

# Unification of Some Literature Models of Aromaticity: Computational and Conceptual Study of a Set of One-Ring Species<sup>†</sup>

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Numerous models have been suggested for the important concept of aromaticity. In the current study, a set of recently suggested models of aromaticity/homoaromaticity/anti-aromaticity for one-ring species [e.g. pyridazine, oxazole, tropilidene (cycloheptatriene), 1,4-dithiin, [8]-annulene (cyclooctatetraene)] is shown to have a common mathematical framework from which a new, unifying quantitative equation has been derived. Computational and conceptual application is made to a well defined set of one-ring carbocycles.

Aromaticity is one of the oldest and most important concepts in organic chemistry. Aromaticity and related concepts, the ‘hyphenated’ versions such as homoaromaticity and anti-aromaticity, remain an active area for research. Over the past few years, several new and well defined models have been presented based on a variety of geometric, energetic, electronic magnetic and (less well defined) reactivity criteria.<sup>1–5</sup> The current study discusses some of these more recent thermochemically based models<sup>6–9</sup> for aromaticity (and associated versions), as opposed to alternative criteria, and then provides a common mathematical and logical structure for these particular models. All of these models make extensive use of isodesmic reaction reasoning and are based upon relative stabilities within related series of compounds, as they appear from gas-phase experimental and/or computed enthalpies of formation. While initially these models were used mostly for heterocyclic species, the current application is made exclusively for carbocycles. Nonetheless, it is hoped that the currently enunciated conceptual unity both legitimizes the models themselves and extends their future utility.

## The models and their generalization

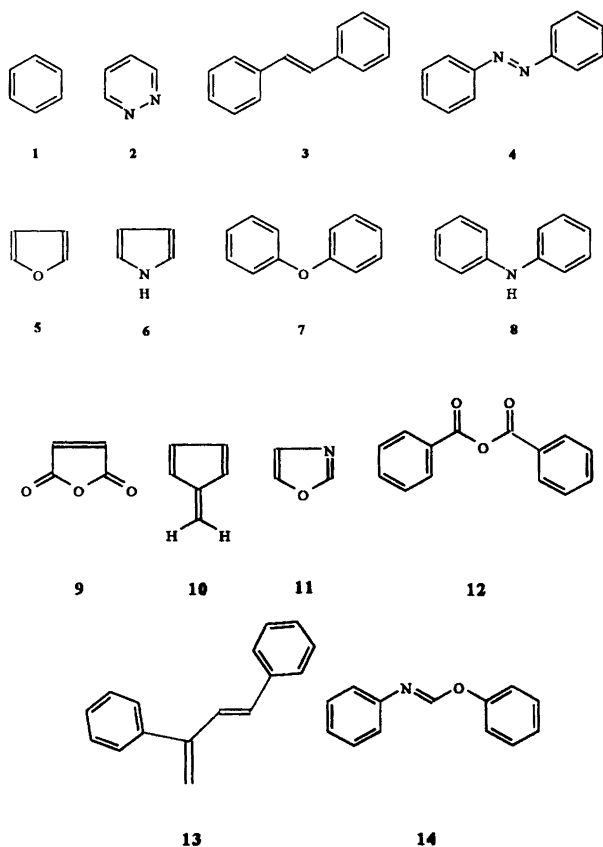
The first model<sup>6</sup> to be discussed here thermochemically contrasted some six-membered ring species such as ben-

zene (1) and pyridazine (2) with the ‘acyclic’ *trans*-stilbene (3) and *trans*-azobenzene (4), respectively, as well as contrasting some five-membered ring species such as furan (5) and pyrrole (6) with diphenyl ether (7), and diphenylamine, (8) respectively. (All of the above ring or ‘cyclic’ species may be described by the line formula *cyclo*-[(CH=CH)<sub>2</sub>X], in which X equalled –CH=CH–, –N=N–, –O and –NH, respectively, and found in a ring. By contrast, the corresponding ‘acyclic species’ were all diphenyl derivatives of the type (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>X, so labelled ‘acyclic’ because the group X is not found in a ring.) The numerical difference of the gas-phase enthalpies of formation of a given cyclic and acyclic species was taken as a quantitative index of the aromaticity of the former.

The second study<sup>7</sup> dealt solely with the aromaticity of five-membered ring species and considerably extended the list of species found in Ref. 6. These different species included maleic anhydride (9), fulvene (10) and oxazole (11), species that could not be written as *cyclo*-[(CH=CH)<sub>2</sub>X] for any choice of X. Enthalpies of formation were compared for these cyclic species with those of benzoic anhydride (12), (*E*)-1,3-diphenyl-1,3-butadiene (13) and N,O-diphenyl formamidate (14), respectively. By contrast, all of the ‘cyclic species’ discussed herein were recognized as *cyclo*-[(CH=CH)X] wherein X = –C(O)OC(O)–, –CH=CH(C=CH<sub>2</sub>)– and –N=CH–O–, while the ‘acyclic species’ were still of the type (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>X, or more correctly, the ‘difference’ of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>X and ethylene. The aromaticity of the cyclic species was taken to be the difference of the enthalpy of formation of this species and of that of the sum of the acyclic species and of ethylene.

