



## Facts and artifacts about aromatic stability estimation

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The paper is dedicated to Professor Dr H. C. Lucjan Sobczyk (Wrocław University, Poland) on the occasion of his 75th birthday

**Abstract**—The stability of a set of 105 five-membered  $\pi$ -electron systems (involving aromatic, non-aromatic and anti-aromatic species) was evaluated using six isodesmic reactions of which two belong to the subclass of homodesmotic reactions, which are based on cyclic and acyclic reference systems. We demonstrate that the ‘Resonance Energies’ derived from isodesmotic schemes have obvious flaws and do not correct or cancel other contributions to the energy, such as the changes of hybridization, homoconjugation of heterosubstituted cyclopentadienes, conjugative interactions of C=C or C=X (X=N or P) with a  $\pi$  or pseudo  $\pi$  orbital at Y (Y=O, S, NH, PH), strain, etc. as effectively as possible. Likewise, ‘aromatic stabilization energies (ASE)’ derived from homodesmotic schemes based on the acyclic reference compounds do not give satisfactory results. We strongly recommend that only cyclic reference compounds should be used for ASE and other aromaticity evaluations. The analysis is based on ab initio optimized geometries at B3LYP/6-311+G\*\*. © 2003 Elsevier Science Ltd. All rights reserved.

### 1. Introduction

Historically, the chemical consequences of increased stability were the main features which distinguished aromatic from other classes of compounds.<sup>1–3</sup> For nearly two centuries, aromaticity has remained one of the central concepts in chemistry and, through ever wider application, is now actually increasing in importance.<sup>4</sup> However, aromaticity is not a directly measurable or computable quantity. ‘Aromaticity’ is generally evaluated on the basis of energetic, geometric, and magnetic criteria.<sup>4a,b,5,6</sup> These usually require comparisons with non-aromatic model compounds or are derived from the non-additivity of evaluations based on data for non-aromatic reference species judged to be appropriate. However well chosen for the purpose, such selections are arbitrary.

Nevertheless, some evaluation procedures (and criteria) may be more soundly conceived than others and are more effective in dissecting the effects of cyclic  $\pi$ -electron delocalization (aromaticity) from other influences. This paper is concerned with the choice of the ‘best’ methods for the quantitative evaluation of ‘aromatic stabilization

energies (ASE),’ arguably the most basic operational criterion influencing the reactions and the physicochemical behavior.<sup>4a,b,6–10</sup> It is important to realize that ASE’s, while being among the largest deviations from additivity found chemically, are at most only 3–4% of the total atomization energy of typical aromatic systems.<sup>4c</sup> This emphasizes the difficulty in disentangling ASE from other important, but complicating effects. ‘Strain’ is an obvious example. Since this ‘disentangling’ has not been done adequately, there is considerable variation in the ASE’s derived from various schemes (e.g. ‘isodesmic’<sup>11</sup> and ‘homodesmotic’<sup>12</sup>) which have been applied in the literature. While it has been pointed out often that ‘resonance energies’, even for benzene, have ranged over 50 kcal/mol,<sup>4a,b,13,14</sup> this large range is due to some ill-conceived choices of evaluation methods (often dictated earlier by the availability of experimental data). Many of these methods have employed acyclic reference species, which do not compensate for ring strain. Mono-hetero five-membered ring systems provide an example. The ASE’s of Nyulaszi et al.<sup>15</sup> which were based on acyclic reference compounds, are, on average, 8.5 kcal/mol higher than the values of Ref. 7 which agree well with those of Chesnut and Davis.<sup>16</sup>

Such discrepancies are either due to (i) differences in the choice and definition of reference molecules and the defining equations (the energies may be perturbed by additional effects such as strain, topological charge

**Keywords:** ab initio calculations; aromaticity; five-membered heterocycles; homodesmotic reactions; stabilization energies.

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**Table 1.** Calculated ASE and RE in kcal/mol, for polyaza five-membered rings (including the parent systems)








































