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A Theoretical and Experimental Scale of Aromaticity. The First Nucleus-Independent Chemical Shifts (NICS) Study of the Dimethyldihydropyrene Nucleus[⊥]

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Abstract: Nucleus-independent chemical shift (NICS) values were calculated at several locations for a series of dimethyldihydropyrenes (DDPs). These NICS values were used to assess the relative aromaticities of the dimethyldihydropyrene nucleus (DDPN) of these DDPs and to construct a NICS scale of aromaticity. The NICS and experimentally determined relative aromaticities of these DDPNs are in complete agreement, verifying that NICS can be used not only to classify a compound as aromatic but also to determine the degrees of aromaticity of structurally related systems.

Introduction

Classically, aromaticity is attributed to the complete cyclic delocalization of $(4n+2)\pi$ electrons. However, as a consequence of the lack of a universally acceptable/applicable definition for aromaticity, the term is understandably controversial.[1] This ill-defined property of aromaticity results in the aromatic molecule enjoying a "special stability" relative to an appropriate nonaromatic model compound. Many attempts have been made to quantify this special stability through variously defined stabilization energies.[1] Depending on the model chosen and the method of calculation, a bewildering array of stabilization energies resulted.[2,3] These energies were used to construct scales of aromaticity. Unfortunately, the exact ordering of compounds depended more on the nature of the earlier models and methods used than it did on any intrinsic property of the compounds being ordered. Similarly, and often with an equal lack of success, other properties associated with aromaticity, such as reactivity,[2] structural features,[4] and magnetic properties,[5] have been used to construct scales of aromaticity.[4b] Despite the difficulties in defining the term and in consistently establishing the degree of aromaticity, identifying a compound as aromatic is often straightforward. Experimentally, nuclear magnetic resonance (NMR) spectroscopy is the key technique used in deciding whether a compound is aromatic or not.[6] Supporting the use of magnetic properties in classifying a molecule as aromatic, Hess, Schaad, and Nakagawa demonstrated that resonance energy and chemical shift are correlated, and Haddon derived a relationship linking the induced ring current with resonance energy.[7,8] Further Bird[9] and Fowler and Steiner[10] also linked magnetic properties with aromaticity, and recently Schleyer even proposed a definition of aromaticity based solely on magnetic susceptibility exaltation and asserted that such properties are the only measurable properties uniquely associated with aromaticity.[11]

For many years Mitchell has championed the use of the dimethyldihydropyrene nucleus (DDPN) as a sensitive experimental probe for measuring aromaticity.[12] The internal methyl groups of dimethyldihydropyrene (DDP) (**1**) are ideally situated within its nearly planar completely delocalized 14 π periphery to serve as exquisitely sensitive NMR probes for aromaticity. We have shown that the ^{1}H chemical shifts of the internal methyl groups of DDP (**1**) and its annelated derivatives serve to assess the aromaticity of the dimethyldihydropyrene nuclei (DDPNs).[13] This methodology also permits the quantitative assessment of

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[⊥] Dedicated to Professor Ian Fleming on the occasion of his retirement from the University of Cambridge.

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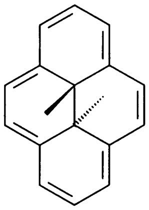
the relative degree of aromaticity of the annelating aromatic rings by comparing the magnitude of the downfield shift they induce in the internal methyl groups of the DDP with that induced by the corresponding benzannelation.[14] An *experimental* scale of aromaticity for a large range of DDPNs is available from this work.



1

Schleyer et al. introduced nucleus-independent chemical shifts (NICS),[15] the negative of the absolute magnetic shieldings, usually computed at the ring centers, as a means of evaluating the aromaticity/antiaromaticity of appropriate candidates. Negative NICS values correspond with aromaticity (e.g., -11.5 for benzene), while positive values are associated with antiaromaticity (e.g., $+28.8$ for cyclobutadiene) and values near zero for nonaromatics (e.g., -2.1 for cyclohexane).[15a] Not surprisingly, NICS values are basis set dependent; those cited above for benzene, cyclobutadiene, and cyclohexane were calculated using the GIAO-HF/6-31G*//B3LYP/6-31G* methods, while for the GIAO-HF/6-31+G*//B3LYP/6-31G* methods the corresponding values are -9.7, $+27.6$, and -2.2, respectively.[15a] NICS appears to be not only an ideal discriminator for aromaticity but also a valuable predictor for the degree of aromaticity.[15] In a limited demonstration of the effectiveness of NICS in predicting the degree of aromaticity, Schleyer et al. showed that there was excellent agreement between the magnitude of the NICS for a range of five-membered ring heterocycles (**2**) and the corresponding aromatic stabilization energies (ASEs) for these compounds.[15a]

2

X = SiH$^+$, BH, AlH, CH$_2$, PH, SiH$^-$, O, S, NH, CH$^-$

In another study, the ASEs of these same compounds were correlated with their magnetic susceptibility exaltations, magnetic susceptibility anisotropies, and Julg parameters,[16a] and more recently, these parameters were directly compared with the NICS values for **2** (X = O, S, NH, and CH$^-$) and variously 5,5-disubstituted cyclopenta-1,3-dienes.[16b] Unfortunately, all of these discriminators were determined by theoretical calculations (albeit of high-order and proven reliability). Consequently, the resulting NICS scale of aromaticity is theoretically derived and has not been calibrated against experiment. Schleyer et al. also used NICS to evaluate the aromaticity of individual rings in fused polycyclic aromatic/antiaromatic systems by determining NICS values at the centers of each ring.[15] Thiel and Patchkovskii use semiempirical methods to calculate NICS values for a very wide range of compounds and compare their results with those obtained by others using ab initio and DFT methods.[17] In many studies, the NICS values are calculated at points out of the ring plane in order to minimize local anisotropies associated with the σ-bonds of the ring.[17] To more effectively probe the individual effects of the various σ- and π-bonds along with those of the core electrons, Schleyer et al. introduced dissected NICS in which these contributions to the total NICS are separated out and determined individually.[18] Krygowski et al. have shown that NICS measures of aromaticity correlate well with their reliable structure-based harmonic oscillator model of aromaticity (HOMA)[4] and that, for a large enough set of molecules, there is statistically significant correlation between NICS, HOMA, and a variety of other calculated indices of aromaticity.[4b] Some concern has been expressed regarding the use of a virtual quantity (NICS) to evaluate such an intangible as aromaticity.[5] In this study, to address the lack of experimental validation of a NICS scale of aromaticity, we calculate the NICS values for a series of annelated DDPs for which the experimental relative aromaticities of each DDPN had already been determined.

So far, the study of the DDPs has been almost entirely confined to the realm of NMR spectroscopy. Supplementing the very few X-ray crystal structures of the dihydropyrene nucleus,[19−27] we were able to obtain well-refined X-ray structures for two important additional DDPs (**3** and **4**) in this study. These additional structures allow for direct points of comparison between experimental and calculated data and presented the opportunity for us to evaluate the appropriateness of our computational methods for the DDPs. Although there have been many theoretical studies using molecular mechanics and (uncorrelated) semiempirical methods, there are very few using correlated methods and none reporting NICS values for this fascinating system.