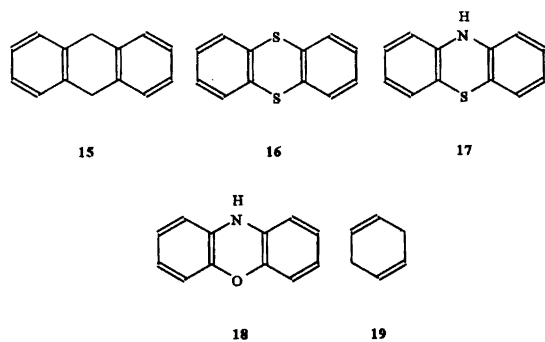
<sup>†</sup>This paper is dedicated to Professor N. L. Allinger on the occasion of his 70th birthday.

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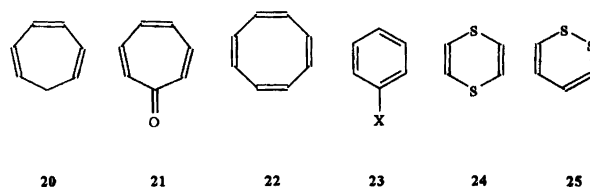


The third paper<sup>8</sup> discussed the energetics of some of the 9,10-dihetero derivatives of 9,10-dihydroanthracene (15). All of these three-ring species were describable by  $X(C_6H_4)_2Y$ : thianthrene (16), phenothiazine (17), phenoxazine (18) and the parent carbocycle (15) have  $X=Y=-S$ ;  $X=-S$ ,  $Y=-NH$ ;  $X=-O$ ,  $Y=-NH$ ; and  $X=Y=-CH_2$ , respectively. Through the process of 'benzo-deannellation' (the conceptual reverse of 'benzo-annellation') to form derivatives of 1,4-cyclohexadiene (19), these 'cyclic species' were then compared with 'acyclic species' of the type  $(C_6H_5)_2X$  and  $(C_6H_5)_2Y$ . The aromaticity of the 9,10-dihetero derivatives of 9,10-dihydroanthracene was thus related to the enthalpies of formation of these three ring species and its acyclic counterparts.

The fourth approach<sup>9</sup> was concerned with tropilidene

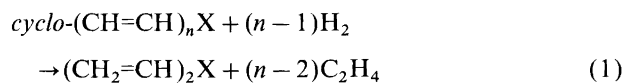


(cycloheptatriene, 20), tropone (21) and cyclooctatetraene (22) and recognized all three carbocycles as being of the type  $[cyclo-(CH=CH)_3X]$  wherein  $X=-CH_2$ ,  $-CO$  and  $-CH=CH-$ , respectively. This study compared these species to the relevant  $(C_6H_5)_2X$ , or more properly the 'sum' of  $(C_6H_5)_2X$  and ethylene, in which the difference of enthalpies of formation of these carbocycles and that of their acyclic analogues and ethylene provided quantitative input into the aromaticity of the ring species.



It may be asked what are the conceptual interrelations of these just enunciated approaches to the understanding of aromaticity, save a relation to diphenyl derivatives. The current paper commences by providing such a unifying link between all of these studies.

Consider the first, second and fourth models. We start by 'reversing' the earlier use of the phenyl-vinyl thermochemical equivalence,<sup>10-12</sup> i.e. the difference of the gas-phase enthalpies of formation of  $C_6H_5X$  (23) and  $CH_2=CHX$  is essentially independent of  $X$ . As such, we compare the various 'cyclic species' with divinyl derivatives rather than the experimentally more feasible (stable, unreactive, conveniently isolable) phenyl species. These three models thus compare  $cyclo-(CH=CH)_nX$  with  $(CH_2=CH)_2X$  either directly ( $n=2$ , model no. 1), with an additional equivalent of  $C_2H_4$  as a reactant ( $n=1$ , model no. 2) or as an additional product ( $n=3$ , model no. 4). Recognizing that the enthalpy of formation of  $H_2$  precisely (by definition, in fact, at all temperatures) equals 0.0 allows us to use this diatomic species as a reactant or product without any numerical thermochemical consequence. Accordingly, the enthalpy change associated with models 1, 2 and 4, the putative aromaticity of  $cyclo-(CH=CH)_nX$  for  $n=2$ , 1 and 3, can be rewritten as the enthalpy of the formal, unique and also balanced reaction



for any  $X$  one chooses.

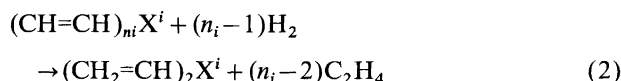
What does one do if there are more than one group  $X$  in a given molecule? By use of the analyses found in Ref. 7 (model no. 2),  $-C(O)OC(O)-$  defines a group  $X$ : by studies 1 and 4 (Refs. 6 and 9), so can  $-CH=CH-$  define a group. By saying there is more than one group, we are also saying that there are more than one  $(CH=CH)_nX$  units in the molecule of interest (i.e. with  $n \neq 0$ ). Such a multi-group molecule may be formally

written

$$\text{cyclo-} \sum_{i=1}^N (\text{CH}=\text{CH})_{ni} X^i,$$

e.g. 1,4-dithiin (**24**) has  $N=2$ ,  $n_1=n_2=1$ ,  $X^1=X^2=\text{S}$  where the isomeric 1,2-dithiin (**25**) has  $n=2$  and  $X=-\text{SS}-$  and so is recognized as having  $N=1$ ,  $n_1=n=2$ ,  $X^1=X=-\text{SS}-$ .

