

# Effects of resonance energy and nonplanar strain energy on the reliability of hyperhomodesmotic reactions for corannulene

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Received 27 October 2006; in final form 29 November 2006

Available online 2 December 2006

## Abstract

The standard heat of formation ( $\Delta H_f^\circ$ ) of corannulene ( $C_{20}H_{10}$ ) is calculated based on 40 hyperhomodesmotic reactions and compared with the existing experimental result. We found that: (1) the reliability of hyperhomodesmotic reactions depends on the construction scheme and the reference molecules; (2) both resonance energy and nonplanar strain energy should be considered during the construction of hyperhomodesmotic reactions. Two principles are proposed for the selection of reference molecules: (i) structurally similar to the object molecule; (ii) simple and small. Due to structural similarity, the above knowledge obtained from  $C_{20}H_{10}$  is of great reference for polycyclic aromatic hydrocarbons and fullerenes.

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## 1. Introduction

Although the calculation of standard heats of formation ( $\Delta H_f^\circ$ ) is usually based on hyperhomodesmotic reactions [1], they are not always reliable for polycyclic aromatic hydrocarbons (PAHs) [2,3]. To improve the accuracy of calculated  $\Delta H_f^\circ$ , Schulman et al. suggested that hyperhomodesmotic reactions should *only* contain aromatic species [2]. Following Schulman,  $\Delta H_f^\circ$  of 139 PAHs and 115 fullerenes were calculated by Cioslowski et al. [4] and Yu et al. [5], respectively. Recently, however, the reliability of Schulman scheme for fullerenes is in doubt, since the values of  $\Delta H_f^\circ$  for a series of fullerenes calculated from three hyperhomodesmotic reactions containing *only*  $C_{60}$  or/and  $C_{70}$  presents remarkable discrepancies [6]. And it was suggested that, for aromatic molecules with strong strain energies ( $E_S$ ), such as nonplanar PAHs and fullerenes, the effects brought by  $E_S$  and resonance energy (RE) should be inves-

tigated [6]. Here four schemes are summarized and the *additional* requirements to hyperhomodesmotic reactions are listed in Table 1. For Schulman scheme (Scheme 1) [2], there is no further requirement except that reactions contain only PAHs, which is also the common feature and basic requirement of the other three. Furthermore, for Schemes 2 and 3,  $E_S$  and RE in reactants and products of the hyperhomodesmotic reaction are balanced, indicated by  $\Delta E_S = 0$  kcal/mol and  $\Delta RE = 0$  kcal/mol, respectively. For Scheme 4, both  $\Delta E_S = 0$  kcal/mol and  $\Delta RE = 0$  kcal/mol are satisfied, as expected in Ref. [6].

How about the reliability and universality of these schemes? To answer these questions, an effective approach is to calculate  $\Delta H_f^\circ$  of one object molecule based on a series of hyperhomodesmotic reactions and compare the calculated values with experimental data. In this letter, corannulene is selected as the object molecule and studied, due to three reasons, (i) its experimental  $\Delta H_f^\circ$  is available and has been widely accepted; (ii) its carbon framework is the basic structural motif in all isolated pentagon rule (IPR) [7] fullerenes; (iii) it has strong nonplanar strain energy which is highly similar to the nonplanar distortion of

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Table 1  
Four schemes and their requirements

Scheme	Requirements	Reference
Scheme 1		[2]
Scheme 2	$\Delta E_S = 0$	[6]
Scheme 3	$\Delta RE = 0$	[6, this work]
Scheme 4	$\Delta E_S = 0$ ; $\Delta RE = 0$	[6, this work]

fullerenes [8]. Based on 40 hyperhomodesmotic reactions containing only PAHs, the value of  $\Delta H_f^\circ$  of corannulene is calculated and compared with its experimental result (110.2 kcal/mol [9]).

