

Aromaticity of annulated benzene, pyridine and phosphabenzene

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Abstract

Cyclopropa-, cyclobutana-, and cyclobutena-annulated benzenes, pyridines, and phosphabenzenes are potentially aromatic compounds. The structures of all mono-, di- and tri-annulated variations are optimized at the B3LYP/aug-cc-pVDZ level. Their aromaticity is evaluated in terms of bond alternation, magnetic properties (NICS), and resonance energy. The cyclopropa systems are aromatic, the cyclobutanana systems express some aromaticity and the cyclobutena systems are not aromatic. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bond alternation; Magnetic properties; Mills–Nixon effect

1. Introduction

The Mills–Nixon effect describes geometric changes of the benzene ring due to annulation by small, strained rings [1]. Arguing in terms of the stability of the Kekulé resonance structures, small ring annulation will favor the resonance structure with the double bonds *exo* to the strained annulated ring. While definitive evidence for or against the concept of the Mills–Nixon effect is likely to be never obtained, recent theoretical work by Siegel and Baldrige [2–4] and Stanger [5,6], along with experimental studies [7–14] by the Vollhardt, Boese and Billups groups have cast extreme doubt on the existence of this effect.

The geometric distortion predicted by the Mills–Nixon effect is oftentimes not observed (as in tricyclopropabenzene **5**) or better understood in terms of a π -effect (as in tricyclobutenabenzene **13**). When bond alternation is observed, such as in tricyclobutenabenzene **9**, Siegel [15] and Stanger [6] have argued that the cause of this is strain induced bond localization (SIBL).

Aromaticity is one of the pillar concepts in organic chemistry, yet is poorly defined. No single measure of aromaticity exists; rather, we associate a number of properties with aromaticity, principally planarity, bond

non-alternation, resonance stabilization energy (RE), and magnetic effects. Theoretical studies of the Mills–Nixon effect have concentrated on the bond distances within the ring, [2–6,16] though a few examinations [17–19] of the magnetic properties (primarily by the nucleus-independent chemical shift NICS [17,20]) have been published. If the Mills–Nixon effect is real, then resonance energy should be diminished due to the dominance of one resonance structure over all others. Until recently, no experimental or theoretical treatment of the energetics of these systems has been reported. Beckhaus et al. determined the heat of hydrogenation of starphenylene and concluded that this reflects a central ring that is essentially a pure cyclohexatriene moiety [14].

Heteroaromatic compounds are well known, though the relative aromaticity of these compounds remains an issue for debate [21–26]. The effect of heteroatoms within the small strained rings annulated to benzene has been examined [6,16], but no study of the potential for the Mills–Nixon effect or SIBL in annulated heteroaromatic compounds has appeared.

In this article, we examine the aromaticity of annulated pyridine and phosphabenzene compounds. Using high-level calculations, the geometries, resonance energies, and magnetic properties of the cyclopropa-, cyclobutana-, and cyclobutenapyridines and phosphabenzenes are compared to the parent benzene analogues.

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2. Computational methods

The cyclopropa-, cyclobutana- and cyclobutena-anneled benzenes, pyridines, and phosphabenzenes examined are schematically drawn in Figs. 1–3. All structures were optimized at HF/6-31G* and B3LYP/

aug-cc-pVDZ [27–30]. All molecules were found to possess a plane of symmetry, i.e. the six-member ring is planar. Analytical frequencies were calculated at the HF/6-31G* level and zero-point vibrational energies (ZPE) were scaled by 0.9135 [31]. All molecules were found to be local minima. All reported energies were