Results and Discussion

All calculations were carried out with a 6-31G* basis set, and the geometries for all of the compounds in this study were optimized using density functional theory (DFT with the B3LYP functional) as implemented in Jaguar 4.0.[28] Analytical energy second derivatives were calculated at the optimized structures (except for the very large **12**) to confirm that these are minima. NICS values were calculated at the points shown using the Hartree−Fock (HF) GIAO method on the B3LYP/6-31G*

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Table 1. Selected Experimental and Calculated Bond Lengths and Bond Alternations for DDPs **1** and **3**−**8** and the Nonaromatic Model Compound **9**

bond	**1**-calc	**1**-expt[a] molecule A	**1**-expt[a] molecule B	3-calc	**3**-expt[b]	**4**-calc	**4**-expt[b]	**5**-calc	**6**-calc	**7**-calc	**8**-calc	**9**-calc
1−2	1.402	1.392	1.396	1.412	1.402	1.443	1.440	1.447	1.428	1.432	1.427	1.504
2−3	1.395	1.389	1.390	1.392	1.387	1.366	1.362	1.426	1.372	1.451	1.462	1.346
3−4	1.403	1.398	1.397	1.405	1.397	1.460	1.463	1.398	1.454	1.376	1.365	1.461
4−5	1.400	1.392	1.390	1.401	1.389	1.433	1.426	1.399	1.435	1.429	1.441	1.353
5−6	1.403	1.397	1.393	1.404	1.393	1.460	1.450	1.405	1.454	1.377	1.365	1.461
6−7	1.395	1.390	1.389	1.395	1.388	1.366	1.364	1.383	1.372	1.421	1.462	1.346
7−8	1.402	1.390	1.388	1.408	1.399	1.443	1.437	1.415	1.428	1.378	1.427	1.504
8−9	1.402	1.392	1.396	1.412	1.402	1.378	1.359	1.447	1.375	1.429	1.447	1.504
9−10	1.395	1.389	1.390	1.392	1.387	1.421	1.429	1.426	1.417	1.373	1.358	1.346
10−11	1.403	1.398	1.397	1.405	1.397	1.379	1.367	1.398	1.381	1.428	1.443	1.461
11−12	1.400	1.392	1.390	1.401	1.389	1.425	1.429	1.399	1.420	1.374	1.364	1.353
12−13	1.403	1.397	1.393	1.404	1.393	1.379	1.351	1.405	1.381	1.433	1.443	1.461
13−14	1.395	1.390	1.389	1.395	1.388	1.421	1.431	1.383	1.417	1.364	1.358	1.346
14−1	1.402	1.390	1.388	1.408	1.399	1.378	1.354	1.415	1.375	1.438	1.447	1.504
Σa[c]	1.400	1.393	1.392	1.402	1.394	1.383	1.369	1.410	1.384	1.433	1.449	1.461
Σb[d]	1.400	1.393	1.392	1.402	1.394	1.439	1.439	1.410	1.431	1.382	1.380	1.348
ΔΣ[e]	0	0	0	0	0	−0.056	−0.071	0	−0.047	0.051	0.069	0.113

[a] Reference 20; there are two crystallographically independent molecules A and B. [b] This work. [c] Average bond length of "a" type bonds. [d] Average bond length of "b" type bonds. [e] $\Delta\Sigma = \Sigma a - \Sigma b$.

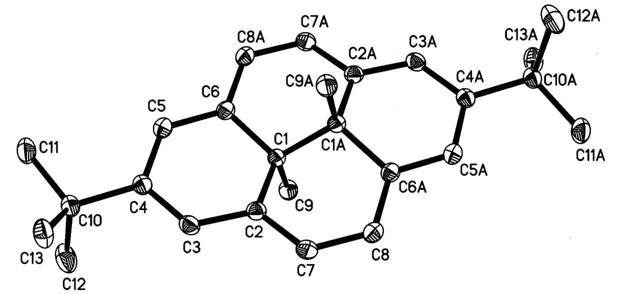

Figure 1. Thermal ellipsoid plot (30% probablility) of **3**. Hydrogen atoms have been omitted for clarity.

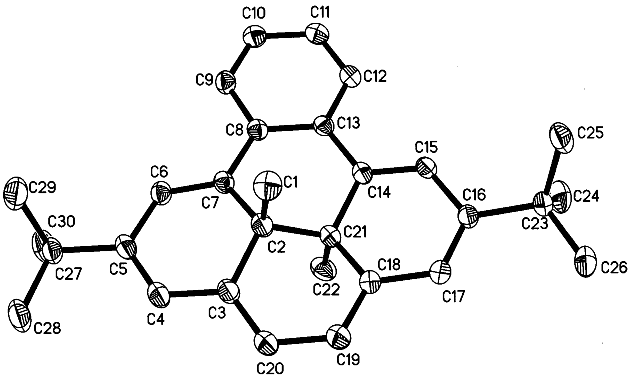

Figure 2. Thermal ellipsoid plot (30% probablility) of **4**. Hydrogen atoms have been omitted for clarity.

Table 2. NICS Values for Compounds **1** and **3**−**9**

point	1	3	5	6	7	4	8	9
1	−19.15	−18.91	−17.80	−6.15	−5.02	−4.40	0.07	0.24
2	−18.15	−17.66	−17.63	−7.23	−5.28	−5.47	−1.02	−0.09
3	−18.15	−17.66	−17.63	−5.98	−6.74	−4.29	−2.45	−0.09
4	−19.15	−18.91	−17.80	−6.15	−5.21	−4.40	0.07	0.24
Av[a]	−18.65	−18.29	−17.71	−6.38	−5.56	−4.64	−0.83	0.07
5			−10.86	−10.95	−11.51	−10.78	−10.49	
6			−10.86				−10.49	

[a] Average value of points *1*−*4*.

Table 3. Relative Aromaticities of the Dimethyldihydropyrene Nuclei (RAs) of **5**−**8**

	RA_{expt} (%)	$RA_{\delta calc}$ (%)	RA_{NICS} (%)[a]
5	87.2	98.0	95.0
6	54.0	40.7	34.5
7	49.2	35.0	30.1
8	18.2	11.8	4.8

[a] Relative aromaticity (%) calculated using NICS Av − the average of NICS points *1*−*4*.

geometry (GIAO-HF/6-31G*//B3LYP/6-31G*) with the Gaussian 94 suite of programs.[29]

Earlier, DDPN presented a significant challenge for computational studies, not only because of its size but also because of the requirement of using extensive electron correlation.[20,22] However, Siegel and Mitchell et al. demonstrated that second-order Möller−Plesset perturbation theory (MP2) and DFT (BLYP and BPW91) provide results in reasonable accord with experiment and expectations for DDP (**1**) and three of its derivatives.[22] Bodwell et al. found that the B3LYP method seemed to overestimate the symmetry and bond equalization of *cis*-DDP, although this apparent discrepancy is perhaps not too surprising, as they compared their calculated results for the parent *cis*-DDP with their experimental X-ray data for a tethered derivative.[27] To evaluate the reliability of the B3LYP/6-31G* method for modeling our *trans*-DDPs, we initially compared our optimized structural parameters of **1** with our previously obtained single-crystal X-ray data for **1** (Table 1).[20] Agreement between experiment and theory is excellent, with a maximum difference between calculated and experimental bond lengths (Δr) of only 0.014 Å. A further comparison of our X-ray data for DDPs **3** and **4** (vide infra) with our B3LYP/6-31G* structures (Table 1), maximum Δr = 0.028 Å, furnished additional reassurance that this method provides excellent modeling of DDPs. Now confident in the reliability of the B3LYP/6-31G* method for DDPs, we used this method exclusively for all geometry optimizations reported in this study.

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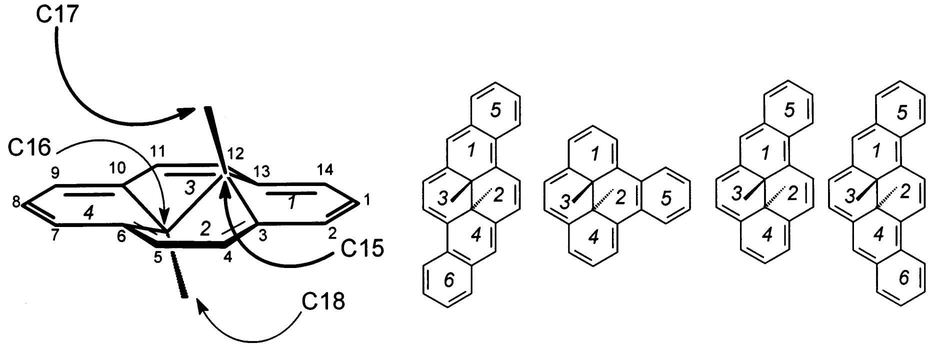
Table 4. Calculated and Experimental ^{13}C Chemical Shifts for Compounds **1** and **3**−**9**