## 2. Calculation methods and details

Structures of object and reference molecules are shown in Fig. 1. To be consistent with previous work [5,8], a code has been assigned to each molecule. Experimental data of

$\Delta H_f^\circ$  are obtained from the CRC handbook [9] and listed in Table 2. Total energies ( $E_T$ ) are collected from Ref. [5]. Details about the calculation of  $E_S$  can be found in Ref. [6]. RE is calculated using the Hückel computational method [10] together with the Hess–Schaad reference structure [11], which can give satisfactory predictions for PAHs [12]. Normally, RE calculated by this method is in unit of  $\beta$ , here  $\beta$  is the Hückel resonance integral,  $\beta = 2.7$  eV [10]. A detailed comparison among different reference structures can be found in a recent review [12].

Forty hyperhomodesmotic reactions involving 15 PAHs are employed and labeled as R1–R40, as listed in the supporting information. In R1–R25, only one reference molecule (F3) contains the five-membered ring (5-MR). To investigate the effect of 5-MR on the calculated results, F5 is introduced into reactions of R26–R40. Through changing the reference molecules and the coefficients, hyperhomodesmotic reactions with different requirements (as illustrated in Table 1) are constructed. To illustrate the

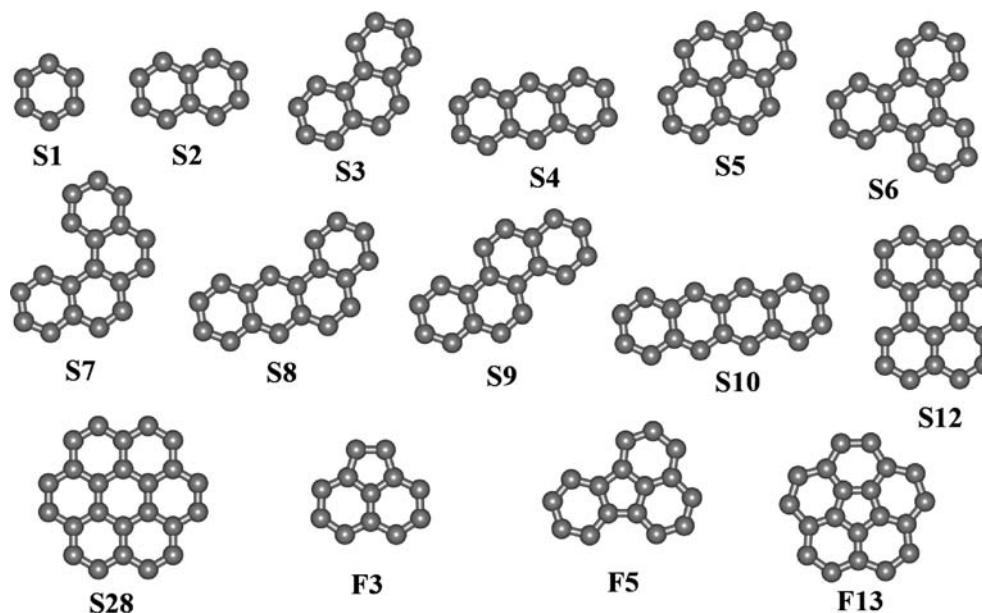


Fig. 1. Frameworks of PAHs used in this work. S-series are PAHs containing only 6-MRs and F-series containing 5-MRs and 6-MRs, as indicated in Ref. [8].

Table 2

Total energy ( $E_T$ , in Hartree), strain energy ( $E_S$ , in kcal/mol), resonance energy (RE, in  $\beta$ ) and standard heats of formation ( $\Delta H_f^{\circ \text{exp}}$ , in kcal/mol) of 15 PAHs, C<sub>60</sub> and C<sub>70</sub>

