



# The influence of aza-substitution on azole aromaticity

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## ABSTRACT

A homogeneous set of values for the aromaticity indices ASE (Aromatic Stabilisation Energy), HOMA (Harmonic Oscillator Model of Aromaticity) and NICS(1) (Nucleus-Independent Chemical Shift) for azoles has been investigated using multiple linear regression analysis. Statistically-significant relationships were found between the aromaticity indices and the number of nitrogen atoms at positions 2/5 and 3/4 of the ring. Aza-derivatives of pyrrole, furan and thiophene all gave similar relationships. For all three indices aza-substitution at positions 2 and/or 5 increases aromaticity. However, aza-substitution at positions 3 and/or 4 decreases classical aromaticity (ASE and HOMA) but increases magnetic aromaticity (NICS(1)). These indices appear to be measuring different properties of the azoles. The influence of aza-substitution on these different aspects of aromaticity is tentatively rationalized in terms of either bond length equalization or uniformity of  $\pi$  electron distribution.

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## 1. Introduction

Although the concept of aromaticity is central to the practice of carbocyclic and heterocyclic chemistry, there is no universally-accepted quantitative measure of aromaticity.<sup>1,2</sup> A number of useful indices of aromaticity have been developed and these enable the relative aromaticities of structures to be discussed quantitatively.<sup>3–6</sup> Although these indices readily discriminate between aromatic, non-aromatic and antiaromatic molecules, sometimes there is poor correlation between energetic, structural and magnetic aromaticity indices for groups of closely related aromatic compounds.<sup>7</sup> Aromaticity can be regarded as being statistically multidimensional.<sup>8</sup> A principal component analysis has provided evidence that there are at least two orthogonal types of aromaticity that have been described as ‘classical’ and ‘magnetic’.<sup>9,10</sup> Nevertheless, there are common trends in the aromaticity of families of molecules and, although a large number of aromaticity index values have now been reported, some general trends in the relationship between structure and aromaticity have not been fully explained. In this paper we demonstrate correlations between the position of aza-substitution of azoles and their aromaticity indices.

For this analysis the following well-established indices have been used: (i) aromatic stabilisation energy (ASE) (an energetic index); (ii) harmonic oscillator model of aromaticity (HOMA) (a structural index); (iii) nucleus-independent chemical shift (NICS(1)) (a magnetic index). Values for ASE, HOMA and NICS(1)

were taken from Ref. 7, which provides a large database with values all derived in the same way. HOMA values are not available for molecules with S–N bonds. ASE values are not available for tetraaza derivatives.

## 2. Results and discussion

It is generally recognised that sequential aza-substitution of benzene results in only small changes to the aromaticity of the ring and indices generally agree that aromaticity is reduced.<sup>5</sup> This small effect of aza-substitution is in agreement with a PMO model of azine aromaticity.<sup>11</sup> In contrast, aza-substitution of pyrrole, furan and thiophene results not only in increases in aromaticity but also in greater variations depending upon the degree and position(s) of substitution. The values of aromaticity indices for a range of azoles are shown in Table 1.

Inspection of Table 1 reveals that complete aza-substitution of pyrazole, furan and thiophene results in a significant increase in aromaticity (entries 1 & 2, 11 & 12, and 21 & 22). All three indices suggest that pyrazole is more aromatic than imidazole (entries 3 and 4). This implies that a nitrogen atom at position 2 makes a greater contribution to aromaticity than a nitrogen atom at position 3. This qualitative observation can be generalised to all the molecules in Table 1, where  $N_{2,5}$  is the number of nitrogen atoms at position 2 and/or 5 (i.e., 0, 1 or 2). A comparison of all the isomeric pairs (entries 3–10, 13–20, and 23–30) suggests the generalisation that the isomer with the greatest number of nitrogen atoms at positions 2 and 5 is the most aromatic of the pair. This qualitative observation raises three questions. (i) Can the relative contributions to aromaticity by nitrogen atoms at different positions of the ring

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**Table 1**  
Aromaticity indices for azoles<sup>a</sup>