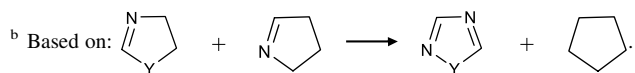
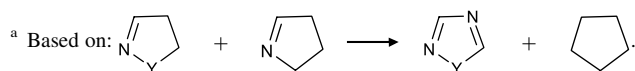
System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)	System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)
	12.26	6.29	–	15.03	14.53	16.17		15.37	11.50	–29.27	17.99	–27.01	–3.20
	15.62	10.90	–	18.39	12.87	17.01		17.07	14.31	6.67	19.69	3.92	13.12
	18.04	5.26	–	20.81	24.22	23.90		22.21	22.46	0.07	24.83	6.24	16.84
	2.73	–0.78	–	5.50	0.23	4.25		2.15	–3.75	7.52	4.77	5.02	6.21
	14.32	8.36	–8.01	16.98	–5.74	–4.20		5.16	7.04	18.69	–9.20	20.96	–1.3
	16.24	11.70	11.04	18.91	8.29	12.33		10.52	8.92	15.35	–3.83	12.59	–2.8
	20.46	13.25	9.39	23.13	15.56	15.14		12.19	–1.22	23.43	–2.16	29.61	6.54
	2.64	–1.36	5.32	5.31	2.83	6.74		1.29	–4.84	–3.00	–13.07	–5.49	–16.46
	9.81	8.12	16.58	10.73	18.85	18.63		6.78	14.83	2.68	–2.40	4.95	–12.13
	14.46	12.10	16.87	15.37	14.12	16.41		10.02	13.22	11.45	0.84	8.70	–1.52
	16.18	3.48	21.79	17.09	27.97	25.80		14.13	10.35	16.46	4.94	22.64	4.75
	2.77	–1.02	0.63	3.69	–1.87	0.30		0.73	–1.91	–1.54	–8.45	–4.04	–9.83
	14.07	12.56	3.21	15.05	5.48	5.32		13.14	17.01	–20.05	16.04	–17.78	6.32
	15.71	13.35	14.73	16.69	11.98	14.33		15.02	17.70	8.84	17.93	6.09	15.57
	20.21	11.11	16.93	21.19	23.11	21.00		21.17	23.23	6.82	24.08	13.00	23.89
	1.91	–2.42	1.78	2.89	–0.72	1.51		1.63	1.49	4.18	4.54	1.69	3.16
	11.42	13.09	–4.13	14.21	–1.86	22.11 <sup>a</sup> (–6.98 <sup>b</sup> )		–	20.88	–	0.96	–	–8.77

Table 1 (continued)

System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)	System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)
	14.57	15.17	11.78	17.35	9.03	18.39 <sup>a</sup> (10.78 <sup>b</sup> )		–	18.56	–	4.11	–	1.76
	18.01	14.48	12.56	20.80	18.74	29.50 <sup>a</sup> (12.81 <sup>b</sup> )		–	22.92	–	10.92	–	10.73
	2.68	2.11	3.22	5.46	0.73	2.07 <sup>a</sup> 6.90 <sup>b</sup>							













stabilization,<sup>17</sup> hybridization, heteroatom interactions like anomeric effects, hyperconjugation, etc.), and/or (ii) inaccuracies in the energies (both experimental and theoretical) employed. While isodesmic reaction schemes demand only equal numbers of formal single and double bonds in products and reactants,<sup>11</sup> the homodesmotic schemes, by definition,<sup>12</sup> require that there be the same number of bonds between given atoms in each state of hybridization both in products and reactants. In addition the number of hydrogen atoms joined to the atoms in given states of hybridization must match.<sup>4a</sup> The homodesmotic reactions are the subclass of isodesmic reactions.<sup>18</sup> The purpose of the present report is to demonstrate, using a comprehensive set of heterocyclic five-membered ring compounds, the great importance of proper selection of the reference systems and of the reaction scheme used for

evaluation in order to achieve credible results. This often has not been appreciated adequately. Since aromatic systems are more stable than their acyclic or cyclic olefinic or conjugated unsaturated analogues, it is commonly believed erroneously that reliable quantitative aromaticity evaluations can be expected if data comparisons are made merely by using the same method and similar reference systems.<sup>4b</sup>

## 2. Methodology



























We have investigated a set of 105 five-membered  $\pi$ -electron systems (see Tables 1–3 and Eqs. (1)–(6)). This comprehensive set of compounds (involving aromatic, non-aromatic and anti-aromatic species) affords an excellent

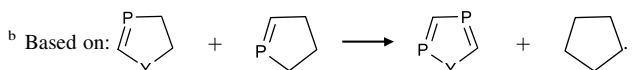
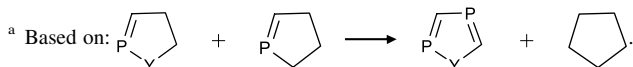
Table 2. Calculated ASE and RE in kcal/mol, for polyphospha five-membered rings

System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)	System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)
	11.91	11.08	22.14	18.78	24.41	30.14		17.72	20.96	30.25	27.59	36.43	36.95
	14.66	15.54	24.05	21.52	21.30	29.54		5.16	8.04	11.33	15.03	8.83	16.87
	18.55	14.68	24.81	25.42	30.99	34.77		8.34	15.91	11.73	14.83	14.00	17.66
	3.52	3.16	6.60	10.39	4.10	12.22		12.26	18.03	17.00	18.76	14.24	19.75
	10.34	13.38	12.03	13.09	14.30	15.92		14.16	13.33	24.08	20.66	30.25	28.7