For each individual unit of the ring  $(\text{CH}=\text{CH})_{ni} X^i$ , i.e. for each individual  $i$ , we could write



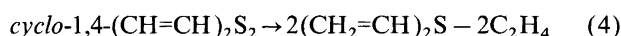
and so, for the entire ring species:

$$\begin{aligned} \text{cyclo-} \sum_{i=1}^N (\text{CH}=\text{CH})_{ni} X^i + \sum_{i=1}^N (n_i - 1) \text{H}_2 \\ \rightarrow \sum_{i=1}^N [(\text{CH}_2=\text{CH})_2 X^i + (n_i - 2) \text{C}_2\text{H}_4] \end{aligned} \quad (3)$$

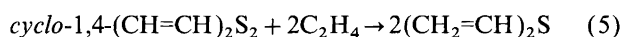
where

$$\sum_{i=1}^N (\text{CH}=\text{CH})_{ni} X^i$$

is recalled to be the compound of interest. For 1,4-dithiin:



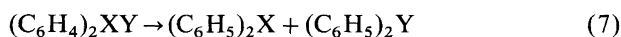
or equivalently (and more conventionally)



Dibenzoannulation of the dithiin, transforming the vinyl groups to phenyls, and ignoring the two ethylene molecules because they are common to the dithiin and other dihetero derivatives of 1,4-cyclohexadiene, gives the new reaction



or more generally



We recognize this as the third model where we allow for the possibility  $X=Y=\text{CH}_2$  as well.

Admittedly, there is the question of the benzoannulation and benzo-deannulation, and how the aromaticity or anti-aromaticity depends on these two affixed rings. For non-aromatic or mildly anti-aromatic rings the thermochemical effect is seemingly generally quite small,<sup>13</sup> and we will continue to assume so here. It is thus seen that all four models of aromaticity presented in Refs. 6–9 are all specific examples of the common relation, eqn. (3). Nonetheless, acknowledging the conceptual and calorimetric virtues of phenyl over vinyl species as explicitly discussed in Refs. 6 and 7, we would thus write

$$\begin{aligned} \sum_{i=1}^N (\text{CH}=\text{CH})_{ni} X^i + \sum_{i=1}^N (n_i - 1) \text{H}_2 \\ \rightarrow \sum_{i=1}^N [(\text{C}_6\text{H}_5)_2 X^i + (n_i - 2) \text{C}_2\text{H}_4] \end{aligned} \quad (8)$$

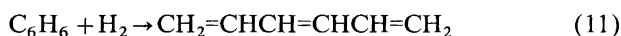
Balancing gives

$$\begin{aligned} \left[ \sum_{i=1}^N (\text{CH}=\text{CH})_{ni} X^i \right] + 2N\text{C}_6\text{H}_6 \\ \rightarrow \sum_{i=1}^N [(\text{C}_6\text{H}_5)_2 X^i + n_i \text{C}_2\text{H}_4 + (1 - n_i) \text{H}_2] \end{aligned} \quad (9)$$

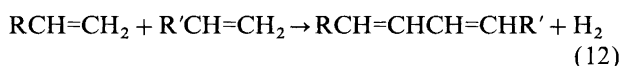
Finally, we recall some studies in which various  $[x]$ -annulenes were compared to ethylene<sup>14</sup> and to [6]-annulene, i.e. benzene (**1**) itself.<sup>14,15</sup> Without loss of generality, let us apply our  $[a]$ -annulene/ethylene analysis to the case of benzene itself. We may choose  $X=-\text{CH}=\text{CH}-$  and let  $n=2$ , reminiscent of the first study above. This gives us the equation



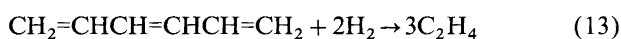
where the three  $\text{C}_6\text{H}_6$  on the left are the [6]-annulene of interest and the two benzenes as found in eqn. (9) when there is but one X group. Use of the aforementioned phenyl–vinyl equivalence returns us to 1,3,5-hexatriene via the reaction



It was earlier suggested<sup>16,17</sup> that the reaction



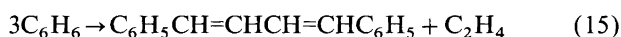
is generally nearly thermoneutral. As such, the theoretically plausible<sup>16,17</sup> and (from the enthalpy of formation of 1,3,5-hexatriene<sup>18</sup>) directly ascertained near thermoneutrality of the reaction



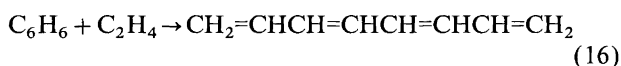
results in the formal reaction



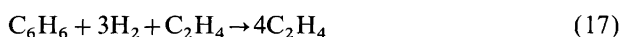
Alternatively, we can let  $X=-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$  and let  $n=1$ , reminiscent of the second study above and so derive



Following the above reasoning we would derive



There is no measured enthalpy of formation for the product of eqn. (16), 1,3,5,7-octatetraene. However, assuming linearity in the series ethylene, 1,3-butadiene, 1,3,5-hexatriene and 1,3,5,7-octatetraene or near thermoneutrality for ‘any’ R and R’ in eqn. (12) results in



or, upon simplification, eqn. (14), once again.

