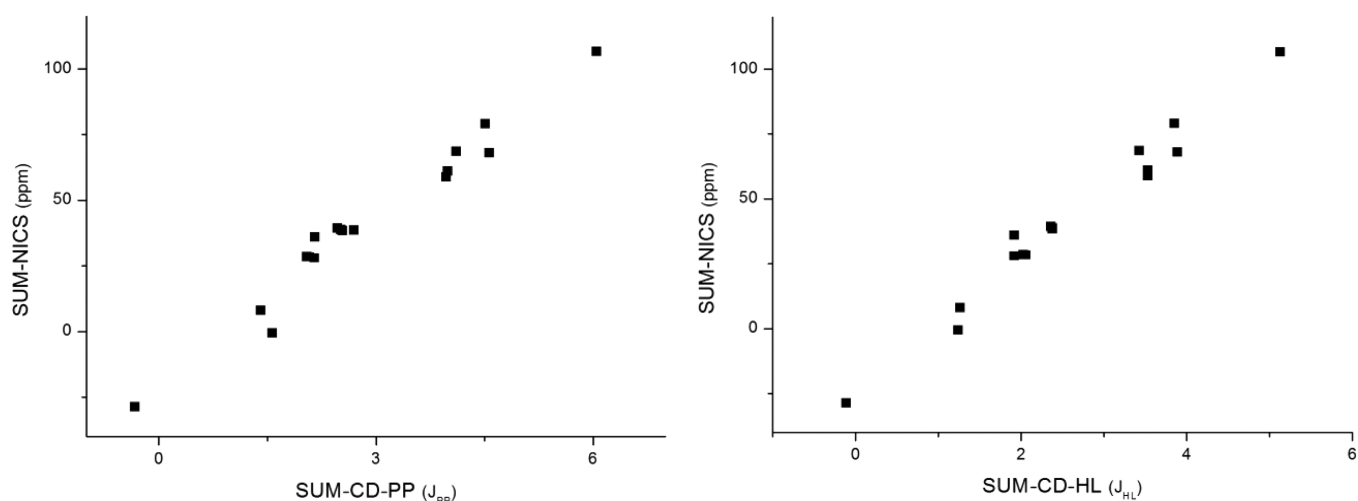
indicated previously, paratropic currents tend to be numerically larger, and so, the summed quantities are dominated by the four-membered rings, even though these are fewer in number. It will be interesting to see how the correlation fares when applied to the benzenoids themselves. It should be noted that a similar correlation between two magnetic indices, namely, magnetic susceptibility exaltation and  $\text{NICS}(1)_{ZZ}$  in a range of antiaromatic neutral and charged systems was previously reported.<sup>21</sup> Note that, in the present work, we consider a simple sum  $\sum \text{NICS}_{\pi_{ZZ}}$  instead of using the normalization by a power of ring area that has been found to work well in other contexts;<sup>21</sup> numerical experimentation indicates that the simple sum gives somewhat better correlations, at least for the phenylene series considered here.

**Comparison between Energy and  $\text{NICS}_{\pi_{ZZ}}$ .** Energy is another often used index of aromaticity, with the assumption being that the more aromatic a compound is, the more stable it is. As mentioned in the Introduction, this index requires a reference system, and this requirement is its greatest disadvantage. By choosing the [N]phenylene family, this difficulty was avoided, since the relative energy of the isomers can be used for comparison. The energy of the different isomers was calculated and subsequently corrected for strain,<sup>38</sup> as it is known that linear and angular annulation are associated with different amounts of strain. As we are dealing with structural isomers, the corrected relative energies obtained by this method should differ primarily because of  $\pi$  electronic considerations, that is, the aromaticity (or antiaromaticity) of the molecule. Hence, a scale of relative energies should correspond to a scale of relative aromaticity. Table 3 displays the strain-corrected, relative ZPE-corrected energies for the [4]- and [5]phenylene subfamilies, respectively.