(continued on next page)

Table 2 (continued)

System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)	System	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)
	13.44	16.23	15.80	16.19	13.05	17.18		3.31	6.10	4.05	9.8	1.55	8.92
	16.07	11.58	21.02	18.82	27.20	26.87		9.7	15.46	21.98	16.20	24.25	27.91
	2.54	4.15	2.91	5.29	0.41	4.42		11.49	16.36	23.98	17.98	21.22	26.73
	10.52	13.27	21.1	14.71	23.37	26.42		14.44	15.61	28.27	20.94	34.45	32.9
	12.14	15.2	22.26	16.32	19.51	25.07		4.55	6.78	8.66	11.04	6.17	13.54
	16.42	15.17	25.29	20.60	31.46	32.56		11.7	15.11	32.51	17.29	34.78	29.01
	2.49	5.22	6.24	6.68	3.74	9.18		12.03	17.81	31.54	17.61	28.79	26.36
	10.55	16.60	22.47	15.52	24.74	18.35 <sup>a</sup> (26.88 <sup>b</sup> )		15.7	19.85	30.84	21.29	37.02	33.25
	12.91	19.42	24.67	17.88	21.92	18.87 <sup>a</sup> (25.90 <sup>b</sup> )		5.56	8.78	12.39	11.15	9.89	13.65
	16.03	18.62	27.25	21.00	33.42	29.04 <sup>a</sup> (30.35 <sup>b</sup> )		11.37	13.33	32.53	17.31	34.8	29.02
	4.37	7.81	7.82	9.34	5.32	(8.46 <sup>a</sup> ) (11.17 <sup>b</sup> )		10.5	13.70	30.74	16.43	27.99	25.18
	11.90	13.56	32.35	21.77	34.61	33.13		14.02	15.84	31.77	19.95	37.94	31.91
	13.66	18.81	32.44	23.53	29.69	31.54		7.34	9.21	14.83	13.28	12.34	15.77

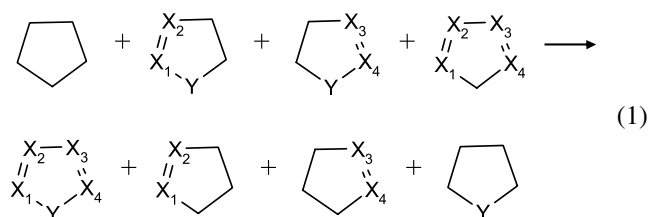


**Table 3.** Calculated ASE and RE in kcal/mol for mono-hetero five-membered rings (C<sub>4</sub>H<sub>4</sub>X)

X	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)	X	ASE(1) Eq. (1)	ASE(2) Eq. (2)	RE(3) Eq. (3)	RE(4) Eq. (4)	RE(5) Eq. (5)	RE(6) Eq. (6)
BeH <sup>-</sup>	-8.39	-23.14	-	-5.62	-1.25	-2.05	P <sup>-</sup>	18.97	-2.57	-	21.74	39.96	32.23
B	5.00	-40.45	-	7.77	11.27	10.91	PH <sub>2</sub> <sup>+</sup>	-9.37	-19.52	-	-6.6	-14.2	-9.02
BH	-24.01	-29.77	-	-21.24	-13.68	-16.08	GaH	-10.84	-17.76	-	-8.07	-5.68	-5.49
BH <sub>2</sub> <sup>-</sup>	0.29	-16.22	-	3.06	7.06	6.45	GaH <sub>2</sub> <sup>-</sup>	-0.77	-13.81	-	2.00	0.04	2.40
CH <sup>-</sup>	20.45	-18.07	-	23.22	58.77	42.38	GeH <sup>-</sup>	4.70	-10.55	-	7.47	6.83	8.53
CH <sub>2</sub>	0.00	-3.04	-	2.77	0.00	2.77	GeH <sup>+</sup>	-25.22	-41.94	-	-22.45	-14.5	-17.09
CF <sub>2</sub>	-12.4	-11.55	-	-9.63	-14.49	-10.67	GeH <sub>2</sub>	-3.28	-7.47	-	-0.51	-6.14	-1.94
N <sup>-</sup>	18.22	-13.20	-	20.99	55.62	39.69	As <sup>-</sup>	17.29	-3.06	-	20.06	30.51	26.67
NH <sub>2</sub> <sup>+</sup>	-2.54	-8.48	-	0.23	-13.82	-5.41	AsH	0.88	-2.48	-	3.65	-3.33	1.55
Al <sup>-</sup>	-7.04	-16.60	-	-4.27	-1.45	-1.47	AsH <sub>2</sub> <sup>+</sup>	-8.16	-17.73	-	-5.39	-16.04	-9.33
AlH	-10.83	-17.55	-	-8.06	-3.91	-4.6	Se	13.67	9.31	-	16.44	8.39	13.8
AlH <sub>2</sub> <sup>-</sup>	-1.65	-14.02	-	1.12	1.32	2.61	C=CH <sub>2</sub>	-5.10	-5.07	-	-2.33	2.74	1.59
SiH <sup>-</sup>	8.68	-11.41	-	11.45	11.66	12.94	C=O	-16.31	-18.99	-	-13.54	-11.41	-11.09
SiH <sup>+</sup>	-28.72	-45.38	-	-25.95	-12.87	-18.02	C=S	-16.3	-16.47	-	-13.53	-4.64	-7.70
SiH <sub>2</sub>	-4.75	-8.28	-	-1.98	-4.75	-1.98	C=Se	-17.61	-16.32	-	-14.84	-2.62	-7.35