	1		**3**		**4**		**5**		**6**		**7**		**8**		**9**	
	δcalc[a]	δexpt[b]	δcalc[a]	δexpt[b]	δcalc[a]	δexpt[c,d]	δcalc[a]	δexpt[c,e]	δcalc[a]	δexpt[c,f]	δcalc[a]	δexpt[c,g]	δcalc[a]	δexpt[c,e]	δcalc[a]	δexpt[h]
C1	125.20	122.97	148.08	145.47	147.52	144.3	130.77	129.9	125.34	122.1	131.64	133.7	133.79	131.6	30.03	27.8
C2	125.14	123.38	123.43	120.62	119.80	116.9*	128.73		119.48	117.0	129.59	128.5	131.33	129.5	127.34	122.5
C3	137.27	136.76	137.16	136.64	137.94	134.6	134.74		137.82	134.7	136.70	137.0	140.39	136.2	143.72	138.7
C4	126.01	123.45	125.79	122.67	131.72	129.2	121.28	119.5	131.33	128.9	120.34	117.0	120.16	116.7	129.38	125.4
C5	126.01	123.45	125.79	122.67	131.72	129.2	126.80	126.0	131.33	128.9	124.73	121.2	120.16	116.7	129.38	125.4
C6	137.27	136.76	137.16	136.64	137.94	134.6	136.68	137.0	137.82	134.7	140.67		140.39	136.2	143.72	138.7
C7	125.14	123.38	123.43	120.62	119.80	116.9*	127.57	127.8	119.48	117.0	127.02	123.6	131.33	129.5	127.34	122.5
C8	125.20	122.97	148.08	145.47	147.52	144.3	130.77	129.9	125.34	122.1	126.34	123.5	133.79	131.6	30.03	27.8
C9	125.14	123.38	123.43	120.62	123.00	119.6*	128.73		127.25	125.7	125.06	122.0	128.59	127.2	127.34	122.5
C10	137.27	136.76	137.16	136.64	139.94	138.3	134.74		139.42	138.1	140.42	139.2	141.39	138.5	143.72	138.7
C11	126.01	123.45	125.79	122.67	125.41	120.9*	121.28	119.5	125.64	122.7	128.49	126.2	130.44	127.7	129.38	125.4
C12	126.01	123.45	125.79	122.67	125.41	120.9*	126.80	126.0	125.64	122.7	129.13	127.0	130.44	127.7	129.38	125.4
C13	137.27	136.76	137.16	136.64	139.94	138.3	136.68	137.0	139.42	138.1	138.42	138.7	141.39	138.5	143.72	138.7
C14	125.14	123.38	123.43	120.62	123.00	119.6*	127.57	127.8	127.25	125.7	127.65	126.2	128.59	127.2	127.34	122.5
C15	29.74	29.92	29.28	29.56	36.21	35.1	31.64	32.8*	35.41	35.2*	35.91	35.5*	42.12	39.5*	44.34	39.2
C16	29.74	29.92	29.28	29.56	36.21	35.1	31.64	32.8*	35.41	35.2*	36.41	36.0*	42.12	39.5*	44.34	39.2
C17	11.70	13.97	11.87	14.33	15.45	17.3*	12.67	15.9*	14.31	16.8*	14.99	17.0*	18.40	19.2*	24.91	23.6
C18	11.70	13.97	11.87	14.33	15.45	17.3*	12.67	15.9*	14.31	16.8*	15.57	17.7*	18.40	19.2*	24.91	23.6
C19			39.52	35.95	126.48	124.4*	132.20	132.6	126.67	125.7	131.12	130.3	130.59	128.2		
C20			32.88	31.98	126.43	125.5*	126.64	125.6	126.41	124.5	127.53	125.5	128.41	127.1		
C21			32.88	31.98	126.43	125.5*	126.46	124.7	126.41	124.5	127.11	123.6	127.89	124.4		
C22			32.88	31.98	126.48	124.4*	126.21	124.4	126.67	125.7	125.51	123.5	125.14	123.2		
C23			39.52	35.95	38.94	35.3	132.20	132.6					125.14	123.2		
C24			32.88	31.98	31.23	30.6*	126.64	125.6					127.89	124.4		
C25			32.88	31.98	31.23	30.6*	126.46	124.7					128.41	127.1		
C26			32.88	31.98	31.23	30.6*	126.21	124.4					130.59	128.2		
C27					38.94	35.3										
C28					31.23	30.6*										
C29					31.23	30.6*										
C30					31.23	30.6										

[a] Empirically scaled ^{13}C chemical shifts from the GIAO-B3LYP/6-31G*//B3LYP/6-31G* absolute shieldings.[31] [b] Experimental chemical shifts determined and unambiguously assigned with the aid of HMBC correlation spectroscopy, this study. [c] Only the resonances marked * were specifically assigned in the cited work, and here the remaining signals are assigned by best fit to the calculated data. [d] Reported in ref 32. [e] Of the expected 13 resonances, only 10 signals are reported in ref 33. [f] Of the expected 11 resonances, only 10 signals are reported in ref 34, with the one at 125.7 designated as double intensity. [g] Of the expected 22 resonances, only 18 signals are reported in ref 35, with those at 126.2, 123.6, and 123.5 designated as intensity >1. [h] Reported in ref 36.

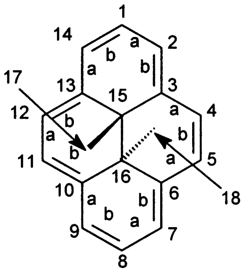
Chart 1. Location of the NICS Points



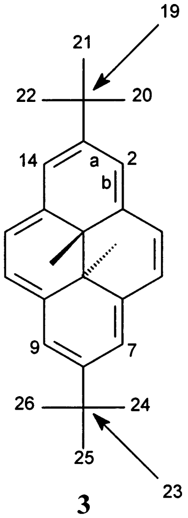
NICS points are shown in *italic* type

X-ray Structures of 3 and 4. The molecular structures of **3** and **4** were determined by X-ray crystallography (Figures 1 and 2). Selected bond lengths are given in Table 1, and further information for the data collection and refinement are given in Table 12. The parent molecule, **1**,[20] is triclinic, and both **3** and **4** show higher symmetry, crystallizing in the following respective space groups: monoclinic *C*2/*c* and orthorhombic *Pbca*. Disubstitution with ^{t}Bu groups leads to little difference between the bond lengths in **3** and **1** (see Table 1). The addition of the annelation in **4**, however, gives rise to greater bond length alternation than seen in either **1** or **3**, which is in excellent agreement with calculated values. Comparing the planarity of the peripheral carbon atoms also highlights the similarities between the parent, **1**, and **3**. Both systems display a mean displacement of ca. 0.02 Å from the plane of the peripheral carbon atoms, with the interior carbon atoms (C1 and C1a, X-ray numbering) extending ca. 0.36 Å out of this plane. Compound **4** is similar and has a mean displacement of ca. 0.05 Å, with the interior atoms (C2, C21 X-ray numbering) extending ca. 0.31 and 0.43 Å out of this plane. It is also notable that the ^{t}Bu groups adopt a conformation in which one carbon atom of the methyl group almost eclipses an adjacent aromatic C−C bond. In compound **3** this is represented by the torsion angle C11−C10−C4−C5 (X-ray numbering) of ±14° and in **4** by C4−C5−C27−C28 (X-ray numbering) = −3.1° and C26−C23−C16−C17 (X-ray numbering) = 0.3°. In these eclipsing conformations favorable hyperconjugative interactions are presumably maximized. Our calculations show that the conformation of **4** with the eclipsing interactions away from the annelating benzene ring is favored by 2 kcal/mol over the conformation with the eclipsing interactions toward the ring.

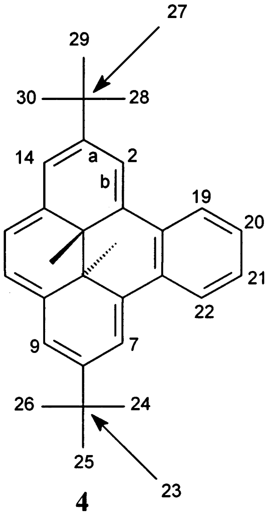
There are only a handful of X-ray structures reported in the literature for *trans*-dimethyldihydropyrene derivatives.[20−24,27] These six compounds all show mean deviations from planarity of the peripheral carbons from 0.02 to 0.05 Å, with the interior carbon atoms out of plane by 0.34−0.40 Å. The only other ^{t}Bu-DDP structure[23] displays an eclipsing similar to that seen in **3** and **4**. However, in this compound only one of the two ^{t}Bu groups is eclipsed (torsion angle 4.7°), while the other ^{t}Bu group is staggered relative to the peripheral carbon atom plane.