Energy is a molecular property and should be compared to another property of the molecule as a whole. The magnetic criterion chosen for comparison here is the  $\sum \text{NICS}_{\pi_{ZZ}}$  which was shown in the previous section to correlate well with the sum of  $J$ . Figure 6 shows  $\sum \text{NICS}_{\pi_{ZZ}}$  of the five isomers of the [4]phenylene subfamily, plotted against the relative energy. The correlation is satisfying, as is evident from the correlation coefficient. Figure 7 shows the  $\sum \text{NICS}_{\pi_{ZZ}}$  of the 12 isomers of the [5]phenylene subfamily, plotted against the relative energy. Though the coefficient is less impressive, there is clearly a close relationship between the two properties.

It appears that, within subfamilies, the aromaticity (or antiaromaticity) of the [N]phenylene isomers is a cumulative property. These systems, with their cancellation of mutual enhancing effects, may be especially suited to use of  $\text{NICS}_{\pi_{ZZ}}$ . The correlations suggests that the same considerations that were in play for the magnetic criterion apply also for the energetic criterion. In other words, the balance between avoiding cyclobutadiene rings and maximizing delocalization of the benzene rings also decides the overall stability of each compound. Compounds in this family with more aromatic (less antiaromatic) character on the magnetic criterion are lower in energy. This conclusion extends the range of systems for which correlations among energetic-, magnetic-, and delocalization-based criteria and indices of aromaticity have been found (e.g., see the discussion in ref 39).

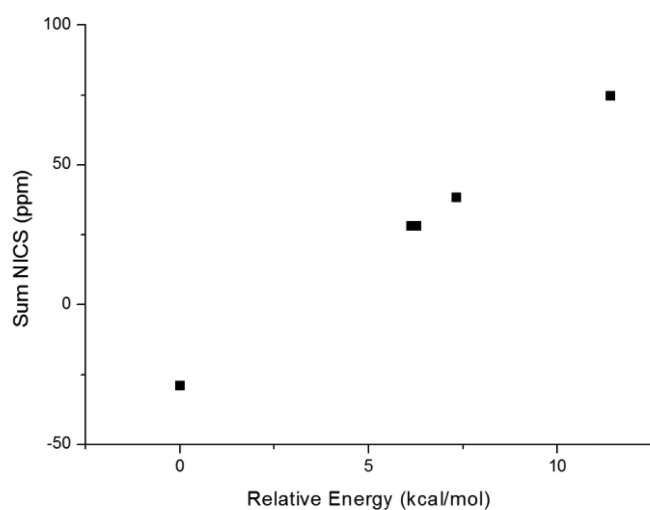
The next step is to examine the generality of the correlation by combining the results for the two subfamilies. In order to do this, one must first calibrate the ZPE- and strain-corrected energies of the different compounds. The structural difference between the [5]phenylenes and the [4]phenylenes is one  $\text{C}_6\text{H}_2$



**Figure 5.** Plot of  $\sum \text{NICS}_{\pi_{zz}}$  against (a)  $\sum J(\text{CD-PP})$  ( $R^2 = 0.9537$ ), (b)  $\sum J(\text{CD-HL})$  ( $R^2 = 0.9635$ ). Scaled dimensionless currents are used as in Figure 3.