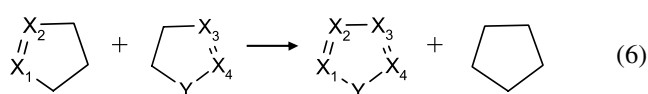
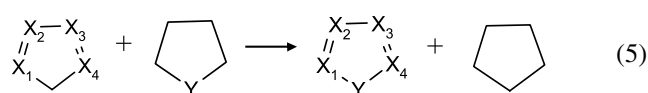
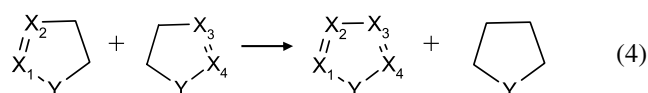
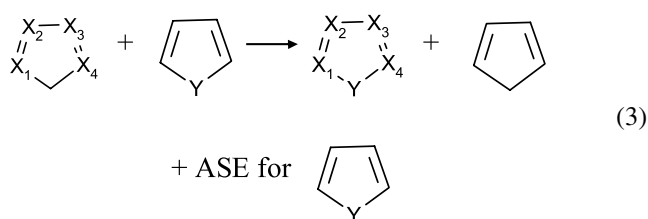
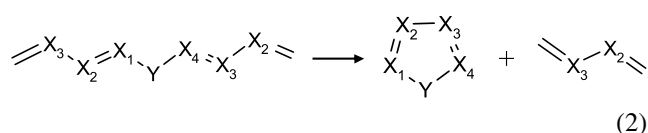
opportunity to evaluate the aromaticity of systems with one or more heteroatoms. We have employed six schemes to estimate the stabilization energy:

- Homodesmotic reactions<sup>6</sup> (Eq. (1))<sup>†</sup> based on cyclic olefinic and conjugated unsaturated analogues: The five-membered  $\pi$ -electron ring systems (the first product molecule in Eq. (1)) are regarded as being comprised of three unsaturated units, represented by the three unsaturated reference molecules on the reactant side of Eq. (1). The remaining reference molecules provide the necessary homodesmotic balance. The resulting ASE(1) have recently been applied to address the question, 'Is aromaticity statistically a one- or multidimensional phenomenon?'<sup>6</sup> Systems with strongly positive ASE are aromatic, while those with strongly negative ASE are anti-aromatic.
- Homodesmotic reactions (Eq. (2)) based on the acyclic analogues: This evaluation model is similar to the frequently used schemes for estimating the ASE of benzene, for example, by employing butadiene and ethene.<sup>19–22</sup> The resulting values, ASE(2), also have been denoted as 'Aromatic Stabilization Energies'.
- (vi) Four isodesmic reaction schemes (Eqs. (3)–(6))<sup>‡</sup> which are simplified versions of Eq. (1). The resulting Resonance Energies (RE(3)–RE(6)) are perturbed to some extent by additional effects mainly involving the changes in hybridization, except in some cases (as discussed below). They should not be expected to give reliable ASE, even though such models are often used.<sup>4a,c,22,23</sup>



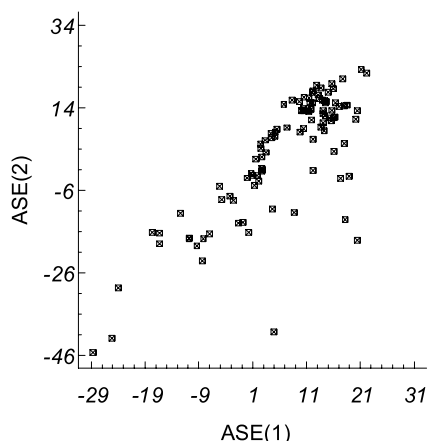
<sup>†</sup> The 2,3,4,5-tetraaza derivatives could not be evaluated by Eq. (1) since the ring of the necessary reference compound (2,3,4,5-tetraazacyclopentadiene) opened during optimization.