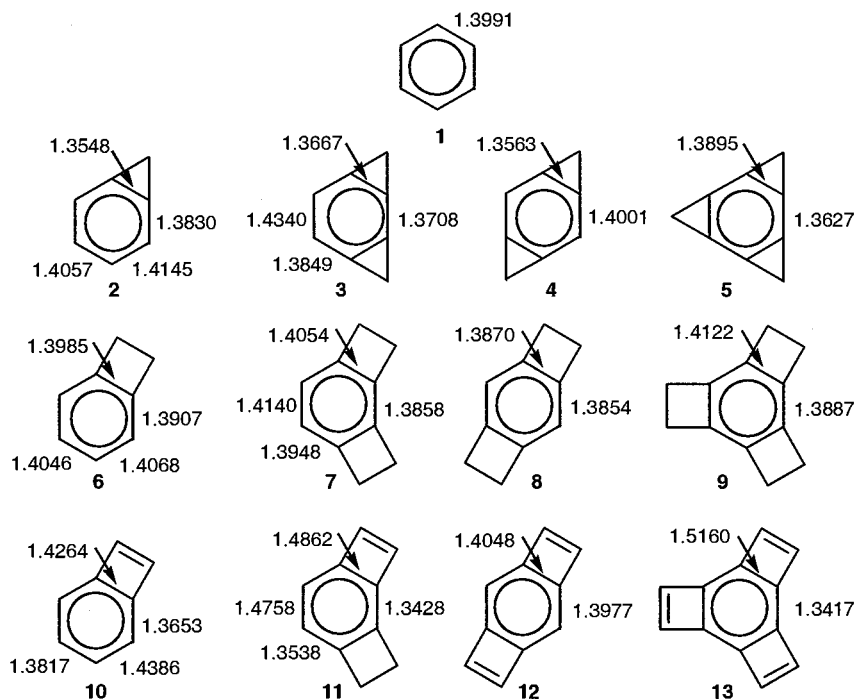


Fig. 1. Selected bond distances (Å) for 1–13.

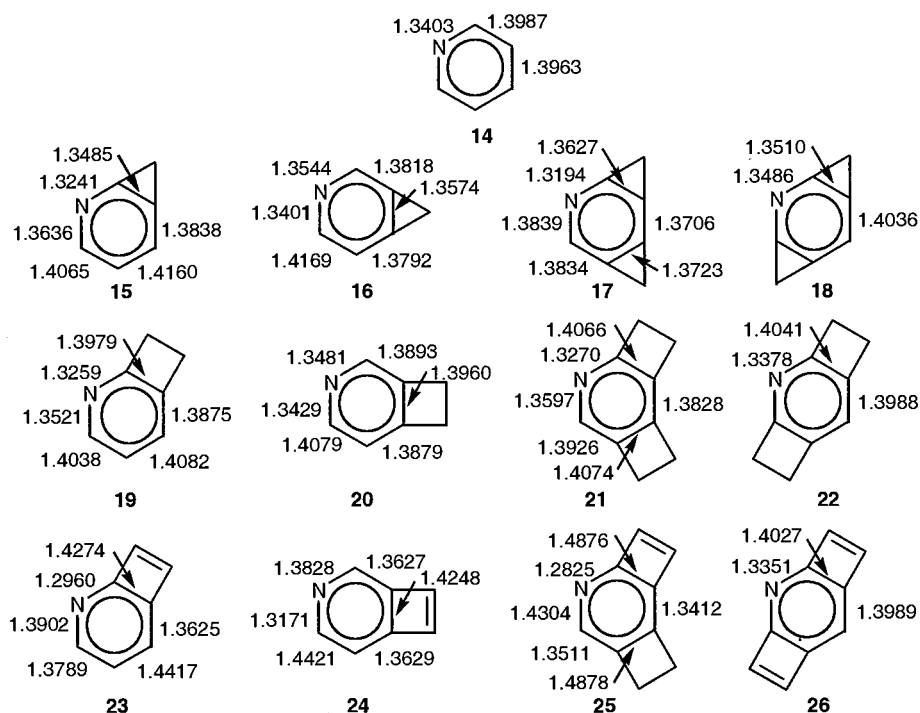


Fig. 2. Selected bond distances (Å) for 14–26.