Entry		$N_{2,5}$	ASE	HOMA	NICS(1)	Entry		$N_{2,5}$	ASE	HOMA	NICS(1)
1		0	20.57	0.876	-10.60	2		2	—	0.950	-16.59
3		1	23.70	0.926	-11.93	4		0	18.78	0.908	-10.83
5		1	24.37	0.931	-13.51	6		2	26.66	0.960	-13.61
7		1	21.33	0.940	-11.84	8		0	14.96	0.823	-11.52
9		1	18.26	0.897	-14.12	10		2	26.49	0.960	-14.64
11		0	14.77	0.298	-9.36	12		2	—	0.500	-15.34
13		1	17.29	0.527	-10.58	14		0	12.37	0.332	-9.45
15		1	17.20	0.443	-11.99	16		2	20.19	0.677	-12.52
17		1	14.23	0.553	-10.40	18		0	7.78	0.243	-10.00
19		1	9.65	0.413	-12.29	20		2	18.71	0.586	-13.84
21		0	18.57	0.891	-10.79	22		2	—	—	-17.48
23		1	20.18	—	-11.66	24		0	17.43	0.905	-11.37
25		1	20.48	—	-13.72	26		2	22.67	—	-12.96
27		1	18.28	—	-11.96	28		0	13.69	0.849	-12.34
29		1	14.72	—	-14.65	30		2	21.62	—	-14.96

<sup>a</sup> All values of ASE, HOMA and NICS(1) taken from Ref. 7.

be quantified? (ii) Why is there a positional dependence of the contribution to aromaticity by nitrogen atoms? (iii) Is the contribution of a nitrogen atom the same for classical and magnetic aromaticity?

In the context of the last question, the analysis below suggests that there is a difference in the contribution of nitrogen to classical aromaticity (ASE, HOMA) and magnetic aromaticity (NICS(1)) and the following discussion is sub-divided accordingly.

## 2.1. Classical aromaticity of azoles

**2.1.1. Aromatic stabilisation energy (ASE).** The ASE is a measure of stability relative to localised bond structures and is a measure of aromaticity similar to that provided by the resonance energy.<sup>7,12</sup> For

pyrrole and the azapyrroles in Table 1 (entries 1, 3–10), multiple regression analysis<sup>13</sup> gives Eq. 1, which shows a statistically-significant relationship between ASE and the number of nitrogen atoms at position 2 and/or 5 ( $N_{2,5}$ ) and position 3 and/or 4 ( $N_{3,4}$ ). In particular nitrogen atoms at positions 2 and 5 increase aromaticity and nitrogen atoms at positions 3 and 4 decrease aromaticity. A similar analysis of furan and the oxazoles (Eq. 2) and thiophene and the thiazoles (Eq. 3) gives similar, statistically-significant results suggesting that the influence of nitrogen is essentially the same in all the heterocycles. Combination of the three sets of data gives the relationship shown in Eq. 4, in which [O] and [S] are dummy variables (0 or 1) that allow for the different aromaticities of the parent systems. This effect of nitrogen at positions 2 and 5 is consistent with the rule that aromaticity increases with the

decrease in electronegativity difference between a heteroatom and its neighbouring atoms.<sup>6,14</sup>