<sup>‡</sup> Eq. (6) is not applicable for the 2,4-diaza- and 2,4-diphospha-derivatives.



where (i) X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub> are (C or N) or X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub> are (C or P) and Y=O, S, NH, PH; or (ii) X<sub>1</sub>=X<sub>2</sub>=X<sub>3</sub>=X<sub>4</sub>=C and Y=BeH<sup>-</sup>, B<sup>-</sup>, BH, BH<sub>2</sub><sup>-</sup>, CH<sup>-</sup>, CH<sub>2</sub>, CF<sub>2</sub>, N<sup>-</sup>, NH<sub>2</sub><sup>+</sup>, Al<sup>-</sup>, AlH, AlH<sub>2</sub><sup>-</sup>, SiH<sup>-</sup>, SiH<sup>+</sup>, SiH<sub>2</sub>, P<sup>-</sup>, PH<sub>2</sub><sup>+</sup>, GaH, GaH<sub>2</sub><sup>-</sup>, GeH<sup>-</sup>, GeH<sup>+</sup>, GeH<sub>2</sub>, As<sup>-</sup>, AsH, AsH<sub>2</sub><sup>+</sup>, Se, C=CH<sub>2</sub>, C=O, C=S, C=Se.

All geometries used here were fully optimized at the B3LYP/6-311+G\*\* DFT level,<sup>24</sup> expected to be quite accurate for molecules of this type.<sup>25</sup> Except for ASE(2), B3LYP/6-311+G\*\* zero point energies were applied, but these usually were very small (about 0.7 kcal/mol and the correlation between the ZPE corrected and uncorrected ASE was excellent, correlation coefficient cc=0.9996). In view of a large number of molecules the polyene systems were not corrected for ZPE. All five-membered species are the lowest energy minima at B3LYP/6-311+G\*\*, with no imaginary frequencies. Tables 1–3 list the aromatic stabilization and resonance energies of the systems.



**Figure 1.** The dependence between ASE(2) and ASE(1); correlation coefficient: 0.796 (102 data).

### 3. Results and discussion

Although the ASE(1) derived earlier at the MP2/6-311+G\*\* level<sup>6</sup> are slightly larger (by about 2.4 kcal/mol) than the B3LYP/6-311+G\*\* ASE(1) data, the relative stabilities agree very well (the correlation coefficient is 0.992). Hence the level of theory, if adequately high, should not affect the relative stabilization energy values appreciably. The most interesting comparison involves the ASE given by the two different homodesmotic models. Figure 1 shows considerable scatter in the ASE(1) vs. ASE(2) plot. The correlation coefficient is only 0.796. The plot is essentially useless for the practical purpose of deriving one value from another accurately. Nevertheless, according to the standards of statistical correlation analysis,<sup>26</sup> this correlation corresponds to what is considered to be a significant<sup>§</sup> linear dependence. Therefore, ASE(1) and ASE(2) contain only very roughly similar information.