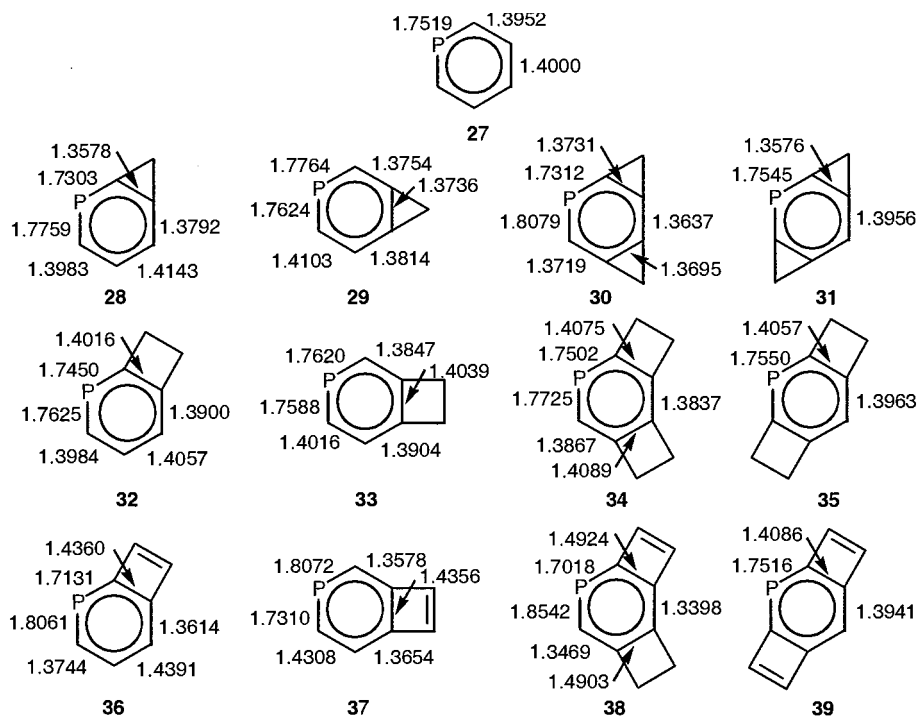


Fig. 3. Selected bond distances (Å) for 27–39.

obtained using the B3LYP electronic energies and the corrected HF ZPEs. Bond distances about the six-member ring (calculated at B3LYP) are shown in Figs. 1–3. NICS [17] values were obtained using the GAIO method and evaluated at the ring critical point, as defined within the ‘atoms in molecules’ [32] procedure. The ring critical point is defined purely by the electron density and resolves the arbitrary decision of evaluating NICS at the geometric center of a ring. All calculations were performed with GAUSSIAN-98 [33].

3. Results and discussion

3.1. Geometries

The distances about the six-member ring of the annulated benzenes **1–13** are shown in Fig. 1. Most of these structures were reported by Stanger at the B3LYP/6-31G* level. These geometries differ insignificantly from the structures obtained here at B3LYP/aug-cc-pVDZ-distances differ by typically less than 0.004 Å. To reiterate the conclusions of Baldrige and Siegel [2] and Stanger [6], SIBL is evaluated by comparing the distances of the bonds inside (*endo*) the small ring with the distance of the bond outside (*exo*) the ring. For **5**, the *endo* distance is 1.3895 Å while the *exo* distance is 1.3627 Å, a difference (or ΔR) of 0.0268 Å. The value of ΔR for **9** is 0.0235 Å. For all of the saturated annulated benzene (**2–9**), the value of ΔR is very small

(see Table 1), indicating a small distortion, but not the dramatic distortion implied by the Mills–Nixon effect. On the other hand, bond alternation is severe in the cyclobutenabenzenes with ΔR as large as 0.1743 Å in **13**. This bond alternation is the result of a π -effect, whereby the geometry reflects an avoidance of the formally antiaromatic cyclobutanadiene fragment(s).

The values of ΔR for the pyridines (**15–26**) and phosphabenzenes (**28–39**) are listed in Table 1 and the bond distances are shown in Figs. 2 and 3, respectively. For simplicity’s sake, ΔR is defined such that the C–N and C–P bond is never considered as the *exo* bond (avoiding the problem of directly comparing the lengths of C–C, C–N and C–P bonds), and for the asymmetric compounds the average of the two *exo* or two *endo* bonds is used.