*pyrrole and azapyrroles :*

$$ASE = 20.62(\pm 1.02) + 3.64(\pm 0.65)N_{2,5} - 2.45(\pm 0.65)N_{3,4},$$

$$n = 9, r = 0.952, s = 1.407, F = 28.79, p < 0.001 \quad (1)$$

*furan and oxazoles :*

$$ASE = 15.03(\pm 1.05) + 3.04(\pm 0.67)N_{2,5} - 3.43(\pm 0.67)N_{3,4},$$

$$n = 9, r = 0.954, s = 1.442, F = 30.22, p < 0.001 \quad (2)$$

*thiophene and thiazoles :*

$$ASE = 18.90(\pm 0.87) + 2.15(\pm 0.56)N_{2,5} - 2.45(\pm 0.56)N_{3,4},$$

$$n = 9, r = 0.938, s = 1.200, F = 22.12, p = 0.002 \quad (3)$$

*all azoles :*

$$ASE = 21.53(\pm 0.69) + 2.94(\pm 0.37)N_{2,5} - 2.78(\pm 0.37)N_{3,4}$$

$$- 7.00(\pm 0.65)[O] - 3.05(\pm 0.65)[S],$$

$$n = 27, r = 0.962, s = 1.379,$$

$$F = 67.84, p = 0.0001 \quad (4)$$

**2.1.2. Harmonic oscillator model of aromaticity (HOMA).** The HOMA parameter is a geometry-based index of aromaticity.<sup>4,15–18</sup> Like ASE and resonance energy, HOMA can be regarded as a measure of classical aromaticity and we have found similar and significant relationships between HOMA values and the positions and number of ring nitrogen atoms. Eq. 5 shows the relationship for pyrrole and its aza derivatives. Again, nitrogens at positions 2 and 5 make a positive contribution to aromaticity and nitrogens at positions 3 and 4 make a negative contribution. A similar relationship is found for furan and the oxazoles (Eq. 6). Insufficient HOMA values for thiazoles are available for regression analysis. Eq. 7 shows the correlation for the combined azoles.

*pyrrole and azapyrroles :*

$$HOMA = 0.889(\pm 0.015) + 0.044(\pm 0.009)N_{2,5}$$

$$- 0.015(\pm 0.009)N_{3,4},$$

$$n = 10, r = 0.883, s = 0.023,$$

$$F = 12.40, p = 0.005 \quad (5)$$

*furan and oxazoles :*

$$HOMA = 0.367(\pm 0.033) + 0.148(\pm 0.021)N_{2,5}$$

$$- 0.058(\pm 0.021)N_{3,4},$$

$$n = 10, r = 0.946, s = 0.051,$$

$$F = 29.76, p = 0.0004 \quad (6)$$

*combined azoles :*

$$HOMA = 0.858(\pm 0.032) + 0.096(\pm 0.018)N_{2,5}$$

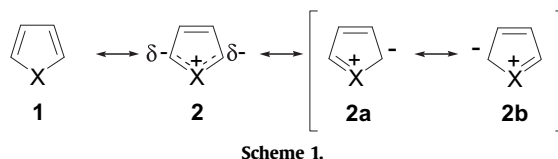
$$- 0.037(\pm 0.018)N_{3,4} - 0.460(\pm 0.027)[O],$$

$$n = 20, r = 0.976, s = 0.061,$$

$$F = 105.87, p = 0.0001 \quad (7)$$

**2.1.3. Resonance structures and classical aromaticity.** The different contributions of ring nitrogens to classical aromaticity implicit in Eqs. 1–7 can be rationalised in terms of their influence on bond equalisation. Consider the resonance hybrids shown in Scheme 1. There will be a greater contribution of the form 2 (which is a hybrid of 2a and 2b) if a nitrogen atom is at position 2 and/or 5 because these will stabilise negative charge at these positions. The ‘1,3-dipole’ resonance form 2 has opposite bond orders to the Kekulé structure 1, i.e., double bonds in 1 are single bonds in 2 and vice versa. The greater the contribution of resonance form 2 then the more bond equalisation in the overall structure, and this can be equated to greater classical aromaticity. Based on this analysis, the

2,5-diaza-heterocycles can be expected to have shorter bonds between the ring atoms at positions 3 and 4 due to greater double bond character at that position. Based on the data shown in Table 2, this appears to be the case.



Scheme 1.

**Table 2**  
The effect of aza-substitution on bond length

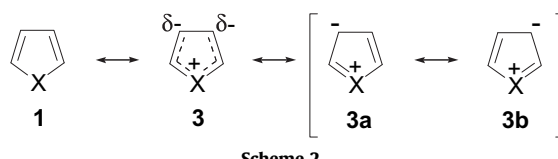
X	Bond lengths (r) (Å) <sup>a</sup>		Δr
O	1.430	1.421	0.009
NH	1.417	1.405 <sup>b</sup>	0.012
S	1.423	1.417	0.006
O	(1.384) <sup>c</sup>	(1.372)	0.012
NH	(1.365)	(1.326)	0.039
S	—	—	—

<sup>a</sup> Unless otherwise stated, bond lengths (microwave spectroscopy) are taken from Ref. 19.

<sup>b</sup> Ref. 20.

<sup>c</sup> Values in parentheses are calculated values taken from Ref. 21.

A similar analysis of aza-substitution at positions 3 and 4 (Scheme 2) implies that even with a greater contribution of the form 3 there will be (i) no increase in double bond character between atoms 3 and 4 and (ii) reinforcement of the double bonds in the Kekulé structure 1. These factors may account for the adverse contribution of nitrogen atoms at these positions to classical aromaticity.