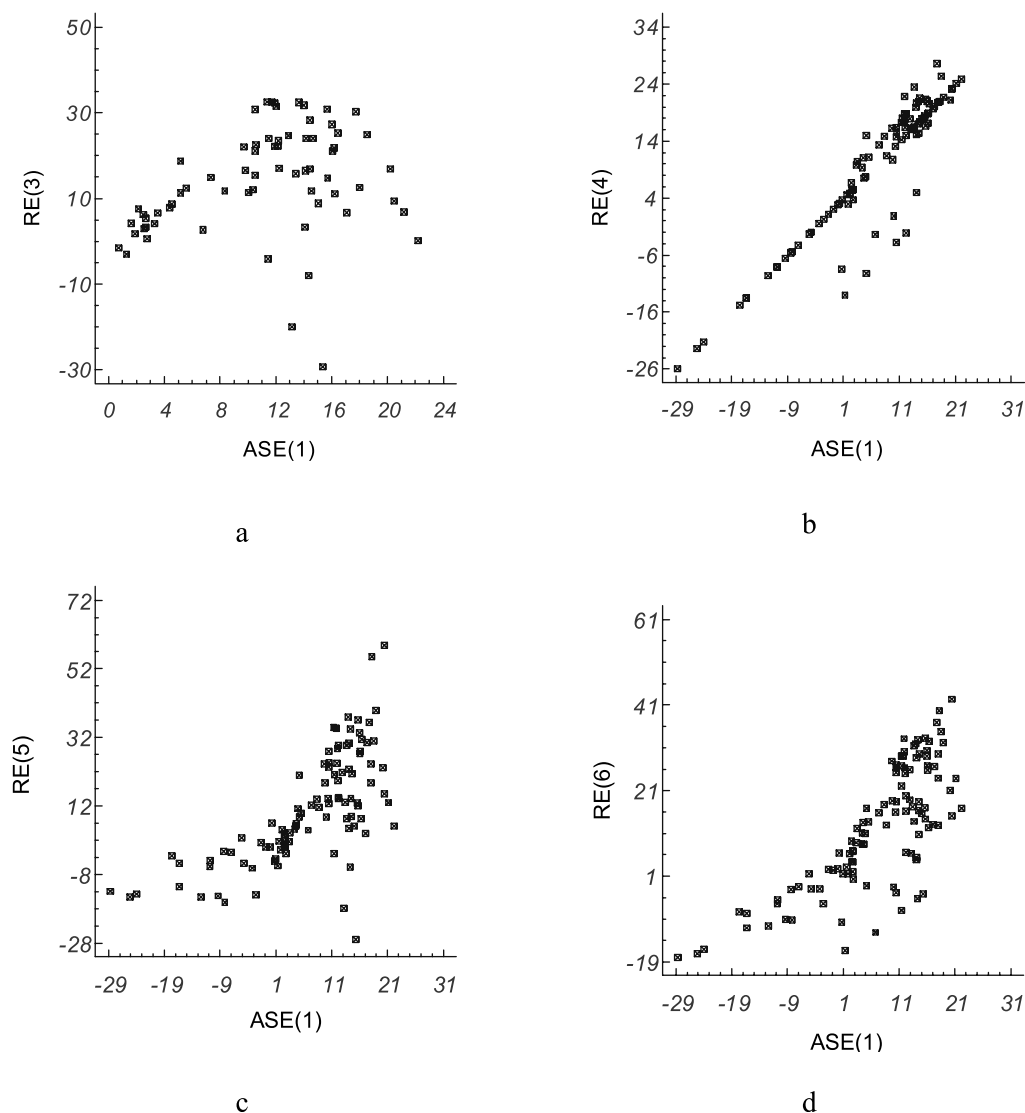
However, a closer inspection of data in Tables 1–3 reveals many subtle deviations between the data compared. The classical problem of the aromaticity of phosphole, furan, thiophene and pyrrole has long been discussed.<sup>7,9</sup> While the ASE(1) values, in line with chemical expectations and recent analyses<sup>6</sup> show nicely that phosphole is the least aromatic while pyrrole the most aromatic in the series, ASE(2) gives an inconsistent order. An independent magnetic index, NICS(0)<sup>10</sup> calculated at the center of the rings,<sup>6</sup> reveals the same qualitative order as the homodesmotic ASE(1) values. This comparison can be extended to all polyaza and polyphospha derivatives (with one exception, pentaphosphathiophene). NICS<sup>6</sup> supports the same order for all polyaza derivatives. The homodesmotic reaction scheme (1) reveals the aromaticity of most polyaza derivatives to be increased, but that of most polyphospha derivatives to be decreased, with respect to their parent systems.<sup>28,29</sup> This exemplifies the rule that aromaticity increases with the decrease in the electronegativity difference between a heteroatom and its neighbouring atoms.<sup>4a</sup> Hence, replacement of a CH fragment by nitrogen at position (2) causes a substantial increase while replace-

ment at position (3) results in a decrease of aromaticity. Consequently, 2,5-diaza species have the highest aromaticity and 3,4-diaza systems have the lowest aromaticity among the whole set of polyaza derivatives. These generalizations are fully supported by NICS values.<sup>6</sup> Also the aromaticity of 2,5-diphospha systems is substantially higher than that of their 3,4 isomers. Hence, it is not surprising that all the 2,3,4-trisubstituted species have lower aromaticity than the 2,3,5-trisubstituted systems. The increase in aromaticity in polyphosphole systems is due to the well-known decrease in pyramidalicity of the tricoordinate phosphorous;<sup>27,28</sup> pentaphosphole is known to be planar and aromatic.<sup>27,29</sup>