The value of ΔR for the annulated pyridines and phosphabenzenes parallel their benzene analogues quite closely. The mono- and dicyclopropa-annulated rings actually have an inverse-Mills–Nixon distortion, with the *endo* bond shorter than the *exo* bond, likely originating from the very bent bonds of the three-member ring leading to a shorter internuclear distance. The mono- and dicyclobutana-annulated rings show a small, but distinct, bond alternation. This distortion is best described as SIBL due to the hybridization change necessary to accommodate the small ring. In all of these cases (compounds **2–9**, **15–22** and **28–35**), the magnitude of ΔR is small, always less the 0.05 Å. Lastly, a considerably larger distortion is seen for the cy-

clobutena-annulated systems. This distortion is best understood in terms of the avoidance of the cyclobutanadiene resonance structure. Most importantly, for all of the substitution patterns examined, the trends in the values of DR for the pyridine and phosphabenzene systems parallel those for benzene, indicating that these three core six-member rings are responding to the substituents in the same way.

3.2. Nucleus-independent chemical shift

Magnetic properties of rings are often a key signature for aromaticity. The downfield shifts for exocyclic atoms and upfield shifts of endocyclic atoms are identifiers of aromaticity. However, chemical shifts of aromatic systems can fall in a broad range. Recently, Schleyer has advocated the use of the nucleus-independent chemical shift (NICS) as a probe for aromaticity [17,20,34–36]. Negative values of NICS indicate aromaticity, and within close sets of compounds (such as same ring size), the value of NICS can gauge relative aromaticity. Application of NICS to annulated aromatics is limited. Schleyer et al. report the NICS value (at HF/6-31 + G*) for the six-member ring of **10** is -2.5 and -5.1 for biphenylene [17]. Alkorta and Elguero [19] have investigated NICS at B3LYP/6-31G* of **5** and a number of bicyclo-annulated systems (including **40**) which should express SIBL. The NICS values for all of these are negative, and the values for **9** and **40** are -10.1 and -7.3 . Another study of **40** found the NICS value to be -8.0 at HF/6-31 + G** [18].

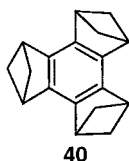


Table 1
 ΔR (Å) for compounds 2–39^a

Compounds	ΔR	Compounds	ΔR	Compounds	ΔR
2	-0.0282	15	-0.0353	28	-0.0214
3	-0.0041	16	-0.0231	29	-0.0048
4	-0.0438	17	-0.0031	30	0.0076
5	0.0268	18	-0.0526	31	-0.0380
6	0.0078	19	0.0104	32	0.0116
7	0.0196	20	0.0074	33	0.0164
8	0.0016	21	0.0242	34	0.0245
9	0.0235	22	0.0053	35	0.0094
10	0.0611	23	0.0649	36	0.0746
11	0.1434	24	0.0620	37	0.0740
12	0.0071	25	0.1465	38	0.1516
13	0.1743	26	0.0038	39	0.0145

^a ΔR defined as the *endo* distance minus the *exo* distance. For compounds with the small rings in the (a,c) positions, the bond between the two rings is used as the *exo* bond. For the pyridine and phosphabenzene compounds, the *exo* bond is never taken as the C–N or C–P bond, and the average of the two *exo* or two *endo* bonds are used for the asymmetric compounds.

The NICS values evaluated at the ring critical point of the six-member ring for compounds **1–39** at B3LYP/ aug-cc-pVDZ are listed in Table 2. The NICS values for benzene, pyridine and phosphabenzene are -7.4 , -6.3 and -6.4 , respectively. All three clearly express aromatic character, but comparison of these values with each other is not a valid operation due to their differing size. All of the compounds with saturated annulated rings have negative NICS values of comparable magnitude to their unsubstituted parents. Therefore, these compounds possess an aromatic central ring, essentially as aromatic as the parents.

The cyclobutena-annulated compounds all have positive NICS values, except for **38** which is just barely negative. The magnitude of these NICS values is quite small, certainly much smaller than antiaromatic compounds like cyclobutanadiene and planar cyclooctatetraene which have values of 27.6 and 30.1 at HF/6-31 + G* [17]. The central six-member ring in these compounds, including the compounds with just one annulated cyclobutenyl ring, show non-aromatic magnetic properties as evaluated by NICS. This is consistent with the geometric parameter ΔR , which also indicated strong bond localization.