The comparison with [6]-annulene is tautological (i.e. it involves an identity reaction), and thus has no new information content for benzene. However, for general  $[x]$ -annulenes, it follows quite directly from the comparison with ethylene. After all, all of the various  $[a]$ -annulenes may be rewritten  $(\text{CH}=\text{CH})_{a/2}$ , and so the

earlier formal reaction



follows from comparing  $x/2$  CH=CH groups in different environments: all of the extra species we would write as part of eqn. (9), i.e. the additional  $C_6H_6$ ,  $(C_6H_5)_2X$ ,  $C_2H_4$  and  $H_2$  appear in equal numbers on the two sides of the reaction and so cancel.

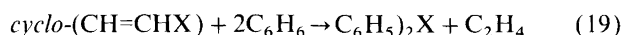
Before presenting the application of our unifying equation at some length, it is perhaps desirable to discuss two largely conceptual, if not philosophical, points. The first point is the need for phenyl derivatives in lieu of their vinyl counterpart. We acknowledge that the latter, in principle, is more direct in terms of our model. The vinyl group is also quite 'small', and so is amenable to quantum chemical calculation and derived energetics. It may be argued that for such species measurements are superfluous as well as often unrealizable. Finally, there are structural features that are not shared between the two such as a pair of *ortho*-hydrogens of the two phenyl groups being really quite near, while the divinyl compound can escape the derived repulsion by being in an extended W configuration as opposed to the likewise strained U configuration. The second point concerns this strain and its presence in many, if not most, of the cyclic species of interest. While both points are acknowledged, we nonetheless generally prefer to accept experimentally measured quantities over those that are calculated and, having adopted this philosophy, will generally not try to disentangle the often competing roles of strain and aromaticity even in one-ring species that are considered in the current study.

### Application to one-ring carbocycles

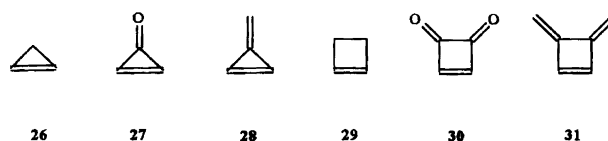
We commence the discussion of aromaticity with a variety of one-ring carbocycles, all of which may be described as of the generic type  $(CH=CH)_mX_n$  where  $X = -CH_2$ ,  $-CO$  and  $-C=CH_2$  ( $m = 1, 2$  and  $3$ ;  $n = 1$  and  $2$ ). In what follows we accept the recommended enthalpies of formation of these species from the recent, largely computational, theoretical paper,<sup>19</sup> which also followed this organizational structure. That paper provided a uniform level of calculation (MP2/6-31G\*\*//MP2/6-31G\*, zero-point energies at HF/6-31G\*),<sup>20</sup> computational protocol<sup>21,22</sup> and thermochemical understanding for all of the species above described. Likewise, in the name of uniformity, all other (but unreferenced) enthalpies of formation given in this paper are taken from the common archival Ref. 23 unless otherwise explicitly said: we find generally theory and experiment are in good agreement for the cyclic species of direct interest to the current study. Cases of alternative references and/or poor theory/experimental agreement will be cited directly when the compound is discussed.

The first three species we discuss are the cyclopropenoid  $m=n=1$  as well as  $N=1$  for which we consider

the formal reaction



For  $X = -CH_2$  (**26**) the enthalpy of formation of  $(C_6H_5)_2CH_2$  is derived by summing the value for the solid from Ref. 23 with the enthalpy of sublimation determined in Ref. 24. (This procedure was also used in Ref. 7.) The other entries are taken from Ref. 23, giving a reaction energy of  $-255$  kJ mol<sup>-1</sup>. For  $X = -CO$  (**27**) we deduce the energy of reaction of  $-187$  kJ mol<sup>-1</sup> based upon the enthalpy of formation of cyclopropanone from Ref. 19. For  $X = -C=CH_2$  (**28**), we find an exothermicity of 290 kJ mol<sup>-1</sup> if we use the recommended 'experimental' measurement<sup>25</sup> of the enthalpy of formation of methylenecyclopropene (**28**) of 423 kJ mol<sup>-1</sup> value, and an exothermicity of 245 kJ mol<sup>-1</sup> using the very disparate calculated<sup>19</sup> value of 378 kJ mol<sup>-1</sup>. There are several immediate questions. Why is reaction (19) so exothermic for all three species? Why, in particular, is it so exothermic for cyclopropanone (**27**): is it not aromatic? Why are the theoretical and experimental values for the enthalpy of formation of methylenecyclopropene so different, and dare we choose the theoretical value over the experimental?

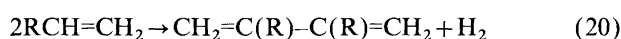


That all three reactions are so exothermic is less surprising than it first seems: we recall<sup>26</sup> the considerable strain energy of cyclopropane ( $>100$  kJ mol<sup>-1</sup>) and the increase derived from the presence of trigonal carbons (ca. 50 kJ mol<sup>-1</sup>/carbon) that contributes to the relative destabilization of all cyclopropene derivatives (cf. Ref. 27). That is, had it not been for this three-membered ring strain energy and the additional trigonal carbon induced destabilization, we would have found eqn. (19) to be ca. 35 kJ mol<sup>-1</sup> exothermic for cyclopropene. This value is not insignificant, but at least it is much smaller than before. The amended value is ca. 60 kJ mol<sup>-1</sup> endothermic for cyclopropanone. Equivalently, cyclopropanone enjoys some 95 kJ mol<sup>-1</sup> stabilization over cyclopropene or nearly 50 kJ mol<sup>-1</sup> per  $\pi$  electron. By contrast, benzene only has ca. 30 kJ mol<sup>-1</sup> stabilization per  $\pi$ -electron.