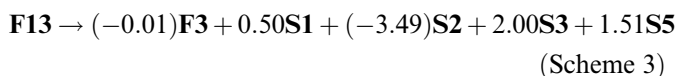
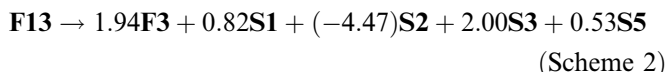
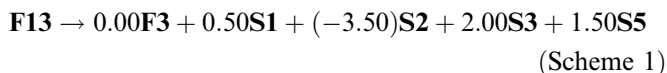
No.	$E_T^a$	$E_S^b$	RE	$\Delta H_f^{\circ \text{expc}}$	No.	$E_T^a$	$E_S^b$	RE	$\Delta H_f^{\circ \text{expc}}$
S1	−232.25	0.00	0.39	19.8	S10	−693.17	1.41	0.69	79.3
S2	−385.89	0.45	0.55	36.0	S12	−769.41	1.40	0.91	76.4
S3	−539.54	0.95	0.76	48.1	S28	−921.90	1.53	1.26	73.6
S4	−539.53	0.95	0.65	55.2	F3	−462.09	31.79	2.54	61.7
S5	−615.77	1.01	0.81	53.9	F5	−615.75	44.63	0.77	69.8
S6	−693.18	1.31	1.00	65.5	F13	−768.15	62.20	0.98	110.2
S7	−693.17	2.93	0.95	69.6	C <sub>60</sub>	−2286.17	483.90	1.87	598.6
S8	−693.18	1.58	0.89	69.6	C <sub>70</sub>	−2667.30	494.70	2.30	659.1
S9	−693.18	1.37	1.01	63.0					

<sup>a</sup> Ref. [5].

<sup>b</sup> Ref. [8].

<sup>c</sup> Ref. [9].

construction process and the determination of the coefficients, R1 is presented as an example:



Obviously, for each reaction, there are three sets of coefficients corresponding to three schemes, producing three calculated results of  $\Delta H_f^\circ$  for corannulene, labeled as  $\Delta H_{f1}^\circ$ ,  $\Delta H_{f2}^\circ$  and  $\Delta H_{f3}^\circ$ . The subscripts indicate the schemes.

### 3. Results and discussion

The calculation error is defined by

$$\text{Error}_i = \Delta H_{fi}^\circ - \Delta H_f^{\circ \text{exp}} \quad (i = 1, 2 \text{ and } 3) \quad (1)$$

where,  $\Delta H_f^{\circ \text{exp}} = 110.2$  kcal/mol [9]. The errors (Error<sub>1</sub>, Error<sub>2</sub> and Error<sub>3</sub>) are listed in Table 3. The bold numbers indicate the optimal schemes for each reaction. From Table 3, we can see, (1) Error<sub>1</sub>, Error<sub>2</sub> and Error<sub>3</sub> keep similar changing tendencies for R1–R25, but vary remarkably from each other for R26–R40, suggesting that the introduction of **F5** into the reactions of R26–R40 makes the results complicated and unstable. (2) Error<sub>1</sub> is quite close to Error<sub>3</sub> for R1–R25. (3) For R1–R25, Scheme 2 is the best, while for R26–R40, Scheme 1 is the best. Based on the above results, we can see that Scheme 1 approximately implies the requirement of  $\Delta RE = 0\beta$ . From the Supporting Information

(Table S1) of the unbalanced terms for R1–R40 under these three schemes, it is noted that  $\Delta RE$  is close to zero for most reactions under Scheme 1. And this is the reason why hyperhomodesmotic reactions containing only PAHs can produce good results for normal PAHs [2]. Thus, it is necessary to consider the resonance contribution during the construction of hyperhomodesmotic reactions for PAHs and fullerenes, which can be approximately satisfied by constructing reactions containing *only* PAHs. From Table 3, it is clear that Scheme 2 produces much better results than Schemes 1 and 3 for R1–R20, although the unbalanced *RE* (the difference of resonance energy between the reactant and the product) is high, from  $2.83\beta$  to  $3.89\beta$ . Thereby, the effect of  $E_s$  is also important.