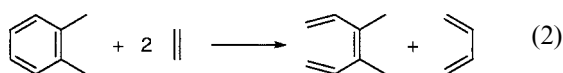
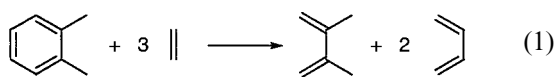
3.3. Resonance energy

Resonance energy quantifies the stability of aromatic species relative to some reference. Homodesmotic and superhomodesmotic reactions are typically employed for this purpose [37,38]. Unfortunately, there is no ideal set of reference compounds, and heteroatoms and substituents complicate matters further. For example, in order to evaluate the RE of *o*-xylene, one has two

Table 2
NICS values (ppm) for compounds 1–39

Compounds	NICS	Compounds	NICS	Compounds	NICS
1	–7.4	14	–6.3	27	–6.4
2	–7.4	15	–5.2	28	–6.1
3	–7.4	16	–6.7	29	–7.0
4	–7.0	17	–6.4	30	–7.4
5	–10.7	18	–5.2	31	–5.9
6	–7.9	19	–6.1	32	–6.6
7	–8.4	20	–6.9	33	–7.2
8	–8.4	21	–6.6	34	–7.4
9	–9.0	22	–6.3	35	–6.8
10	0.0	23	2.0	36	1.1
11	3.6	24	0.9	37	0.2
12	1.3	25	4.7	38	–0.1
13	1.3	26	3.4	39	1.8

choices (Eqs. (1) and (2)) for homodesmotic reactions, depending on the Kekulé structure chosen. The reaction energy is $+33.38 \text{ kcal mol}^{-1}$ for Eq. (1) and $+32.13 \text{ kcal mol}^{-1}$ for Eq. (2). Which is the Eq. (2) correct (or better) value?



A simple solution is to use a 50:50 average of these two Kekulé structures and thus an average of the energies from Eqs. (1) and (2). However, this choice presupposes that the two structures will participate equivalently, a supposition that is opposite the contention of the Mills–Nixon effect and contrary to structural evidence for the cyclobutena-annulated rings. Perhaps a better approach is to use these two methods as extremes, recognizing that the ‘true’ resonance energy lies somewhere in between these limits, with the average taken as an estimate.

Another issue of concern is the choice of reference compound(s). Our approach is to maintain as much structure of the molecule of interest within the references, except for cyclic delocalization. Adopting the principle of conservation of Benson’s group equivalents, [39] reference molecules must contain some delocalization, as a butadiene or hexatriene fragment. The butadiene fragments are in the *cisoid* conformation to mimic their strict *cis* arrangement in 1–39. The annulated rings are also conserved. Therefore, we report in Table 3 the RE for 1–39 using the two homodesmotic methods, which are sketched in Fig. 4. As a baseline, the REs of the parent compounds are $33.35 \text{ kcal mol}^{-1}$

for benzene, $30.82 \text{ kcal mol}^{-1}$ for pyridine and $31.48 \text{ kcal mol}^{-1}$ for phosphabenzene.

Examining the RE for 1–5, one sees a steady decrease with increasing annulation. The RE for cyclopropabenzene 2 is about $6.7 \text{ kcal mol}^{-1}$, suggesting the compound is mildly aromatic. However, further annulation with cyclopropyl rings decreases the stability of the system such that it is less stable than the references. On the basis of energetics, 3–5 are not aromatic, though their geometries and magnetic properties are consistent with aromaticity.

The cyclobutanabenzene 6–9 all possess positive resonance energies, except for 9 where the average of the two methods is only $-0.8 \text{ kcal mol}^{-1}$. Apparently, the four-member ring allows for more delocalization than the three-member ring.