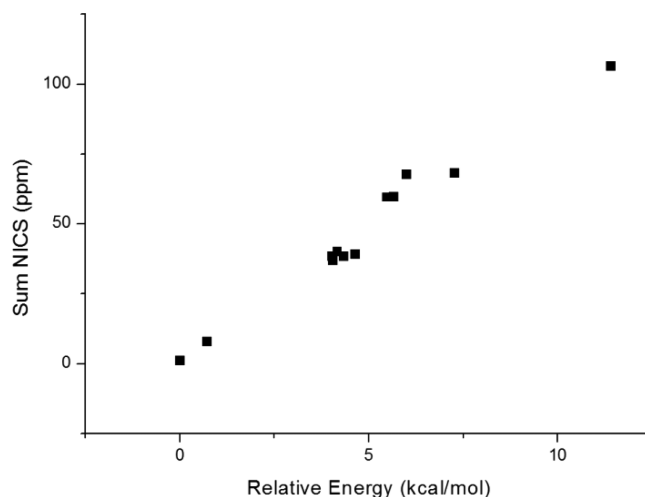
**Table 3. Relative Strain-Corrected, ZPE-Corrected Energies and  $\sum \text{NICS}_{\pi_{zz}}$  for [4]Phenylene and [5]Phenylene Isomers**

compd	rel energy (kcal mol <sup>-1</sup> )	$\sum \text{NICS}_{\pi_{zz}}$ (ppm)	compd	rel energy (kcal mol <sup>-1</sup> )	$\sum \text{NICS}_{\pi_{zz}}$ (ppm)
T1	11.387	74.76	P1	13.500	106.59
T2	0.000	-28.79	P2	9.110	68.30
T3	7.305	38.50	P3	7.845	67.97
T4	6.117	28.29	P4	5.963	39.33
T5	6.259	28.41	P5	5.621	38.68
			P6	5.631	37.09
			P7	7.328	59.80
			P8	5.659	38.63
			P9	5.489	40.38
			P10	0.000	1.40
			P11	0.447	8.05
			P12	7.241	59.94



**Figure 6.**  $\sum \text{NICS}_{\pi_{zz}}$  against relative energy for the [4]phenylene isomers ( $R^2 = 0.9996$ ).

unit. Thus, the simplest form of correction would be to subtract the energy of T1 from P1 and to add the energetic value of this unit to the energies of all the [4]phenylene isomers, or alternatively, to subtract it from all the energies of the [5]phenylene isomers. However, the difference between the