1

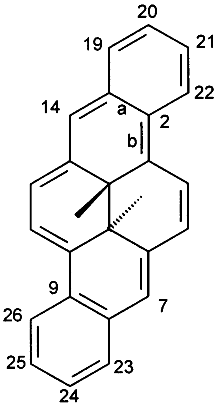


3

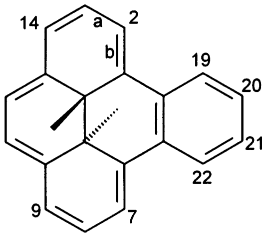


4

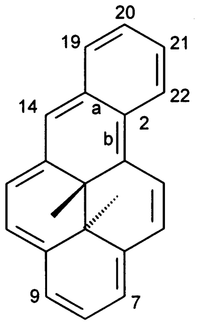
A NICS Scale of Aromaticity. Twenty years ago, we determined the experimental relative aromaticities of the DDPNs of **1** and **5**−**8** to be **1** > **5** $\gg$ **6** > **7** $\gg$ **8**, with only marginal difference in the aromaticities of the DDPNs of **6** and **7**.[13] These DDPs appeared to be the ideal starting point for our probe of NICS as a quantitative as well as qualitative measure of aromaticity. We optimized the structures of **5**−**9** (Table 1) and used the resulting geometries along with that for **1** to calculate NICS values (Table 2).



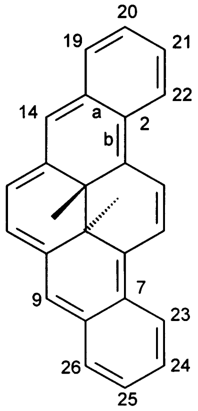
5



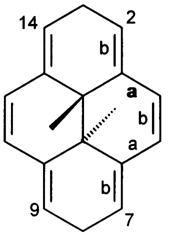
6



7



8



9

We calculated NICS values at the centers of the six-membered rings (points *1*−*6*), Chart 1. Due to the proximity of the C15−C16 bond, NICS points at the center of the 14-membered DDP rings would yield distorted NICS values.[15] Consequently, we used the simple arithmetic average of the NICS values at points *1*−*4* as representative of the aromaticity of each DDPN, the larger negative NICS value indicating greater aromaticity. These NICS Av values (average of the NICS at points *1*, *2*, *3*, and *4*) are in perfect agreement with the experimental order of aromaticity for the DDPNs of **1** and **5**−**8** (Table 2). NICS Av, in agreement with experiment, indicates that **8** is somewhat aromatic in comparison with the nonaromatic **9**.

We also calculated NICS at other points including numerous locations out of the mean DDPNs planes (see the Supporting Information for locations and NICS values). These NICS points all give the correct relative aromaticities of the DDPNs of **1** and **5**−**8**, but offer no advantage over the operationally simpler expedient of considering only NICS Av. In agreement with experiment NICS indicate:[13]

NICS decreasing order of aromaticity
of the DDPNs of **1** > **5** $\gg$ **6** > **7** $\gg$ **8**

Table 5. Calculated and Experimental ^{1}H Chemical Shifts for Compounds **1** and **3**−**9**

	1		**3**		**4**		**5**		**6**		**7**		**8**		**9**	
	δcalc[a]	δexpt[b]	δcalc[a]	δexpt[c]	δcalc[a]	δexpt[d]	δcalc[a]	δexpt[e]	δcalc[a]	δexpt[f]	δcalc[a]	δexpt[g]	δcalc[a]	δexp[e]	δcalc[a]	δexpt[h]
H1	9.07	8.11							7.39	7.25					2.46	2.97
H1′[i]															2.65	2.97
H2	9.72	8.62	9.71	8.54	8.17	8.28			8.34	8.3					5.67	5.70
H3																
H4	9.76	8.67	9.64	8.46			10.80	9.29			8.10	8.11	7.29	7.40	6.21	5.96
H5	9.76	8.67	9.64	8.46			10.04	8.39			7.31	7.38	7.29	7.40	6.21	5.96
H6																
H7	9.72	8.62	9.71	8.54	8.17	8.28	10.16	8.90	8.34	8.3	7.69	7.70			5.67	5.70
H8	9.07	8.11							7.39	7.25	7.17	7.14			2.46	2.97
H8′[i]															2.65	2.97
H9	9.72	8.62	9.71	8.54	7.37	7.35			7.84	7.59	7.25	7.37	6.93	7.16	5.67	5.70
H10																
H11	9.76	8.67	9.64	8.46	6.96	7.13	10.80	9.29	7.35	7.36	7.78	7.52	7.05	7.05	6.21	5.96
H12	9.76	8.67	9.64	8.46	6.96	7.13	10.04	8.39	7.35	7.36	7.84	7.62	7.05	7.05	6.21	5.96
H13																
H14	9.72	8.62	9.71	8.54	7.37	7.35	10.16	8.90	7.84	7.59	7.80	7.90	6.93	7.16	5.67	5.70
H15																
H16																
H17	−6.30	−4.25	−6.16	−4.04	−1.28	−1.58	−6.15	−3.58	−1.92	−1.85	−1.51	−1.60	0.22	0.02	1.09	0.97
H18	−6.30	−4.25	−6.16	−4.04	−1.28	−1.58	−6.15	−3.58	−1.92	−1.85	−1.49	−1.60	0.22	0.02	1.09	0.97
H19					9.00	8.77	9.18	8.70	9.16	8.81	8.05	7.99	7.58	7.58		
H20			1.58	1.69	7.92	7.61	8.37	7.76	7.99	7.62	7.93	7.69	7.65	7.46		
H21			1.58	1.69	7.92	7.61	8.44	7.80	7.99	7.62	7.94	7.70	7.65	7.49		
H22			1.58	1.69	9.00	8.77	10.41	9.39	9.16	8.81	9.02	8.75	8.45	8.25		
H23							9.18	8.70					8.45	8.25		
H24			1.58	1.69	1.54	1.49	8.37	7.76					7.65	7.49		
H25			1.58	1.69	1.54	1.49	8.44	7.80					7.65	7.46		
H26			1.58	1.69	1.54	1.49	10.41	9.39					7.58	7.58		
H27																
H28					1.54	1.49										
H29					1.54	1.49										
H30					1.54	1.49										

[a] Calculated ^{1}H chemical shifts from the GIAO-HF/6-31G*//B3LYP/6-31G* absolute shieldings. [b] Reported in ref 34. [c] Experimental chemical shifts from this study. [d] Reported in ref 32. [e] Reported in ref 33. [f] Reported in ref 34. [g] Reported in ref 35. [h] Reported in ref 36. [i] H1′ is syn to Me (C17), and H8′ is syn to Me (C18).

Table 6. Selected Experimental and Calculated Bond Lengths and Bond Alternations for DDPs **10**−**17**

bond	**10**-calc	**11**-calc	**12**-calc	**13**-calc	**14**-calc	**15**-calc	**15**-expt[a]	**16**-calc	**17**-calc
1−2	1.399	1.404	1.446	1.435	1.449	1.448	1.44	1.437	1.451
2−3	1.390	1.391	1.364	1.366	1.362	1.459	1.52	1.365	1.360
3−4	1.432	1.433	1.462	1.464	1.467	1.370	1.38	1.466	1.469
4−5	1.444	1.445	1.438	1.450	1.450	1.435	1.50	1.459	1.459
5−6	1.432	1.434	1.462	1.464	1.467	1.372	1.36	1.466	1.469
6−7	1.390	1.387	1.364	1.366	1.362	1.428	1.46	1.365	1.360
7−8	1.399	1.409	1.446	1.435	1.449	1.372	1.32	1.437	1.451
8−9	1.398	1.404	1.375	1.370	1.373	1.435	1.49	1.367	1.371
9−10	1.391	1.391	1.425	1.424	1.427	1.369	1.42	1.427	1.429
10−11	1.431	1.433	1.376	1.376	1.375	1.435	1.46	1.374	1.373
11−12	1.445	1.445	1.429	1.426	1.430	1.369	1.36	1.429	1.433
12−13	1.431	1.434	1.376	1.376	1.375	1.440	1.46	1.374	1.373
13−14	1.391	1.387	1.425	1.424	1.427	1.360	1.31	1.427	1.429
14−1	1.398	1.409	1.375	1.370	1.373	1.444	1.43	1.367	1.371
Σa[b]	1.412	1.415	1.442	1.439	1.445	1.380	1.37	1.441	1.447
Σb[c]	1.412	1.415	1.381	1.382	1.381	1.439	1.47	1.382	1.381
ΔΣ[d]	0	0	0.061	0.057	0.064	−0.059	−0.10	0.060	0.066

[a] Reference 23. Due to poor diffraction and crystal quality, only the carbon skeleton was determined and C−C bond values show high error levels. [b] Average bond length of “a” type bonds. [c] Average bond length of “b” type bonds. [d] $\Delta\Sigma = \Sigma a - \Sigma b$.