Analysis of the REs of 10–15 requires a great deal of care. For 10–12, method 2 gives a positive RE indicating that the annulated system is more stable than its references. This reflects the extreme instability of the reference compounds, particularly divinylcyclobutadiene, which is formally antiaromatic. A positive RE simply indicates that the annulated system is likely localizing the π -density into the *exo* bonds. Method 1 shows an increasingly more negative RE with annulation, indicating decreasing stability, and the RE of 12 (where there is no ambiguity on the reference due to symmetry) is negative. 10 likely has small aromatic energy stabilization, but the other cyclobutenabenzene 11 have no resonance stabilization.

A similar pattern exists for the annulated pyridines and phosphabenzene. Annulation of pyridine or phosphabenzene with a single three-member ring diminishes the RE, but they still possess resonance stabilization. A second annulation removes any resonance stabilization. Annulation of pyridine or phosphabenzene with a satu-

rated four-member ring reduces the resonance stabilization. However, unlike with the cyclopropa-systems, a second four-member ring can be accommodated with preservation of resonance stabilization. **23** and **26**, like **10**, show some small resonance energy. The other cyclobutena-annulated compounds, while difficult to unambiguously assess, appear to strongly favor the resonance structure having *exo* double bonds and therefore have no resonance stabilization. In all cases, the RE of the phosphabenzene is more positive than the analogously substituted pyridine or benzene.

4. Conclusions

Rather than attempting to quantify the degree of aromaticity, we have examined whether annulated benzenes, pyridines and phosphabenzenes express three properties (lack of bond alternation, negative NICS values, and resonance energy) associated with aromaticity. These properties reflect geometric, magnetic, and energetic manifestations of aromaticity. The first major conclusion is that the nature of the core six-member ring is insensitive to heteroatom substitution. In other words, analogously annulated benzenes, pyridines, and

phosphabenzenes express very similar aromatic properties.

All of the cyclopropa-annulated compounds show very small bond alternation, and large negative NICS values. Previously, the slight bond alternation has been argued as strain-induced bond localization [2,6]. The mono-annulated compounds (**2**, **15**, **16**, **28**, **29**) have positive resonance energies, and therefore are aromatic on all three grounds. The di- and tri-annulated compounds have large negative REs.

All of the cyclobutana-annulated compounds have a greater bond alternation than their cyclopropa-annulated analogues. Again, this is a manifestation of SIBL [2,6]. The alternation is still rather small, being no more than 0.025 Å. They all have large negative NICS values, and so express both magnetic and geometric aromaticity. However, they have positive REs, indicating no energetic stabilization due to delocalization.

The cyclobutena-annulated compounds differ quite dramatically from the other annulated systems. They show substantial bond alternation, evidence for a π -interaction that disfavors the resonance structure containing the cyclobutanadiene fragment [2,6]. Their central six-member ring has positive NICS value, indicative of non-aromatic character. Lastly, single annulated com-

Table 3
Resonance energy^a (kcal mol⁻¹) for compounds **1–39**

Compounds	RE	Compounds	RE	Compounds	RE
1	33.35	14	30.82	27	31.48
2	8.15	15	1.47	28	12.42
	5.33		1.22		11.07
		16	4.31	29	11.85
3	-20.41		3.28		7.56
	-26.06	17	-27.92	30	-11.16
4	-17.82		-29.20		-16.80
5	-48.30	18	-25.69	31	-6.51
	-56.79				
6	25.05	19	20.12	32	25.54
	19.47		18.79		21.09
		20	21.53	33	26.80
7	16.48		16.06		19.45
	5.32	21	10.92	34	20.00
8	12.66		4.12		8.21
9	7.55	22	9.71	35	16.15
	-9.20				
10	4.60	23	-2.54	36	6.21
	27.16		24.25		29.91
		24	1.22	37	8.41
			24.05		26.48
11	-13.64	25	-18.87	38	-7.25
	31.48		30.75		34.53
12	-6.77	26	-11.09	39	-1.80
13	-24.70				
	42.99				

^a RE calculated by Method 1 listed on top, by Method 2 listed at the bottom.