The above conclusions are logical and reasonable. Essentially, the inherent limitation of hyperhomodesmotic reactions (including Scheme 1) is attributed to two approximations: (1) PAHs are localized and the carbon–carbon bond is described by C–C and C=C; (2) the bond structures are described universally using a set of bonds, for instance, if the hybridization of each carbon atom and hydrogen effect are taken into account, there are six types of carbon–carbon bonds, C=C ( $\alpha$ ), CH=CH ( $\beta$ ), C=CH ( $\gamma$ ), CH–CH ( $\delta$ ), C–CH ( $\xi$ ), and C–C ( $\lambda$ ). The first approximation fails to consider the resonance contribution in PAHs, and the second one neglects the details of bonds (bond length, bond angle, and rehybridization led by nonplanar distortion), whose derivations from ideal values directly result in strain energies, which is the source of destabilization. Therefore, for hyperhomodesmotic reactions, the types of bonds and the hybridization of carbon atoms are just *approximately* conserved. Originally, Schulman et al. clearly stated that difficulty should be

Table 3  
Errors (kcal/mol) defined by Eq. (1) on the basis of Schemes 1–3<sup>a</sup>

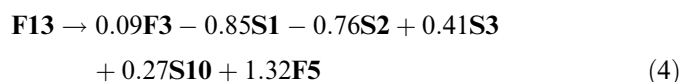
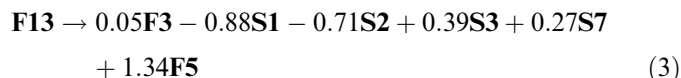
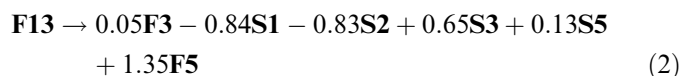
Reaction	Error <sub>1</sub>	Error <sub>2</sub>	Error <sub>3</sub>	Reaction	Error <sub>1</sub>	Error <sub>2</sub>	Error <sub>3</sub>
R1	5.68	<b>0.01</b>	5.72	R21	−4.57	−13.20	<b>−4.27</b>
R2	6.13	<b>0.35</b>	6.15	R22	11.14	<b>6.98</b>	10.99
R3	22.69	<b>6.05</b>	19.67	R23	<b>45.37</b>	50.57	48.40
R4	13.44	<b>2.73</b>	12.85	R24	11.72	<b>7.70</b>	11.54
R5	15.72	<b>3.49</b>	15.95	R25	13.49	<b>9.94</b>	13.54
R6	5.98	<b>0.63</b>	6.01	R26	<b>−3.08</b>	15.06	12.02
R7	11.54	<b>5.90</b>	11.48	R27 <sup>b</sup>		17.03	<b>14.28</b>
R8	17.02	<b>11.38</b>	16.25	R28	<b>0.91</b>	15.52	13.06
R9	10.85	<b>5.17</b>	10.65	R29	<b>3.06</b>	20.27	10.00
R10	12.37	<b>6.65</b>	12.46	R30	<b>2.78</b>	15.76	13.53
R11	4.14	<b>2.11</b>	4.15	R31	<b>14.10</b>	18.01	15.45
R12	20.70	<b>7.91</b>	18.39	R32	<b>7.93</b>	19.04	12.33
R13	11.45	<b>4.60</b>	11.08	R33	<b>9.45</b>	18.77	13.34
R14	13.73	<b>5.38</b>	13.90	R34	<b>−0.70</b>	14.92	12.33
R15	7.34	<b>2.12</b>	7.52	R35	26.12	<b>14.10</b>	13.28
R16	23.64	<b>7.90</b>	21.05	R36	<b>6.89</b>	14.46	13.18
R17	12.97	<b>4.09</b>	12.43	R37	<b>12.28</b>	13.98	14.44
R18	15.24	<b>4.85</b>	15.35	R38	−17.72	<b>16.02</b>	10.39
R19	12.65	<b>8.90</b>	12.66	R39	<b>4.72</b>	14.59	12.89
R20	6.74	<b>2.64</b>	6.72	R40	39.87	14.41	<b>9.49</b>

<sup>a</sup> Error<sub>1</sub>, Error<sub>2</sub> and Error<sub>3</sub> are in units of kcal/mol.