Mitchell has demonstrated that substituents on the DDPN have little effect upon the diatropicity as measured by the ^{1}H chemical shifts of the internal methyl groups.[6] Entirely consistent with this finding, our calculated NICS values for the ^{t}Bu-substituted DDPs, **3** and **4**, are similar to those of the corresponding DDPs **1** and **6** (Table 2), which lack the ^{t}Bu substituents.

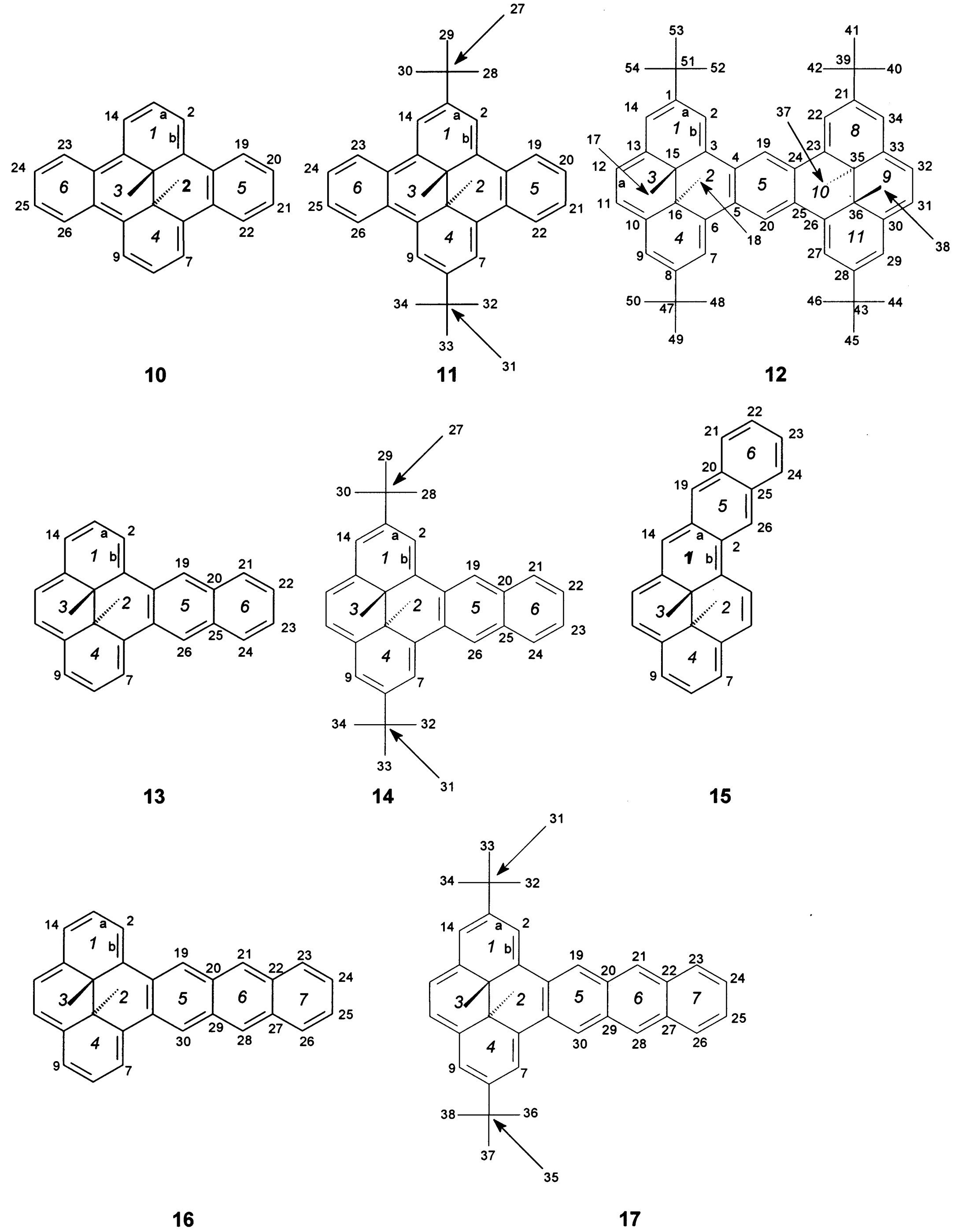
The experimental relative aromaticities of the DDPNs of **1** and **3**−**8** can be expressed quantitatively using eq 1 (Tables 3 and 9).[6] Similarly, relative aromaticities can be determined from calculated chemical shifts using eq 2, and NICS scales of aromaticity for the DDPNs can be derived from eq 3 (Tables 3 and 9).

$$\mathrm{RA}_{\mathrm{expt}} = \frac{\delta(\mathbf{9}) - \delta(\mathbf{n})}{\delta(\mathbf{9}) - \delta(\mathbf{1})} \times 100\% \qquad (1)$$

$$\mathrm{RA}_{\delta\mathrm{calc}} = \frac{\delta\mathrm{calc}(\mathbf{9}) - \delta\mathrm{calc}(\mathbf{n})}{\delta\mathrm{calc}(\mathbf{9}) - \delta\mathrm{calc}(\mathbf{1})} \times 100\% \qquad (2)$$

$$\mathrm{RA}_{\mathrm{NICS}} = \frac{\mathrm{NICS}\ \mathbf{9} - \mathrm{NICS}\ \mathbf{n}}{\mathrm{NICS}\ \mathbf{9} - \mathrm{NICS}\ \mathbf{1}} \times 100\% \qquad (3)$$

Chart 2. Location of the NICS Points and Atom Numbering



NICS points are shown in *italic* type

where RA_{expt} = experimental relative aromaticity of the DDPN of DDP **n** (compared to **1**), $\delta(\mathbf{9})$ = experimental ^1H chemical shift of Me groups on **9** (0.97 ppm), $\delta\mathbf{n}$ = experimental ^1H chemical shift of Me groups (average if different) on annelated DDP, $\delta(\mathbf{1})$ = experimental ^1H chemical shift of Me groups on **1** (−4.25 ppm), $RA_{\delta calc}$ = calculated relative aromaticity of the DDPN of DDP **n** (compared to **1**), $\delta calc(\mathbf{9})$ = calculated ^1H chemical shift of Me groups on **9** (0.97 ppm), $\delta calc\mathbf{n}$ = calculated ^1H chemical shift of Me groups (average if different) on annelated DDP, $\delta calc(\mathbf{1})$ = calculated ^1H chemical shift of Me groups on **1** (−4.25 ppm), RA_{NICS} = NICS relative aromaticity of the DDPN of DDP **n** (compared to **1**), NICS **9** = NICS Av for **9** (0.07), NICS **n** = NICS Av for **n**, and NICS **1** = NICS Av for **1** (−18.65).

The absolute magnitudes of RA_{expt}, $RA_{\delta calc}$, and RA_{NICS} diverge somewhat (Tables 3 and 9); however most importantly, the relative ordering of aromaticities is identical.