Scheme 2.

## 2.2. Magnetic aromaticity of azoles

**2.2.1. Nucleus-independent chemical shift (NICS).** NICS values are the negative of the absolute magnetic shielding and can be calculated at the centre or above rings.<sup>2</sup> NICS(1) values are calculated 1 Å above the centre of the ring and are considered to be good measures of π-electron magnetic effects and aromaticity.<sup>22</sup> Rings with negative NICS values are aromatic.

Using the data in Table 1, statistically-significant relationships between NICS(1) values and the position and number of ring nitrogen atoms have been established. Eqs. 8, 9 and 10 show the relationships for the azapyrroles, oxazole and thiazoles, respectively. For each subset the relationships are similar. Eq. 11 shows the relationship for the combined sets.

*pyrrole and azapyrroles :*

$$NICS(1) = -9.92(\pm 0.42) - 1.98(\pm 0.26)N_{2,5}$$

$$- 1.02(\pm 0.26)N_{3,4},$$

$$n = 10, r = 0.956, s = 0.633,$$

$$F = 37.11, p = 0.0002 \quad (8)$$

furan and oxazoles :

$$\begin{aligned} \text{NICS}(1) &= -8.57(\pm 0.43) - 2.15(\pm 0.27)N_{2,5} \\ &\quad - 0.86(\pm 0.27)N_{3,4}, \\ n &= 10, r = 0.956, s = 0.656, \\ F &= 37.40, p = 0.0002 \end{aligned} \quad (9)$$

thiophene and thiazoles :

$$\begin{aligned} \text{NICS}(1) &= -9.86(\pm 0.51) - 1.82(\pm 0.32)N_{2,5} \\ &\quad - 1.51(\pm 0.32)N_{3,4}, \\ n &= 10, r = 0.943, s = 0.772, \\ F &= 28.11, p = 0.0005 \end{aligned} \quad (10)$$

all azoles :

$$\begin{aligned} \text{NICS}(1) &= -9.81(\pm 0.31) - 1.98(\pm 0.16)N_{2,5} \\ &\quad - 1.13(\pm 0.16)N_{3,4} + 1.34(\pm 0.31)[O] \\ &\quad - 0.27(\pm 0.31)[S], \\ n &= 30, r = 0.950, s = 0.684, \\ F &= 58.05, p = 0.00001 \end{aligned} \quad (11)$$

In contrast to the relationships for ASE and HOMA (Eqs. 1–7), the NICS(1) relationships (Eqs. 8–11) show that all ring nitrogens make a positive contribution to increasing the aromaticity of the ring. The nitrogens at positions 2 and 5 make the biggest contribution but those at positions 3 and 4 also make a significant contribution. The contribution of nitrogen at positions 3 and 4 to aromaticity measured by NICS(1) is opposite to that measured by ASE and HOMA. Figure 1 illustrates the difference between the aromaticity index/aza-substitution profiles for pyrrole and the azapyrroles. The values for  $N_{2,5}=N_{3,4}=1$  are the average for entries 5 and 7 (Table 1). The ASE value for pentazole (Fig. 1(b),  $N_{2,5}=N_{3,4}=2$ ) is the value predicted by Eq. 1.

**2.2.2. Resonance structures and magnetic aromaticity.** Since all the relationships in Eqs. 1–11 are statistically significant and consistent within their subgroups, it must be concluded that the aromaticity measured by NICS(1) (Fig. 1a) is a different property to the aromaticity measured by ASE (Fig. 1b) and HOMA. This conclusion is consistent with the findings of principal component analysis, which suggest that aromaticity is a multidimensional property and that classical and magnetic aromaticities are orthogonal.<sup>9</sup>

Although pyridine-type nitrogen atoms in five-membered rings appear to increase the NICS(1) aromaticity regardless of position, this is not an intrinsic property of pyridine-type nitrogens. As noted above, the influence of aza-substitution on the aromaticity of azines

is small but, if there is an effect, it is a tendency to reduce aromaticity relative to benzene, and this appears to be the case for NICS(1) values for azines. NICS(1) values for contiguous-N azabenzene have been reported to be: benzene (–12.81), pyridine (–12.38), pyridazine (–12.50), 1,2,3-triazine (–12.48), 1,2,3,4-tetrazine (–12.47), pentazine (–12.14) and hexazine (–14.79).<sup>23</sup> The influence of aza-substitution is therefore a characteristic of the type of ring, although the enhanced aromaticity calculated for planar hexazine is noteworthy (see below).