However, the largest discrepancies between the two homodesmotic models (Eqs. (1) and (2)) involve most of the anionic systems. The cyclopentadienyl anion is a good example: this prototypal 5-membered ring system has 6 $\pi$ -electrons, follows the Hückel rule,<sup>30</sup> and has long been considered to be aromatic. Indeed, ASE(1) confirms its considerable aromatic character (+20.5 kcal/mol stabilization), as does the strongly negative NICS (−14.0 ppm).<sup>10</sup> In contrast, the homodesmotic scheme based on Eq. (2) (and the acyclic pentadienyl anion) erroneously suggests strong antiaromatic character with a negative ASE(2) of −18.1 kcal/mol. Similar discrepancies are found for C<sub>4</sub>H<sub>4</sub>N<sup>−</sup>, C<sub>4</sub>H<sub>4</sub>B<sup>−</sup>, C<sub>4</sub>H<sub>4</sub>SiH<sup>−</sup>, C<sub>4</sub>H<sub>4</sub>P<sup>−</sup> or C<sub>4</sub>H<sub>4</sub>GeH<sup>−</sup> where the homodesmotic model based on Eq. (1) and NICS reveal substantial aromatic character, whereas the homodesmotic reaction based on Eq. (2) suggests the opposite (see Table 3). In some cases, e.g. C<sub>4</sub>H<sub>4</sub>BeH<sup>−</sup>, C<sub>4</sub>H<sub>4</sub>BH<sub>2</sub><sup>−</sup>, C<sub>4</sub>H<sub>4</sub>SiH<sup>+</sup> or C<sub>4</sub>H<sub>4</sub>GeH<sup>+</sup>, both models predict similar trends, but the quantitative stabilization/destabilization energy estimates are very different (with deviations of about 16 kcal/mol). Apart from many other cases where the homodesmotic reaction scheme of Eq. (2) evidently gives incorrect results (e.g. the aromaticity of 3,4-diazapyrrole), it is also possible to find related molecules where the agreement between the two homodesmotic schemes is impressive—for example selenophene, fulvene and cyclopentadienone. The aromatic stabilization energies derived from the homodesmotic reaction (1) revealed a good dependence on NICS<sup>6,10</sup> and on geometry-based index HOMA<sup>6,31</sup> while the ASE(2) correlations with these indices are much worse.

What is responsible for such great divergence between ASE(1) and ASE(2)? Strain effects are an important factor. These should cancel to a large extent in the homodesmotic Eq. (1) where all the reference molecules are five-membered rings computed in their most stable conformations. In contrast, the polyene reference systems used in Eq. (2) have different conformations and bond angles, compared with the rings. Another important factor is that the reference systems used in the homodesmotic Eq. (2) may be perturbed considerably by additional effects—for example the negative charge may be better accommodated by a greater degree of delocalization to the ends of polyene chains, and benefit from better minimization of coulombic charge repulsion. Hence, such non-aromatic acyclic compounds are more stable than their aromatic cyclic analogues. Consequently, Eq. (2) is biased and cannot be expected to give reliable ASE results. Moreover, both ASE(1) and ASE(2) can be

<sup>§</sup> At significance level 0.01.

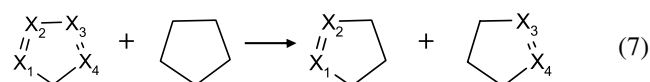


**Figure 2.** Dependences between (a) RE(3) vs ASE(1) (correlation coefficient: 0.291; 68 data); (b) RE(4) vs ASE(1) (correlation coefficient: 0.920; 102 data); (c) RE(5) vs ASE(1) (correlation coefficient: 0.681; 102 data) and (d) RE(6) vs ASE(1) (correlation coefficient: 0.767; 110 data).

perturbed by additional effects, like topological charge stabilization<sup>17</sup> and/or heteroatom–heteroatom interactions. These effects may be minimized but not completely eliminated even by careful formulation of the homodesmotic reactions.

Comparisons of the stabilization energies derived from the isodesmic schemes (3), (5) and (6) with the values of ASE(1) do not give good correlations (see Fig. 2). The one exception, Eq. (4) for monoheteropentatomic systems (see the main linear subset in Fig. 2(b)), is successful<sup>7,23</sup> because the reference molecules, cyclopentane, cyclopentene, and cyclopentadiene, truncated from Eq. (4) are not critical as they are the same for all the monoheteropentatomic systems. Further examination of Figure 2(b) reveals several sets of parallel lines, indicating successful local correlations among related molecules. These include, e.g. the 3,4-diaza and the 2,3,4-triaza subgroups (where Y=PH, O, NH, and S) and arise for the same reason as the monohetero rings: the truncated reference molecules are the same in each set. While each subgroup of these truncated molecules contributes a constant amount to each set, these amounts differ

from set to set and give rise to the parallel lines seen in Figure 2(b). The scatter of the lines comes from the different stabilization energies of heterosubstituted cyclopentadienes. This can be deduced from the difference between Eqs. (1) and (4), which results in Eq. (7).