We doubt that methylenecyclopropene would have less stabilization than the parent cyclopropene. Correcting for the additional trigonal carbon reduces the exothermicity to ca. 195 and 240 kJ mol<sup>-1</sup> depending whether we choose, respectively, the theoretical or experimental value for the enthalpy of formation of methylenecyclopropene. The choice of the former number places

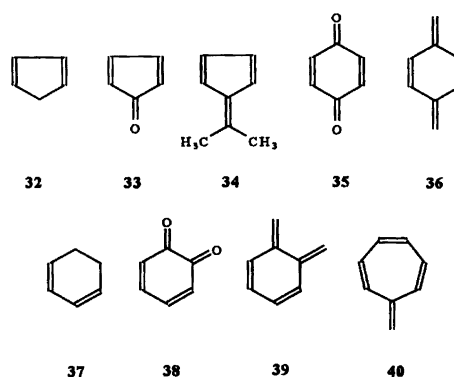
the stabilization of methylenecyclopropene between that of cyclopropene and cyclopropenone, an altogether plausible and so satisfying result. Choosing the latter suggests there is no stabilization for methylenecyclopropene, a conclusion we are unwilling to make. We therefore prefer the theoretically determined enthalpy of formation in this case and note that enthalpies of formation determined from the use of appearance energies must be investigated carefully before they are accepted. Of course the same applies to any enthalpy of reaction measurement where we additionally note that 'more reliable' enthalpy of combustion or of hydrogenation measurements are not available in the current case.

We now turn to the cyclobutenoid  $(\text{CH}=\text{CH})\text{X}_2$  with  $m=1$ ,  $n=2$ , and  $N=1$ . Even though we write  $\text{X}_2$  here to be in accord with the formalism in Ref. 19, by the definition of the current paper these species also have but one X group, admittedly larger and more complicated  $-\text{CH}_2\text{CH}_2-$  (**29**),  $-\text{C}(\text{O})\text{C}(\text{O})-$  (**30**) or  $-\text{C}(\text{CH}_2)\text{C}(\text{CH}_2)-$  (**31**). As such eqn. (10) may be used directly to find exothermicities of 127 and 90  $\text{kJ mol}^{-1}$  for the first two cases using experimentally measured enthalpies of formation for cyclobutene and 3-cyclobutene-1,2-dione. Concerning the third of these species we know of no experimentally measured enthalpy of formation for the necessary 2,3-diphenyl-1,3-butadiene,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_2)\text{C}(\text{CH}_2)\text{C}_6\text{H}_5$ . We hesitate to estimate this number, since we know the enthalpies of formation of no 2,3-disubstituted 1,3-butadienes except the methyl and *tert*-butyl cases, for which reactions (20) are, respectively, nearly thermoneutral and 40  $\text{kJ mol}^{-1}$  endothermic. These latter values are simply too disparate to be useful at this time.

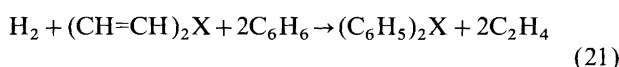


We are quite confident of the values of the enthalpy of formation of cyclobutene<sup>23</sup> and cyclobutenedione,<sup>19</sup> and conclude that cyclobutenedione is stabilized by some 35  $\text{kJ mol}^{-1}$  relative to cyclobutene. This demonstrates that there does not appear to be any destabilization in four-membered rings associated with the introduction of trigonal carbons (as opposed to three-membered rings).<sup>27</sup> We also find that reaction (20) has nearly identical enthalpies for cyclopropene and cyclobutene when the 50  $\text{kJ mol}^{-1}$  correction for trigonal carbons in the former is made. Interestingly, the strain energies of the saturated cyclopropane and cyclobutane are nearly the same,<sup>27-29</sup> a combined result of CH bond eclipsing, 1,3-repulsions, angle strain, relative C-H bond strengths and ring atom hybridization.

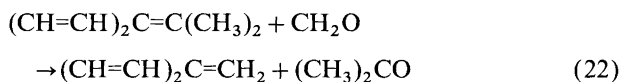
The next series of compounds is the cyclopentadienoid species  $(\text{CH}=\text{CH})_2\text{X}$  with  $m=2$ ,  $n=1$ ,  $N=1$  for which  $\text{X}=\text{CH}_2$  (**32**),  $\text{CO}$  (**33**) and  $\text{CCH}_2$  (**10**). We here distinguish these species from the 1,2-cyclohexadienoid  $(\text{CH}=\text{CH})_2\text{X}_2$  (since the related 1,4-cyclohexadienoid species would have  $m=n=N=2$ ). The relevant cyclo-



pentadienoid reaction is



For  $\text{X}=\text{CH}_2$  (**32**), this reaction is 42  $\text{kJ mol}^{-1}$  exothermic, a value that is very nearly identical to those for  $\text{CO}$  (**33**) and  $\text{CCH}_2$  (**10**), which are 36 and 39  $\text{kJ mol}^{-1}$ . It is interesting to note that the reaction enthalpies of two hydrocarbon cases are nearly the same. At the very least we are forced to conclude that fulvene is not more aromatic than cyclopentadiene (**32**). This violates our earlier conclusion in Ref. 7, but note that our earlier suggested value for the enthalpy of formation of fulvene was quite seriously in error, our having earlier assumed thermoneutrality for the transmethylation reaction