The RAs (Table 3), whether determined from experimental chemical shifts or calculated parameters, are in remarkable agreement with the order of aromaticity for **5**−**8**. However, even though there is little difference between the chemical shifts and NICS values for **3** and **4** and those for **1** and **6**, the RA of **4** is less than that of **7**, while the DDPN of **6** is more aromatic than that of **7**. The discrepancy between the RAs of the parent and

Table 7. NICS Values for Compounds **10**−**17**

point	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
1	−18.02	−17.73	−3.60	−2.18	−1.28	−1.49	−0.46	−0.83
2	−16.56	−16.05	−3.97	−3.82	−2.78	−2.09	−2.47	−1.67
3	−16.56	−16.05	−2.80	−2.43	−1.53	−3.49	−0.89	−0.23
4	−18.02	−17.73	−3.60	−2.18	−1.28	−1.40	−0.46	−0.83
Av[a]	−17.29	−16.89	−3.50	−2.65	−1.72	−2.12	−1.07	−0.89
5	−9.12	−9.10	−10.98	−12.51	−12.11	−12.07	−11.27	−10.81
6	−9.12	−9.10		−10.38	−10.39	−10.79	−14.21	−14.11
7							−8.95	−9.01
8			−3.60					
9			−2.80					
10			−3.97					
11			−3.60					

[a] Average value of points *1*−*4*.

Table 8. Relative Aromaticities of the Dimethyldihydropyrene Nuclei (RAs) of **10**, **13**, **15**, and **16**

	RA_{expt} (%)	$RA_{\delta calc}$ (%)	RA_{NICS} (%)[a]
10		97.8	92.7
13	28.0	21.8	14.5
15	27.0	17.3	11.7
16		13.4	6.1

[a] Relative aromaticity (%) calculated using NICS Av − the average of NICS points *1*−*4*.

Table 9. Relative Aromaticities of the Dimethyldihydropyrene Nuclei (RAs) of **3**, **4**, **11**, **12**, **14**, and **17**

	RA_{expt} (%)	$RA_{\delta calc}$ (%)	RA_{NICS} (%)[a]
3	96.0	98.1	98.1
11	83.9	96.1	90.6
4	48.9	32.1	25.2
12	39.1[b]	23.1	19.07
14	28.9	17.3	9.6
17	18.6	10.1	5.1

[a] Relative aromaticity (%) calculated using NICS Av − the average of NICS points *1*−*4*. [b] Based on the single broad resonance observed for the isomeric mixture containing **12**.

^{t}Bu-substituted DDP urges caution in extrapolation to even seemingly closely related systems.

Bond Alternation. Another well-recognized experimental discriminator for aromaticity is the geometry of the cyclically conjugated molecule. Bond equalization is equated with aromaticity, and in general, the more nearly equal the bond lengths around the conjugated system, the more aromatic the molecule. For example, the Julg parameter, a measure of the deviation of the peripheral bond lengths from equality, and HOMA have been used to establish scales of aromaticity.[16,30] Similarly, we have correlated calculated bond orders (as a measure of bond equalization/alternation) with the chemical shifts (as a measure of diatropicity) of the internal methyl groups of a series of annelated DDPs in the construction of a scale of aromaticity of their DDPNs.[13,14] Mitchell and Siegel et al. defined a parameter, $\Delta\Sigma = \Sigma a - \Sigma b$ where Σa is the average length of the "a" type bonds and Σb is the average length of the "b" type bonds, which serves as a measure of bond localization in the DDPNs.[22] The greater the absolute magnitude of ΔΣ, the greater the bond localization (alternation) and the less aromatic the particular DDPN. The order of aromaticity of the DDPNs using ΔΣ values is **1** = **5** > **6** > **7** > **8**. This ordering is almost identical to the experimental and our $RA_{\delta calc}$ and NICS orders. Using ΔΣ, the DDPNs of **1** and **5** are classified as being equally aromatic, which is virtually the case experimentally and by $RA_{\delta calc}$ and NICS. Restricting the bonds considered in **9** to the conjugated pentatrienyl system (shown) still results in very large ΔΣ, indicating significant bond alternation and further confirming the complete lack of aromaticity of our model compound.

Chemical Shifts. Calculated chemical shifts provide another means of comparing theory with experiment. Excellent agreement between the experimental and calculated values is good evidence that the calculated geometry is accurate. The absolute shieldings for **1** and **3**−**9** were calculated using four methods—GIAO-HF/6-31G*//B3LYP/6-31G*, GIAO-B3LYP/6-31G*//B3LYP/6-31G*, CSGT-HF/6-31G*//B3LYP/6-31G*, and CSGT-B3LYP/6-31G*//B3LYP/6-31G*—employing Gaussian 94.[29] We determined the predicted ^{13}C and ^{1}H chemical shifts directly using eq 4 and also from Forsyth's procedure (eq 5) to scale the GIAO-B3LYP/6-31G*//B3LYP/6-31G* ^{13}C absolute shieldings to yield predicted ^{13}C chemical shifts.[31]

$$\delta\text{calc} = \sigma_{\text{TMS}} - \sigma \tag{4}$$

$$\delta\text{calc}\ (^{13}\text{C}) = -1.084\sigma + 203.1 \tag{5}$$

where δcalc = predicted chemical shift, σ_{TMS} = absolute shielding for TMS, and σ = absolute shielding of nucleus under consideration.

Careful examination of our complete series of calculated chemical shifts indicates, not surprisingly,[31] that the scaled ^{13}C shifts give the best agreement with the experimental data (generally within ±3 ppm) and that the GIAO-HF/6-31G*//B3LYP/6-31G* method is the most reliable for ^{1}H shifts (within ±1.7 ppm of experimental values except for the internal Me groups of **1**, **3**, and **5**). Consequently, in Tables 4 and 5 we present only these results and, for comparison, the experimental chemical shifts for **1** and **3**−**9**. The remaining chemical shift data are available in the Supporting Information. All methods provided predicted chemical shifts that are in very good agreement with the experimental values. As the calculated results are for a single conformation of each compound, we averaged the predicted chemical shifts for the symmetry-related ^{1}H's and ^{13}C's made equivalent by rotation of the Me and/or ^{t}Bu groups.

Having established the viability of the B3LYP/6-31G* method for modeling DDPs and NICS, $RA_{\delta calc}$, and the alternation parameter (ΔΣ) for ordering the relative aromaticities of the DDPNs, we next used these techniques to study the DDPs **10**−**17** (Chart 2). Some of these compounds had not been synthesized at the beginning of this study, and others still await preparation. The annelated DDPs **11**,[37] **13**,[14] **14**,[32] **15**,[14] and **17**[32] have all been prepared, and **12** has been made as a component of a mixture of stereoisomers but has not been isolated in a pure state.[38]

Selected bond lengths, NICS values, RAs, ^{13}C chemical shifts, and ^{1}H chemical shifts are reported for DDPs **10**−**17** in Tables

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Table 10. Calculated and Experimental ^{13}C Chemical Shifts for Compounds **10**−**17**