<sup>b</sup> A hyperhomodesmotic reaction cannot be constructed under Scheme 1.

encountered when an aromatic molecule is associated with nonaromatic olefins in a homodesmotic scheme [2]. With respect to conventional hyperhomodesmotic reactions, the essential modification of the Schulman scheme is to take into account of the resonance effect, as indicated above. This is the reason why Schulman's scheme can give quite good results for 16 PAHs even at the SCF level of STO-3G basis set [2]. Schulman's success indicates that the possible optimization of hyperhomodesmotic reactions is supposed to take steps to overcome the shortage of the above two approximations. The Schulman scheme (Scheme 1) is related to the first one and the suggestion given by us previously [6] to the second one.

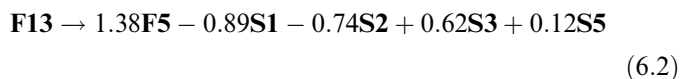
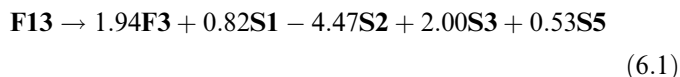
According to the results from R1–R20, Scheme 2 is best among the first three schemes. However, it does not work well for R26–R40. Two possible reasons can be proposed. Firstly, both resonance contribution and the strain energy should be considered simultaneously, as indicated before [6] and as suggested by Scheme 4. Therefore, three hyperhomodesmotic reactions with  $\Delta E_S = 0$  kcal/mol and  $\Delta RE = 0\beta$  are constructed as



The above reactions produce errors of 11.49, 11.49, 12.79 kcal/mol, worse than those from R1–R20 under Scheme 2. Therefore, the failure of Scheme 2 in R26–R40 is NOT resulted by the unbalanced resonance energy. Actually, under Scheme 2, the resonance effect has been considered qualitatively in the calculation of  $E_{np}$  [13],

$$E_{np} = \eta \sum \frac{m}{m+1} \quad (5)$$

Here,  $\eta \approx 100$  kcal/mol, and  $m$  indicates the rehybridization. Based on Eq. (5), we can see that  $E_{np}$  and RE are correlated to each other through  $m$ . Thereby, it is not recommended to satisfy two requirements of  $\Delta E_S = 0$  and  $\Delta RE = 0$  simultaneously because the effect associated with rehybridization will be overcounted. With respect to R1–R25, the main difference of R26–R40 is that **F5** is employed, which may be the essential reason why Scheme 2 fails to produce better results for R26–R40. To compare the qualities of **F3** and **F5**, two reactions are constructed under Scheme 2 and compared,



Eqs. (6.1) and (6.2) produce errors of 0.01 and 11.74 kcal/mol. Obviously, **F3** is a better reference molecule for **F13** than **F5**. This is the reason why Scheme 2 cannot produce good results in R26–R40. Essentially, reference molecules