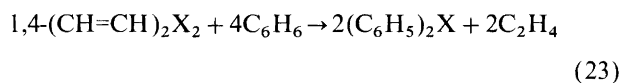


We note that the recommended enthalpies of formation of 6,6-dimethylfulvene are significantly different in the archival Ref. 23 and more recent primary (hydrogenation calorimetry) study.<sup>30</sup> It remains entirely plausible, however, that 6,6-dimethylfulvene (**34**) is more aromatic than fulvene, the two methyl groups stabilizing the fulvene as they do also the carbonyl. In line with this one may note that fulvene is generally considered to be much more fragile/labile than its 6,6-dimethyl derivative. In line with this, fulvene is not a commercial product, whereas 6,6-dimethylfulvene is readily available.<sup>31</sup>

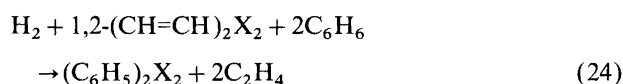
Admittedly, the large error bar (36  $\text{kJ mol}^{-1}$ ) in the  $\text{X}=\text{CO}$  case confounds a definitive comparative analysis of all three species. It allows for the possibility that cyclopentadienone is stabilized compared to fulvene, but that seems most unreasonable. Simultaneously, it allows for the possibility that cyclopentadienone (**33**) is considerably destabilized compared to cyclopentadiene and fulvene. Admitting our prejudices based on the ease of isolability of cyclopropenone but not of cyclopentadienone, we assume this last option where we consider cyclopentadienone to be considerably less stable thermodynamically than cyclopropenone. As such, we now tentatively suggest the 'extreme'  $32+36=68$   $\text{kJ mol}^{-1}$  enthalpy of formation of cyclopentadienone.

Interestingly, our analysis of fulvene allows for a better understanding of its isomer, 3,4-dimethylenecyclobutene (31). The difference of the enthalpies of formation of dimethylenecyclobutene and cyclobutene, per exocyclic methylene group, is nearly identical to the difference of fulvene and cyclopentadiene. We thus conclude that neither non-benzenoid  $C_6H_6$  isomer enjoys any aromatic stabilization.

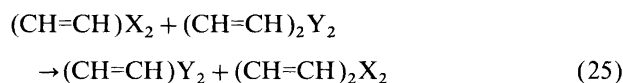
Consider now the isomeric cyclohexadienoid  $(CH=CH)_2X_2$  for both the 1,4- and 1,2- $X_2$  (*p*- and *o*-isomers) with  $X=CH_2$ , CO and  $CCH_2$  and note there is no benzoannulation. These species have  $m=n=2$ , and  $N=2$  and 1, respectively. Let us start with the 1,4-species unto themselves, for which we consider the following equation:



For  $X=CH_2$  (19), CO (35) and  $CCH_2$  (36), respectively, we find this reaction to be exothermic by 21  $\text{kJ mol}^{-1}$  (cf. Ref. 17), endothermic by 8  $\text{kJ mol}^{-1}$  and 59  $\text{kJ mol}^{-1}$  endothermic. We find the results surprising, since 1,4-cyclohexadiene (19) would have been thought to be nonstabilized and *p*-benzoquinone (35) destabilized. For *p*-xylylene (36) it was earlier acknowledged<sup>19</sup> that literature experimental values are conflicting and confusing (i.e. values of 200, 230 and 250  $\text{kJ mol}^{-1}$  may be found). While current computational theory has seemingly not provided definitive clarification, our earlier suggested value of 207  $\text{kJ mol}^{-1}$  is still recommended. For the 1,2-isomers, we can use eqn. (21) with  $X_2=-CH_2CH_2-$  (37),  $-C(O)C(O)-$  (38) and  $-C(CH_2)C(CH_2)-$  (39), although this equation is somewhat more easily used when rewritten as



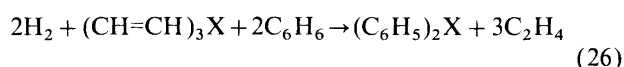
for these latter choices of X. For  $X=CH_2$  and CO we find exothermicities of 22 and 26  $\text{kJ mol}^{-1}$ , respectively. The significant exothermicity for  $X=CH_2$  is still surprising. However, that the value is nearly identical to that for its 1,4-isomer suggests the two isomeric cyclohexadienes are comparably 'normal'. The considerably greater exothermicity for eqn. (24) for *o*- over *p*-benzoquinone, i.e. (38) over (35), is consistent with the greater stability of the *para* form. The omission of a comparison for the remaining  $X=-C(CH_2)C(CH_2)-$  arises from the absence of enthalpy of formation data for 2,3-diphenyl-1,3-butadiene, as earlier noted in the discussion of species of the type  $(CH=CH)X_2$ . Consider now the following formal reaction



The exothermicity of this reaction is the difference of the stabilization of the cyclobutenoid and cyclohexadienoid species and bypasses the need for thermochemical data

on the individual  $(C_6H_5)_2X_2$  species such as the above diphenylbutadiene. For  $X=CCH_2$ ,  $Y=CH_2$  this reaction is exothermic by 50  $\text{kJ mol}^{-1}$ , suggesting that *o*-xylylene (39) is significantly stabilized relative to 3,4-dimethylenecyclobutene (31). This is a surprising result: we would have expected considerably closer to thermoneutrality had both  $X=CCH_2$  species been 'normal'. A comparable exothermicity, ca. 40  $\text{kJ mol}^{-1}$ , is found for  $X=CO$ ,  $Y=CCH_2$ , which is an even more surprising result, since considerable endothermicity would have been expected had the cyclobutenedione been stabilized (cf. aromatic) and the *o*-quinone destabilized (cf. antiaromatic).