	10	**11**	**12**	**13**		**14**		**15**		**16**	**17**	
	δcalc[a]	δcalc[a]	δcalc[a]	δcalc[a]	δexpt[b]	δcalc[a]	δexpt[c]	δcalc[a]	δexpt[b]	δcalc[a]	δcalc[a]	δexpt[c]
C1	124.05	146.44	148.01	126.14	124.2	148.02	144.6*	131.24	129.6	126.70	148.43	144.8
C2	120.32	118.72	120.61	120.36	118.4	120.89	117.6*	129.39	126.1	120.83	121.68	117.9*
C3	135.32	131.05	139.93	140.08	136.8	139.91	139.2*	137.96	134.1	141.18	141.00	136.19
C4	130.59	130.61	129.61	130.68	129.2	131.21	128.7	121.09	117.5	131.22	131.86	129.9
C5	130.59	130.61	129.61	130.68	129.2	131.21	128.7	124.88	121.1	131.22	131.86	129.9
C6	135.32	131.05	139.93	140.08	136.8	139.91	139.2*	143.52	141.0	141.18	141.00	136.19
C7	120.32	118.72	120.61	120.36	118.4	120.89	117.6*	127.97	125.8	120.83	121.68	117.9*
C8	124.05	146.44	148.01	126.14	124.2	148.02	144.6*	127.31	125.6	126.70	148.43	144.8
C9	120.32	118.72	123.25	128.23	127.0	123.57	119.9*	125.49	121.1	128.77	123.96	120.1*
C10	135.32	131.05	140.86	141.21	140.3	141.46	135.7*	142.64	139.9	142.27	142.33	139.7
C11	130.59	130.61	125.65	125.99	123.0	125.72	121.1*	129.40	126.2	126.30	125.94	121.2*
C12	130.59	130.61	125.65	125.99	123.0	125.72	121.1*	130.26	127.8	126.30	125.94	121.2*
C13	135.32	131.05	140.86	141.21	140.3	141.46	135.7*	140.69	138.3	142.27	142.33	139.7
C14	120.32	118.72	123.25	128.23	127.0	123.57	119.9*	128.51	126.9	128.77	123.96	120.1*
C15	31.66	30.99	38.79	39.48	38.8	39.82	37.7	39.71	38.0	41.61	41.79	38.9
C16	31.66	30.99	38.79	39.48	38.8	39.82	37.7	40.67	38.9	41.61	41.79	38.9
C17	10.26	68.76	17.68	17.33	19.2	18.13	19.2*	17.26	18.6	19.04	19.82	20.2*
C18	10.26	68.76	17.68	17.33	19.2	18.13	19.2*	18.11	19.5	19.04	19.82	20.2*
C19	127.11	127.08	123.07	126.05	123.8	125.82	122.6*	129.75	127.4	126.24	125.93	122.5*
C20	125.56	125.21	123.07	131.53	132.6	131.77	131.4	132.83	132.5	129.84	130.16	129.0
C21	125.56	125.21	148.01	130.22	128.6	130.17	127.7*	129.67	126.9	129.33	129.23	125.8*
C22	127.11	127.08	120.61	126.92	126.4	126.82	125.6*	126.91	124.3	132.51	132.56	131.6
C23	127.11	127.08	139.93	126.92	126.4	126.82	125.6*	126.68	124.2	130.74	130.74	128.3*
C24	125.56	125.21	129.61	130.22	128.6	130.17	127.7*	130.47	128.1	126.71	126.64	125.1*
C25	125.56	125.21	129.61	131.53	132.6	131.77	131.4	132.44	132.0	126.71	126.64	125.1*
C26	127.11	127.08	139.93	126.05	123.8	125.82	122.6*	125.34	122.1	130.74	130.74	128.3*
C27		40.23	120.61			38.53	35.1			132.51	132.56	131.6
C28		32.91	148.01			30.59	30.2*			129.33	129.23	125.8*
C29		32.91	123.25			30.59	30.2*			129.84	130.16	129.0
C30		32.91	140.86			30.59	30.2*			126.24	125.93	122.5*
C31		40.23	125.65			38.53	35.1				38.29	35.0
C32		32.91	125.65			30.59	30.2*				30.23	30.0*
C33		32.91	140.86			30.59	30.2*				30.23	30.0*
C34		32.91	123.25			30.59	30.2*				30.23	30.0*
C35			38.79								38.29	35.0
C36			38.79								30.23	30.0*
C37			17.68								30.23	30.0*
C38			17.68								30.23	30.0*
C39			38.88									
C40			31.01									
C41			31.01									
C42			31.01									
C43			38.88									
C44			31.01									
C45			31.01									
C46			31.01									
C47			38.88									
C48			31.01									
C49			31.01									
C50			31.01									
C51			38.88									
C52			31.01									
C53			31.01									
C54			31.01									

[a] Empirically scaled ^{13}C chemical shifts from the GIAO-B3LYP/6-31G*//B3LYP/6-31G* absolute shieldings.[31] [b] Reported in ref 14, no resonances were specifically assigned in the cited work, and here the signals are assigned by best fit to the calculated data. Of the expected 26 resonances for compound **15**, only 24 signals are reported in ref 14. The signals at 126.9 and 122.1 are of higher intensity and are thus assigned to C14 and C21 and to C5 and C9, respectively. [c] Reported in ref 32, only the resonances marked * were specifically assigned in the cited work, and here the remaining signals are assigned by best fit to the calculated data.

6−11. Again, where comparison is possible, agreement between experimental values and the corresponding calculated data is impressive. The relative order of aromaticity for the DDPNs lacking ^{t}Bu substituents is **10** ≫ **13** > **15** > **16**, and that for those DDPNs with ^{t}Bu substituents **3** > **11** ≫ **4** > **12** > **14** > **17**. Just as for **1** and **5**−**8**, the NICS Av, RA$_{\delta\text{calc}}$, and RA$_{\text{NICS}}$ are consistent among themselves and agree with the experimental ordering of aromaticity based on ^{1}H chemical shifts of the known compounds. NICS points *5*−*7* illustrate the correct general trend of increasing aromaticity in the annelating rings going from benz- to naphth- to anthannelated as the aromaticity of the corresponding DDPNs decreases for **10**−**17**,[14] although a quantitative NICS comparison of these different ring systems is, of course, not feasible.

The alternation parameter $\Delta\Sigma$ indicates that the DDPNs of **3**, **10**, and **11** as well as **1** and **5** are completely delocalized ($\Delta\Sigma = 0$) and hence equally aromatic. For the remaining compounds $\Delta\Sigma$ exactly reproduces the order of aromaticity for

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Table 11. Calculated and Experimental ^{1}H Chemical Shifts for Compounds **10**−**17**

	10	**11**		**12**	**13**		**14**		**15**		**16**	**17**	
	δcalc[a]	δcalc[a]	δexpt[b]	δcalc[a]	δcalc[a]	δexpt[c]	δcalc[a]	δexpt[d]	δcalc[a]	δexpt[c]	δcalc[a]	δcalc[a]	δexpt[d]
H1	9.23				6.91	6.70					6.71		
H2	10.65	10.67	9.45	7.24	7.94	7.73	7.92	8.01			7.77	7.78	7.85
H3													
H4									7.72	7.69			
H5									6.74	6.81			
H6													
H7	10.65	10.67	9.45	7.24	7.94	7.73	7.92	8.01	7.12	6.97	7.77	7.78	7.85
H8	9.23				6.91	6.70			6.66	6.66	6.71		
H9	10.65	10.67	9.45	7.35	7.24	7.03	6.90	6.90	6.63	6.77	6.99	6.68	6.68
H10													
H11				7.61	6.70	6.72	6.47	6.66	7.21	7.18?	6.43	6.24	6.43
H12				7.61	6.70	6.72	6.47	6.66	7.30	7.07?	6.43	6.24	6.43
H13													
H14	10.65	10.67	9.45	7.35	7.24	7.03	6.90	6.90	7.46		6.99	6.68	6.68
H15													
H16													
H17	−6.14	−6.01	−3.41	−0.62	−0.52	−0.49	−0.19	−0.54	−0.19	−0.44	0.10	0.34	0.00
H18	−6.14	−6.01	−3.41	−0.62	−0.52	−0.49	−0.19	−0.54	−0.19	−0.44	0.10	0.34	0.00
H19	10.27	10.25	9.37	10.12	9.35	8.94	9.27	9.01	8.27	8.19	9.47	9.38	9.08
H20	8.24	8.20	7.59	10.12									
H21	8.24	8.20	7.59		8.36	7.96	8.35	8.08	8.27	8.03	8.97	8.95	8.68
H22	10.27	10.25	9.37	7.24	7.86	7.41	7.85	7.53	7.84	7.54			
H23	10.27	10.25	9.37		7.86	7.41	7.85	7.53	7.82	7.54	8.42	8.42	8.07
H24	8.24	8.20	7.59		8.36	7.96	8.35	8.08	8.34	8.03	7.75	7.76	7.46
H25	8.24	8.20	7.59								7.75	7.76	7.46
H26	10.27	10.25	9.37		9.35	8.94	9.27	9.01	9.19	8.90	8.42	8.42	8.07
H27				7.24									
H28		2.15	1.79				1.49	1.44			8.97	8.95	8.68
H29		2.15	1.79	7.35			1.49	1.44					
H30		2.15	1.79				1.49	1.44			9.47	9.38	9.08
H31				7.61									
H32		2.15	1.79	7.61			1.49	1.44				1.46	1.41
H33		2.15	1.79				1.49	1.44				1.46	1.41
H34		2.15	1.79	7.35			1.49	1.44				1.46	1.41
H35													
H36												1.46	1.41
H37				−0.62								1.46	1.41
H38				−0.62								1.46	1.41
H39													
H40				1.59									
H41				1.59									
H42				1.59									
H43													
H44				1.59									
H45				1.59									
H46				1.59									
H47													
H48				1.59									
H49				1.59									
H50				1.59									
H51													
H52				1.59									
H53				1.59									
H54				1.59									