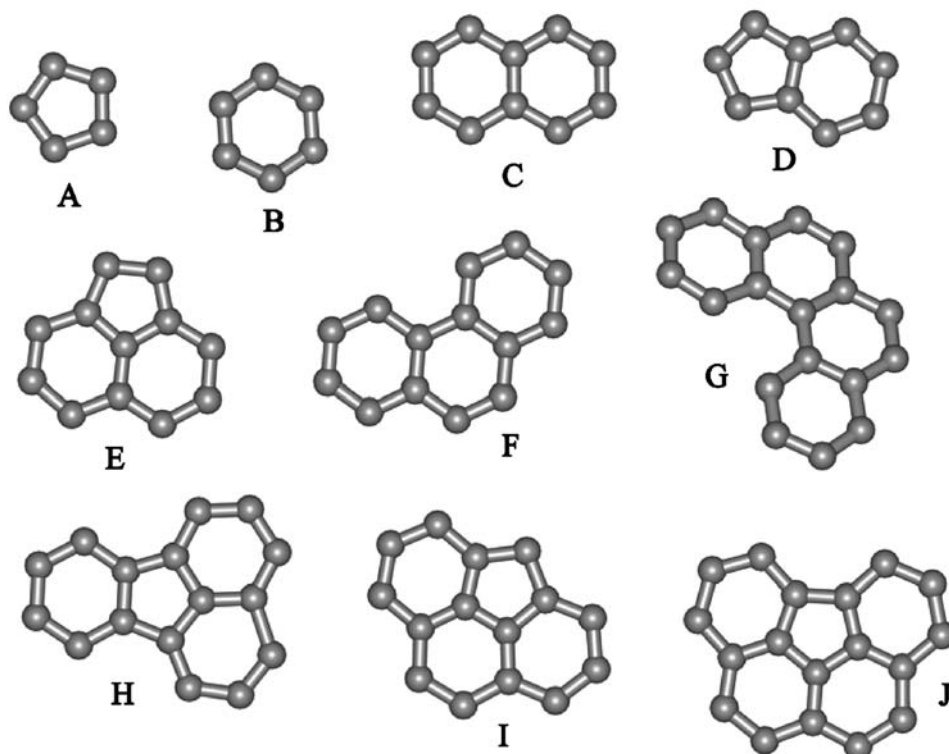


Fig. 2. Frameworks of possible motifs derived from **F13**.

which contain similar rehybridization and delocalization with object molecule are preferred; hence, two principles can be summarized. Firstly, reference molecules are preferred to be structurally similar to object molecules. As shown in Fig. 2, possible basic motifs are derived from F13. Only B, C, E, F and G are directly obtainable from Table 2, corresponding to the frameworks of S1, S2, F3, S3 and S7. H and I are similar to S5 and S6. From Table 3, it is found that reactions composed of S1, S2, S3, S5, S6, S7 and F3 produce quite good results under three schemes. However, reactions containing S10, S12 and S28 produce bigger errors than those containing S1, S2, S3, S5 and S7. Especially, reactions containing S10 (R3, R8, R12, R16, R23, R31 and R40) produce the worst result for each series. Thereby, it is recommended to select reference molecules from the basic motifs derived from the object molecule. Secondly, simple and small reference molecules are preferred. From Table 2, it is clear that reactions containing small reference molecules produce better results, no matter which scheme is employed, such as R1, R2, R6, R11, R15, R20, R26 and R28. For instance, with respect to F5, F3 is better as illustrated above. Moreover, high level SCF optimization and calculations of small reference molecules are computationally cheaper than those of big ones.

#### 4. Conclusions

In conclusion, the standard heat of formation ( $\Delta H_f^\circ$ ) of corannulene ( $C_{20}H_{10}$ ) is calculated based on 40 hyperhomodesmotic reactions and compared with the existing experimental result. It is found that the reliability of hyperhomodesmotic reactions depends on two factors, the construction scheme and the reference molecules, and we further found that, (1) both RE and  $E_S$  play an important role on the construction of hyperhomodesmotic reactions for the calculation of  $\Delta H_f^\circ$ ; (2) among the four schemes listed in Table 2, Scheme 2 is the best; (3) to ensure that the employed reaction can produce reliable results, two

principles should be followed for the selection of reference molecules: (i) structurally similar to the object molecule; (ii) simple and small. Analogically, it is recommended that, for fullerenes, hyperhomodesmotic reactions should involve only fullerenes and reference molecules can be selected on the basis of the basic motifs contained in the object molecule. The above knowledge is of great reference for PAHs and fullerenes.

#### Acknowledgements

This work was supported by NSFC (90606008, 50328204 and 90406012). The financial support from the ARC Centre for Functional Nanomaterials, Australia to this work are acknowledged.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2006.11.105](https://doi.org/10.1016/j.cplett.2006.11.105).

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