We close this section with a discussion of the cycloheptatrienoid  $(CH=CH)_3X$  ( $m=3$ ,  $n=1$ ,  $N=1$ ) for  $X=CH_2$ , CO and  $CCH_2$  [species (20), (21) and (40)] and eqn. (26):



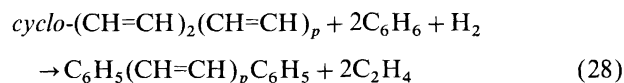
This reaction is, respectively, 37  $\text{kJ mol}^{-1}$  exothermic, 3  $\text{kJ mol}^{-1}$  endothermic and either ca. thermoneutral or 28  $\text{kJ mol}^{-1}$  exothermic, depending on whether the 'experimental' or 'theoretical' value for the enthalpy of formation of heptafulvene with  $X=CCH_2$  is chosen. We expect some conjugative stabilization of this last species, but not so much as with tropone, species (21), and so the theoretically derived 28  $\text{kJ mol}^{-1}$  of stabilization appears more plausible. Tropone, in turn, is less delocalized than cyclopropenone, another reasonable result.

### Benzene and cyclooctatetraene

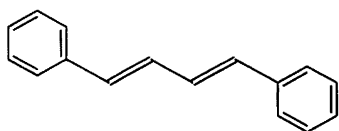
Our next step is to contrast the [*x*]-annulenes, benzene and cyclooctatetraene (22). For the understanding of these conjugated hydrocarbons, there are several approaches we may take from the above analyses. The simplest is the use of eqn. (18) with explicitly the choice of  $x=8$ . This gives us eqn. (27)



for which an exothermicity of 185  $\text{kJ (mol-C}_8\text{H}_8)^{-1}$  is found. Alternatively, an exothermicity of 139  $\text{kJ (mol-C}_6\text{H}_6)^{-1}$  may be deduced. Both values are large and suggest benzene is significantly stabilized and/or cyclooctatetraene is significantly destabilized. That the stoichiometry of eqn. (26) has different numbers of molecules for the two hydrocarbons (1 and 8/6) makes it difficult to ascribe a single number for the relative stabilization or destabilization for these species: do we accept the number as is or multiply it by 6/8? However, we may use eqn. (10) in the form of

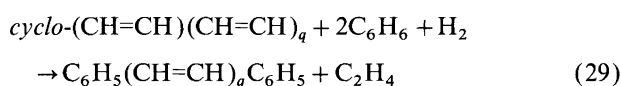


for the cases of  $p=1$  and 2. The gas-phase enthalpy of formation of 1,4-diphenyl-1,3-butadiene (41) is not available from experiment. [As noted in Ref. 14, there are in fact no reliable gas-phase enthalpies of formation of any



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1, $\omega$ -diphenylpolyenes save for *cis*- and *trans*-stilbene, and even for these mono-olefins, there is some acknowledged uncertainty as to the difference of their enthalpies of formation.<sup>32]</sup> However, it should not be too different from that found assuming eqn. (12) is valid for  $R=R'=C_6H_5$ : our recommended value is  $301 \text{ kJ mol}^{-1}$ . Reaction (27) with  $p=1$  and  $2$  is, respectively,  $93 \text{ kJ mol}^{-1}$  endothermic and  $55 \text{ kJ mol}^{-1}$  exothermic. We may say that benzene with  $p=1$  is stabilized relative to cyclooctatetraene with  $p=2$  by  $93 - (-53) = 146 \text{ kJ mol}^{-1}$ . Equation (15) can likewise be modified



for the cases of  $q=2$  and  $3$ . The gas-phase enthalpy of formation of 1,6-diphenyl-1,3,5-hexatriene is not available from experiment.<sup>23</sup> In that our earlier analysis suggested<sup>49</sup> that the enthalpy of formation of a nonaromatic  $-\text{CH}=\text{CH}-$  unit is ca.  $56 \text{ kJ mol}^{-1}$ , the desired triene enthalpy of formation is ca.  $357 \text{ kJ mol}^{-1}$ . Reaction (28) with  $q=2$  and  $3$  is, respectively,  $104 \text{ kJ mol}^{-1}$  and  $43 \text{ kJ mol}^{-1}$  endothermic corresponding to a stabilization of  $104 - (-43) = 147 \text{ kJ mol}^{-1}$  of benzene over cyclooctatetraene.