It is possible that the NICS(1) index is more closely related to the uniformity of distribution of  $\pi$  electron density around the ring rather than the equalisation of bond lengths (ASE and HOMA). This equates to delocalisation of the lone pair and a uniform distribution of  $\pi$  electron density on the atoms of the five-membered ring for optimum aromaticity. If this is the case, location of nitrogen atoms not only at positions 2 and 5 (resonance structure 2) but also at positions 3 and 4 (resonance structure 3) will facilitate optimal redistribution of  $\pi$  electron density around the ring relative to the parent rings (pyrrole, furan and thiophene). This may rationalise why aromaticity measured by NICS(1) is increased by nitrogen at all positions in five-membered rings (Eqs. 8–11). In benzene  $\pi$  electron density is uniformly distributed around the ring but aza-substitution will distort this distribution and this may account for the small decreases in NICS(1) values relative to benzene (see above). The exception is fully symmetrical planar hexazine, where the  $\pi$  electron distribution is again uniform and, against the trend, the magnetic aromaticity (NICS(1) –14.79) is calculated to be greater than that of benzene (NICS(1) 12.81).<sup>23</sup>

### 2.3. Aromaticity and annular tautomerism

The heterocycle with greater aromaticity is not necessarily the most thermodynamically stable because the  $\sigma$  framework is also important. In contrast to their relative aromaticities (Table 1, entries 3 and 4), imidazole ( $\Delta H_f$  132.9 kJ mol<sup>–1</sup>) is thermodynamically more stable than pyrazole ( $\Delta H_f$  179.4 kJ mol<sup>–1</sup>).<sup>24</sup> Schleyer has pointed out that ASE is only 3–4% of the total binding energy of benzene.<sup>2</sup>

Nevertheless, for closely related systems with similar  $\sigma$  frameworks, such as azole annular tautomers, the relative aromaticities can be expected to have a significant influence on the relative thermodynamic stabilities in the gas phase. Since ASE is the most relevant measure of aromaticity in this context, Eqs. 1–4 suggest that the annular tautomer with the most nitrogen atoms at positions 2 and 5 ( $N_{2,5}$ ) will be the most stable of a pair. Another factor is the number of adjacent nitrogens with direct lone pair/lone pair

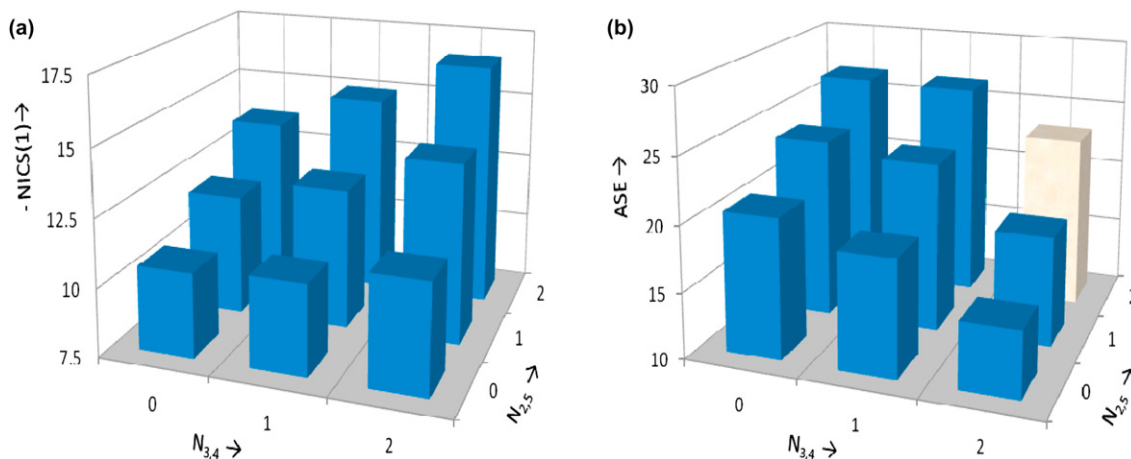


Figure 1. The variation of (a) NICS(1) and (b) ASE with the number and position of ring nitrogen atoms in pyrrole and its aza derivatives.