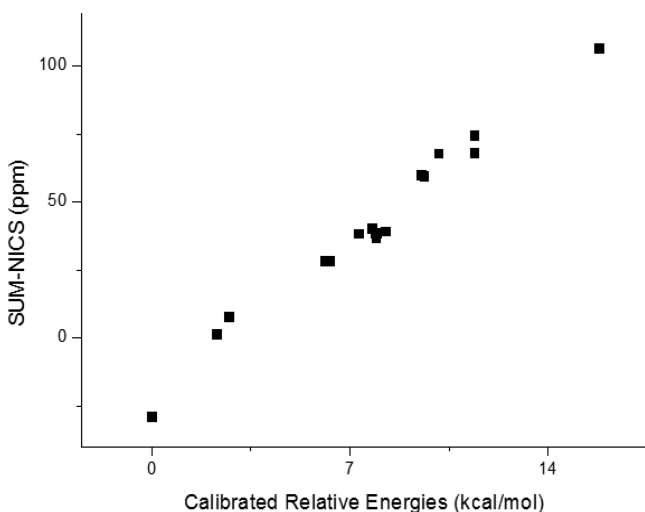


**Figure 7.**  $\sum \text{NICS}_{\pi_{zz}}$  against relative energy for the [5]phenylene isomers ( $R^2 = 0.9710$ ).

T and P families is not solely constitutional, it is also electronic ( $\sum \text{NICS}_{\pi_{zz}} = 106.59$  and  $\sum \text{NICS}_{\pi_{zz}} = 74.76$  for P1 and T1, respectively), and, as shown above, the energy should also reflect this difference. Therefore, the correct way to calculate the constitutional energetic difference cleanly is probably to calculate the difference between two isomers with very similar  $\sum \text{NICS}_{\pi_{zz}}$  values. Three such couples were identified: T3 and P8 ( $\sum \text{NICS}_{\pi_{zz}} = 38.50$  and  $\sum \text{NICS}_{\pi_{zz}} = 38.63$ , respectively); T3 and P5 ( $\sum \text{NICS}_{\pi_{zz}} = 38.50$  and  $\sum \text{NICS}_{\pi_{zz}} = 38.68$ , respectively); and T1 and P2 ( $\sum \text{NICS}_{\pi_{zz}} = 74.76$  and  $\sum \text{NICS}_{\pi_{zz}} = 68.30$ , respectively). The difference in energy (after strain correction) for each pair of isomers was calculated, and the result was added to the strain-corrected ZP energies of all the [4]phenylene isomers. These were plotted, along with the corrected energies of the [5]phenylenes, against the previously calculated  $\sum \text{NICS}_{\pi_{zz}}$  values. Figure 8 displays the relationship found with the difference calculated from the third couple (T1 and P2), which gives  $R^2 = 0.9771$ . The other isomer couples afforded similar results: choosing T3 and P5 gave  $R^2 = 0.9699$ , and choosing T3 and P8 gave  $R^2 = 0.9690$ .

The fact that all three versions gave similar results validates the method chosen to obtain the structural energetic





**Figure 8.** Plot of  $\sum \text{NICS}_{\pi_{zz}}$  of all studied isomers against calibrated relative energy ( $\text{kcal mol}^{-1}$ ).  $R^2 = 0.9771$ .

differences between the two subfamilies. It also supports the conclusion drawn from the plot: that the aromaticity of a compound, as manifested magnetically, goes hand in hand with the energy of the compound. It is in this series interesting to note that the correlation coefficient increases with the geometric similarity between the isomers (number of angular vs linear annulations).

## CONCLUSIONS

The relationship between two methods of evaluating aromaticity, both based on magnetic criteria, has been studied. It is shown that for the [4]- and [5]phenylene subfamilies, the two approaches to magnetic aromaticity, CDA and  $\text{NICS}_{\pi_{zz}}$  show similar trends. In fact, the degree of agreement between the two methods is surprisingly high, considering the differences between the methods. In addition, the relationship between two separate indices of aromaticity, namely, energetic and magnetic, is studied. It is found that, for the [N]phenylenes studied, a correlation does exist: compounds in which  $\sum \text{NICS}_{\pi_{zz}}$  and  $\sum J$  values indicate high overall paratropicity are destabilized compared to compounds with lower overall paratropicity/higher overall diatropicity. These results are explained by analyzing the resonance structures of the studied systems; specifically, identifying those structures in which no cyclobutadiene rings are formed and how this avoidance affects the extent of delocalization in the benzene rings.

The results can be taken to indicate that, for these compounds,  $\text{NICS}_{\pi_{zz}}$  is a good tool for assessing both the integrated local induced fields and the total magnetic character (aromaticity) of the compounds. Another way to look at the success of the correlation between NICS and current density, and between the simplest (HL) and most sophisticated (ab initio) mapping approaches is that, for many purposes, simple Hückel–London theory, involving just diagonalization of a single graph-theoretically defined matrix, and trivial amounts of computer time, gives predictions of similar quality to those obtained from much more onerous methods, and so, summation of HL ring currents seems to offer a simple indicator of global aromaticity of these isomeric polycyclic systems. The surprising ability of Hückel-based models to capture essential features of delocalized systems including patterns of current and semiquantitative evaluations of

multicenter delocalization indices has of course been noted before.<sup>16,20,28,39</sup> All of the above suggests that, within the [4]- and [5]phenylenes, there is a quantitative relationship between aromatic stabilization energy (as manifested by the relative energy) and the magnetic properties (manifested by  $\text{NICS}_{\pi_{zz}}$  or  $J$ ). We are currently studying other systems to determine whether this relationship is more general.

## ASSOCIATED CONTENT

### Supporting Information

NICS distance profiles for the [4]- and [5]phenylenes, CD-Full and CD-PP current-density maps for the [4]phenylene isomers, and Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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