Insight into the relative energies of benzene and cyclo-

octatetraene may be gained from quantum chemical computations. We now report results derived from our calculations with the same protocol<sup>10</sup> as above, namely, MP2/6-31G\*//MP2/6-31G\*, zero-point energies at HF/6-31G\*. At this level, the zero-point energies for benzene and cyclooctatetraene are  $0.10767$  and  $0.14339$  a.u. and the corresponding total energies are  $-231.45773$  and  $-308.52706$  a.u.]. The zero point energy of benzene is within  $10 \text{ kJ mol}^{-1}$  of that of the other  $C_6H_6$  isomers, fulvene and 3,4-dimethylenecyclobutene, while that of cyclooctatetraene is within  $5 \text{ kJ mol}^{-1}$  of its isomers, heptafulvene and the xylylenes. The greater spread of the former series is, however, not due to the aromaticity of benzene, for we find the zero point energy of cyclooctatetraene is less than  $1 \text{ kJ mol}^{-1}$  different from  $8/6$  of that of benzene. (Alternatively said, there is less a  $1 \text{ kJ mol}^{-1}$  difference between cyclooctatetraene and  $4/3$  benzene, where the new count is of  $-\text{CH}=\text{CH}-$  units as opposed to number of carbon atoms.)

The C-C bond alternation of cyclooctatetraene confirms the non-aromatic character of this species. Our structural results are in excellent agreement with the electron diffraction data,<sup>33</sup> except for the dihedral angle CCCC: The structural parameters are found to be (first number being the experimental value)  $R(\text{C}=\text{C})$ ,  $1.340$ ,  $1.323 \text{ \AA}$ ;  $R(\text{C}-\text{C})$ ,  $1.476$ ,  $1.478 \text{ \AA}$ .  $R(\text{C}-\text{H})$ ,  $1.100$ ,  $1.079 \text{ \AA}$ ;  $A(\text{CCC})$ ,  $126.1$ ,  $126.0^\circ$ ;  $A(\text{CCH})$ ,  $117.6$ ,  $117.9^\circ$ ;  $D(\text{CCCC})$ ,  $43.1$ ,  $68.3^\circ$

Let us now see what calculational theory predicts for the interrelating reaction, eqn. (27). The predicted enthalpy of reaction is ca.  $218 \text{ kJ mol}^{-1}$ , some  $30 \text{ kJ mol}^{-1}$  different from experiment. In that there is

Table 1. Summary of herein recommended enthalpies of formation<sup>a</sup> (in  $\text{kJ mol}^{-1}$ ) and comments.

Species	No.	Enthalpy	Comments
Cyclopropene	26	277	Archetypical nonaromatic species
Cyclopropenone	27	130	Correcting for $\text{sp}^2$ carbons, has more aromatic stabilization than benzene per $\pi$ electron
Methylenecyclopropene	28	378	Less aromatic than cyclopropenone
Cyclobutene	29	157	Archetypical nonaromatic species
Cyclobutenedione	30	-78	Less aromatic than cyclopropenone
Dimethylenecyclobutene	31	336	Nonaromatic
Cyclopentadiene	32	137	Archetypical nonaromatic species
Cyclopentadienone	33	68	Considerably destabilized relative to cyclopropenone
Fulvene	10	224	Nonaromatic
Benzene	1	83	Archetypical aromatic species
1,4-Cyclohexadiene	19	104	Archetypical nonaromatic species
<i>p</i> -Benzoquinone	35	-123	Comparable to cyclobutenedione
<i>p</i> -Xylylene	36	207	Comparable to <i>p</i> -benzoquinone
1,3-Cyclohexadiene	37	104	Archetypical nonaromatic species
<i>o</i> -Benzoquinone	38	-90	Destabilized compared to <i>p</i> -isomer
<i>o</i> -Xylylene	39	235	More delocalized than dimethylenecyclobutene
Cycloheptatriene	20	184	Archetypical nonaromatic species <sup>b</sup>
Tropone	21	44	Less delocalized than cyclopropenone
Heptafulvene	40	265	Less delocalized than tropone
Cyclooctatetraene	22	296	Considerably destabilized relative to benzene

<sup>a</sup>See text for source of values. The various compounds are arranged in terms of increasing ring size, with keto derivatives taking precedence over corresponding *exo*-methylene derivatives. <sup>b</sup>In Ref. 9 it was suggested this species 'enjoys' homoaromatic stabilization. Quantitative stabilization for this and other species in terms of our model is under investigation.

some uncertainty in the measured enthalpies of formation of all of the other  $C_6H_6$  and  $C_8H_8$  species, we will not attempt to ascribe 'blame' for this discrepancy by comparing calculated and experimental benzene/(general  $C_6H_6$ ) and cyclooctatetraene/(general  $C_8H_8$ ) isomerization enthalpies. Nonetheless, the message is unequivocal from experiment and both calculational and conceptual theory: benzene is much more stable (read aromatic) than cyclooctatetraene. The result might not be new but it is nonetheless comforting.

## Conclusion

In summary, we find that there is a unifying principle and generalized equation behind several recent thermochemical models for aromaticity. Application is made to gain an increased qualitative and quantitative understanding of the energetics of a series of one-ring carbocyclic species,  $(CH=CH)_mX_n$ , where  $X = -CH_2$ ,  $-CO$  and  $-C=CH_2$  and  $m = 1, 2$  and  $3$ ,  $n = 1$  and  $2$ , and also  $(CH=CH)_m$ , where  $m = 3$  and  $4$ . Our numerical results derived from recent *ab initio* calculations are generally in reasonable accord with experiment and intuition on these compounds, although there are some interesting surprises. To aid the reader, the collected enthalpies of formation of the key carbocyclic species in the present work are found in Table 1, in which there are also brief comments on the degree of aromaticity for the systems considered in the present work.

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