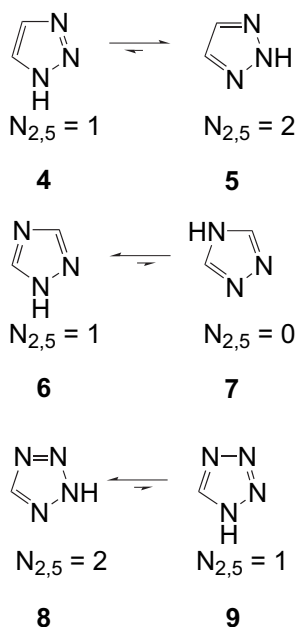


Figure 2. Relative stabilities of annular tautomers in the gas phase.

interactions in the plane of the molecule, since these are destabilising. The two factors are related since maximizing nitrogens at positions 2 and 5 minimises lone pair interactions. Therefore, one might expect  $N_{2,5}$  to be an indicator of relative stability and this appears to be the case (Fig. 2).

Tautomerism of 1,2,3-triazole has been investigated by microwave and photoelectron spectroscopy, which show that in the gas phase the 2H-tautomer **5** strongly dominates over the 1H-tautomer **4**. The ratio estimated from the microwave spectrum of the triple  $^{15}\text{N}$  species is **4:5**  $\approx$  1:1000.<sup>20</sup> For 1,2,4-triazoles, the 1H-tautomers, e.g., **6**, dominate solution chemistry and theoretical studies calculate that in the gas phase the 1H-tautomer **6** is more stable than the 4H-tautomer **7** by  $\sim 7$  kcal mol $^{-1}$ .<sup>25</sup> A UV-photoelectron spectroscopy investigation has confirmed that tetrazole in the gas phase exists predominantly as the 2H-tautomer **8**.<sup>26</sup> A minor contribution (10%) of the 1H-form **9** is also present in low-temperature inert matrices.<sup>27</sup> The parameter  $N_{2,5}$  is therefore a useful *aide-mémoire* when considering annular tautomerism.

### 3. Conclusions

The azoles (Table 1) provide an interesting set of molecules for structure-aromaticity studies. To a first approximation, the contributions to aromaticity of the heteroatoms at the five ring positions appear to be additive. An understanding of the fundamental effect of aza-substitution on aromaticity of the azoles may therefore provide information about the nature of the aromaticity being measured by different indices. Based on the contributions of nitrogen atoms at positions 2, 3, 4 and 5 to the aromaticity of azoles, it is clear that the aromaticity measured by NICS(1) (magnetic aromaticity) is a different aspect of aromaticity to that measured by ASE and HOMA. For the same reason, the aromaticities measured by ASE and HOMA appear to be similar but are not necessarily identical in that they may correspond primarily to one principal component (classical aromaticity) but may contain differing contributions from other principal components. The influence of nitrogen at positions 3 and 4 on HOMA (Eqs. 5–7) while still negative is smaller and less significant than the influence on ASE (Eqs. 1–4). The contributions of  $N_{2,5}$  and  $N_{3,4}$  to other indices can also be expected to vary.

If indices of aromaticity are to be generally useful in the teaching and practice of chemistry their relationship to well-defined molecular properties, rather than abstract principal components or theoretical equations, needs to be demonstrated. Based on the regression analyses described above, we have used resonance structures and  $\pi$  electron distribution to rationalise the difference between aromaticity measured by ASE and HOMA and aromaticity measured by NICS(1). In the former case the electronegativity of nitrogen influences the bond alternation/bond equalisation, whereas in the latter case uniform distribution of the six  $\pi$  electrons around the ring may facilitate the flow of a ring current. In the light of modern quantum mechanical studies, this is a simplistic view but it is consistent with available aromaticity indices of azoles and azines. Other explanations may be correct but the relative electronegativities of carbon and nitrogen are probably the source of these effects. The influence of aza-substitution on aromaticity merits an explanation in the language of practicing organic chemists and the azoles (Table 1) appear to be an excellent data set for structure-aromaticity studies.

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