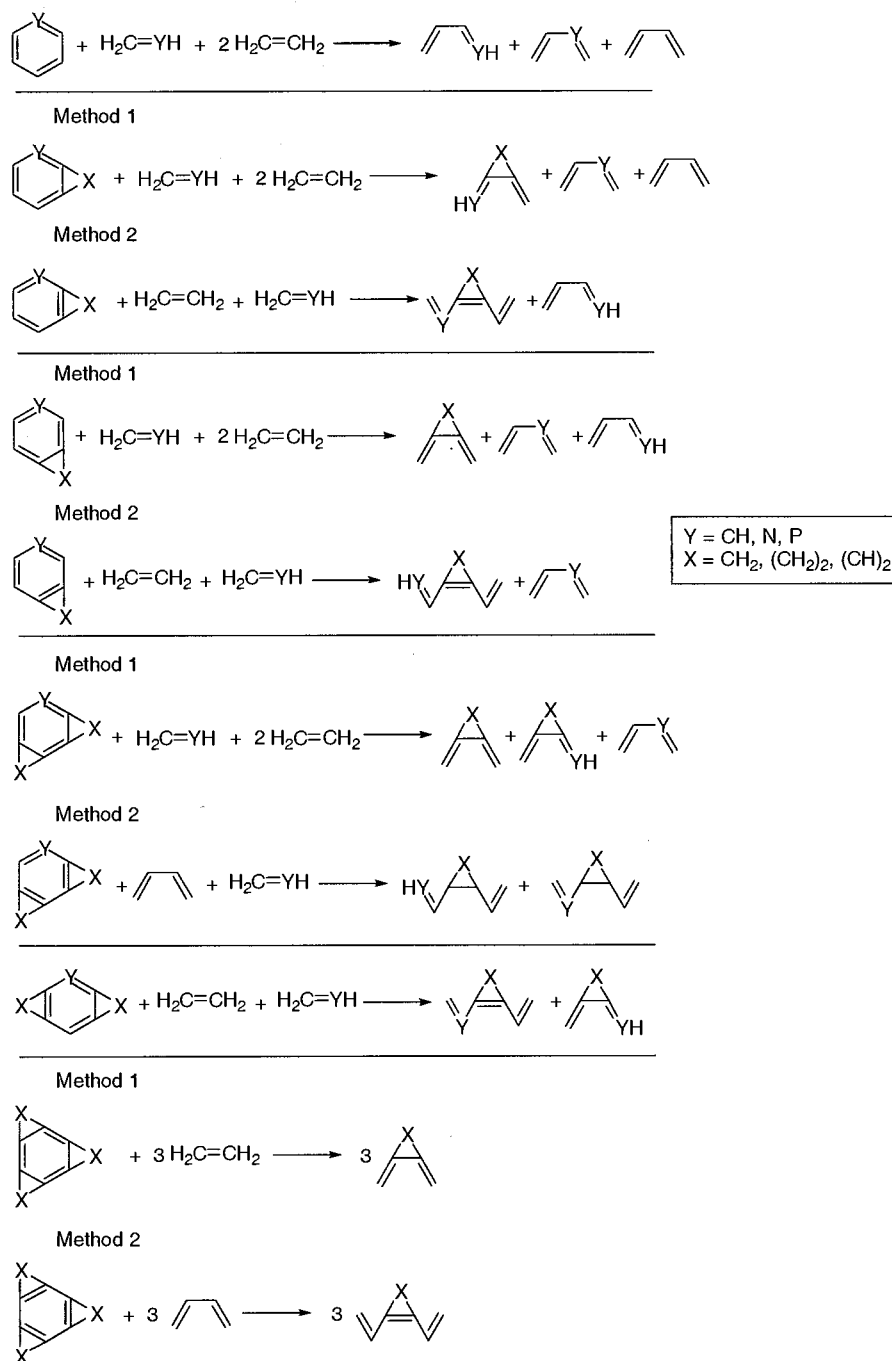


Fig. 4. Homodesmotic reactions used to evaluate resonance energy.

pounds (**10**, **23**, and **36**) have positive RE and the other compounds clearly have no resonance stabilization. The cyclobutena-annulated compounds possess none of these attributes associated with aromaticity.

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