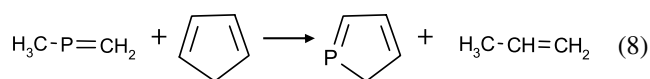


Moreover, the energies are perturbed additionally by the interactions between the atoms in positions 3 and 4. For instance: two 3-azacyclopentadienes disproportionate to 3,4-diazacyclopentadiene and cyclopentadiene endothermically by 13.4 kcal/mol. Likewise, 3,4-diazacyclopentadiene is about 17 kcal/mol less stable than both of its two isomers: 2,4-diazacyclopentadiene and 2,5-diazacyclopentadiene, while 2,3,4-triazacyclopentadiene is 12.1 kcal/mol less stable than its 2,3,5-triazacyclopentadiene isomer. Hence, the lone electron pair repulsion weakening the N–N bond in the 3,4-diaza and the 2,3,4-, triaza subgroups is the common factor which results in the shifting of two of the sets of lines (by 14.4 and 9.2 kcal/mol, respectively). These



deviate towards the bottom of Figure 2(b), away from the general dependence for monohetero ring systems. As expected, the analogous lone pair interactions between the phosphorous atoms are much weaker. The isomerization energy of 2,5-diphosphacyclopentadiene to 3,4-diphosphacyclopentadiene is endothermic by only +3.4 kcal/mol, whereas the disproportionation of two 2-phosphacyclopentadiene into 2,5-diphosphacyclopentadiene and cyclopentadiene is essentially thermoneutral (+1.1 kcal/mol).

Two sets of deviating lines towards the top of Figure 2(b) comprise the 2,5-diphospha and 2-phospha subsystems. The lines are shifted upward from the 'main' line by 9.9 and 6.9 kcal/mol, respectively, mostly as a result of favorable strain effects which are not present in the reference compounds. The 108° average bond angle in planar five membered rings is considerably smaller than the normal 'sp<sup>2</sup>' value. However, the natural bond angles at dicoordinate phosphorous approach 90°; consequently, the other angles in the rings can expand significantly towards their normal values. This strain-reducing effect is even more significant for 2,5-diphosphacyclopentadiene. This is documented by the -7.6 kcal/mol exothermic homodesmotic transfer of a phosphorus atom from 2-phosphapropene (H<sub>3</sub>C-P=CH<sub>2</sub>) to cyclopentadiene to give 2-phosphacyclopentadiene and propene.



Conversely, if the monoheteroring systems are excluded from Figure 2(b), the correlation coefficient deteriorates to 0.759. The other isodesmotic schemes (3), (5) and (6) are even more deficient since they neither balance the homoconjugation of heterosubstituted cyclopentadienes nor the conjugative interactions of C=C or C=X with a  $\pi$  or pseudo  $\pi$  orbital at Y. These flaws are reflected in the poor or very poor correlations between ASE(1) and RE's (the correlation coefficients range from 0.291 to 0.767).

It is important to realize that models simpler than Eq. (1) may, reflect aromatic stabilization well under favorable circumstances<sup>7,23</sup> but only for structurally restricted subgroups of molecules. The poor correlations indicate clearly the deficiency of the isodesmotic reactions, which definitely cannot be expected to give reliable aromatic stabilization estimates. These are perturbed by effects other than aromaticity: changes of hybridization, unbalanced strain, unbalanced heteroatom-hereroatom interactions, topological charge stabilization, etc. Even worse, these additional effects may strongly obscure the properties taken as characteristics for aromaticity.

In view of the present analysis the stabilization energies also derived from even more simplified models, like graph-topological<sup>32</sup> methods based on Hückel  $\pi$ -electron theory,<sup>33,34</sup> should be regarded with skepticism: hypotheses based on qualitative dependencies should be subjected to critical tests<sup>4e</sup> against reliable model reaction schemes based on high level ab initio or thermochemical data.<sup>35,36</sup> Similar implications apply to models and increments devised for calculating magnetic susceptibility exaltation values.<sup>9</sup> Only a reliable homodesmotic reaction scheme

(like Eq. (1)), based on reference systems as unbiased as possible, should be used for such purposes.

#### 4. Conclusions

We conclude that Eq. (1) is not only fundamentally superior conceptually, but also performs best as the ASE evaluation standard. Comparison with Eqs. (3)–(6) (which are truncated version of Eq. (1)), show that only Eq. (4) gives satisfactory results for most compounds (mainly due to its similar conceptual formulation for monoheteropentaatomic systems). Acyclic reference compounds (Eq. (2)) do not give satisfactory results. Hence, we recommend that only cyclic reference compounds should be used for ASE and other aromaticity evaluations.

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