[a] Calculated ^{1}H chemical shifts from the GIAO-HF/6-31G*//B3LYP/6-31G* absolute shieldings. [b] Reported in ref 37. [c] Reported in ref 14. [d] Reported in ref 32.

the DDPNs of both the protio and ^{t}Bu series:

$$\mathbf{10} > \mathbf{13} > \mathbf{15} > \mathbf{16} \text{ (from } \Delta\Sigma)$$

$$\mathbf{3} = \mathbf{11} > \mathbf{4} > \mathbf{12} > \mathbf{14} > \mathbf{17} \text{ (from } \Delta\Sigma)$$

Once again the agreement between our calculated and experimental ^{13}C and ^{1}H chemical shifts is excellent. The fit is so good that we feel confident in assigning the broad resonance at δ −1.07, picked out from a noisy spectrum of the mixture of stereoisomers including **12**, to the internal methyl groups of **12**. As is obvious from the foregoing, $\mathrm{RA}_{\delta\mathrm{calc}}$ closely mimics the experimental orders of aromaticity for the DDPNs of **3**, **4**, and **10**−**17**.

Conclusions

We have shown that there is a direct correlation between a NICS and an experimental scale of aromaticity. Thus, not only can the NICS now be confidently used to identify the presence of aromaticity, but also (provided that the comparison system is chosen carefully) the NICS values themselves can be used to construct a scale of aromaticity. As there is a large body of experimental data available and an established procedure for experimentally ordering the aromaticity of the DDPNs, we chose the DDPs as our comparison system. The average of the NICS values at points *1*−*4* reliably orders the aromaticity of the DDPNs of each of these compounds in complete agreement with

Table 12. Crystal Data and Structure Refinement for **3** and **4**

	3	**4**
empirical formula	$C_{26}H_{32}$	$C_{30}H_{34}$
fw	344.52	394.57
λ (Å)	0.71073	0.71073
cryst syst; space group	monoclinic, *C*2/*c*	orthorhombic, *Pbca*
color, habit	green needle	red block
cryst dim, mm	0.26 × 0.10 × 0.06	0.24 × 0.22 × 0.15
T (K)	203(2)	203(2)
a (Å)	14.3791(11)	12.701(9)
b (Å)	11.7604(9)	9.567(7)
c (Å)	11.7230(9)	38.07(3)
β (deg)	91.02(2)	
V (Å^3)	1982.1(3)	4627(6)
Z	4	8
D_{calc} (Mg m^{-3})	1.155	1.133
μ (mm^{-1})	0.064	0.063
index ranges	$-17 \le h \le 16$; $-13 \le k \le 13$, $-13 \le l \le 13$	$-15 \le h \le 9$, $-11 \le k \le 11$, $-44 \le l \le 45$
no. of reflns collected	7290	23 710
no. of ind reflns	1738 [R(int) = 0.0326]	3942 [R(int) = 0.1584]
no. of data/restraints/ params	1738/0/122	3942/0/279
GOF	1.016	1.023
largest diff peak and hole (e Å^{-3})	0.205/−0.162	0.263/−0.151
final *R* indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0419$, $wR_2 = 0.1007$	$R_1 = 0.0629$, $wR_2 = 0.1383$
R indices (all data)^a	$R_1 = 0.0637$, $wR_2 = 0.1124$	$R_1 = 0.1340$, $wR_2 = 0.1657$

^{a} $R = \sum|F_o| - |F_c|/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

experiment. As Katritzky et al. pointed out,[2] NICS as a discriminator for aromaticity is only quantitatively effective within related sets of compounds which are not affected by other perturbing influences. In this study we have shown that even symmetrically disubstituting the DDPN with ^{t}Bu groups leads to a sufficient perturbation of the NICS values (and the experimental relative aromaticities) so as to render direct extrapolation to the unsubstituted analogues invalid. However, by keeping the probe or comparison system identical, as we have done here by using either DDP **1** or di-^{t}Bu-DDP (**3**), then evaluation of a wide range of different moieties is possible. It is obvious that the "*benzene*" for each series of compounds studied must be identified and its NICS value used as the indicator of maximum possible aromaticity for assessing the relative aromaticities of the remaining members of the series.

The B3LYP/6-31G* method is excellent for modeling DDPs, providing geometries in close agreement with X-ray structures. Using these geometries with the B3LYP- and HF-GIAO methods provides extremely reliable ^{13}C and ^{1}H chemical shifts. Certainly these methods can be used to confidently predict geometries and chemical shifts for unknown DDPs and even aid in the assignment of individual resonances to the appropriate nucleus.

In this paper, by confining our investigations to the DDPNs of a wide range of DDPs, we have determined that there is an excellent correlation between a NICS scale of aromaticity and the already established *experimental* scale for these DDPNs. We made no attempt to probe the *global* aromaticities of the DDPs. Indeed, examination of the relative energies (Supporting Information) for the isomeric pairs **5/8** and **6/7** suggests that the *global* DDP aromaticity order is **8** > **5** and **7** > **6**, the exact reverse of our *local* DDPN scale. We plan to address the issue of the global DDP aromaticities in future work.

Experimental Section

X-ray Crystallographic Studies. Crystals of compounds **3** and **4** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[39] Data for **3** and **4** were collected near 203(2) K using a Siemens SMART 1K instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Siemens LT-2A low-temperature device. The SHELXTL v. 5.10 program package was used for structure solution and refinement.[40] An absorption correction was applied to **3** and **4** using SADABS.[41] The structures were solved by direct methods and refined by full matrix least squares procedures. All non-hydrogen atoms were refined anisotropically. Details of the data collection and refinement are given in Table 12. Further details are provided in the Supporting Information.

Notes Added in Revision. While this paper was in the review process an interesting paper appeared (Schleyer, P. v. R.; Puhlhofer, F. *Org. Lett.* **2002**, *4*, 2876) with recommendations for the evaluation of aromatic stabilization energies (ASEs). This paper presents an excellent overview of the problems previously associated with ASEs and suggests solutions for these problems.

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Supporting Information Available: Tables of NICS values at additional points for **1** and **3**−**17** (Tables S1 and S2), ^{13}C chemical shifts of **1** and **3**−**17** calculated using the GIAO-HF/6-31G*//B3LYP/6-31G*, GIAO-B3LYP/6-31G*//B3LYP/6-31G*, CSGT-HF/6-31G*//B3LYP/6-31G*, and CSGT-B3LYP/6-31G*//B3LYP/6-31G* methods (Tables S3−S8), of ^{1}H chemical shifts of **1** and **3**−**17** calculated using the GIAO-B3LYP/6-31G*//B3LYP/6-31G*, CSGT-HF/6-31G*//B3LYP/6-31G* and CSGT-B3LYP/6-31G*//B3LYP/6-31G* methods (Tables S9−S14), of ^{13}C and ^{1}H absolute shieldings of tetramethylsilane calculated using the GIAO-HF/6-31G*//B3LYP/6-31G*, GIAO-B3LYP/6-31G*//B3LYP/6-31G*, CSGT-HF/6-31G*//B3LYP/6-31G*, and CSGT-B3LYP/6-31G*//B3LYP/6-31G* methods (Table S15), of the Cartesian coordinates of **1** and **3**−**17** optimized using the B3LYP/6-31G* method (Tables S16−S31), and of total energies and zero-point corrections for **1** and **3**−**17** (Table S32). X-ray crystallographic data; files for **3** and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Sheldrick, G. M. *SADABS*: an empirical absorption correction program; Bruker AXS Inc.: Madison, WI, 1999.