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On Structural Dependence of Enthalpy of Formation of Catacondensed Benzenoid Hydrocarbons*

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Abstract

Dependence of the enthalpy of formation (ΔH_f) of catacondensed benzenoid hydrocarbons (CBHs) on structural features was examined. To elucidate the influence of the molecular size (expressed through the number of hexagons, **h**), number of bays (**B**), number of coves (**C**), number of fjords (**F**), and molecular branching (expressed through the number of the A_3-type hexagons, $\mathbf{h_{A3}}$) on ΔH_f, a simple mathematical model was developed. Namely, ΔH_f of CBHs was approximated as a linear combination of first several spectral moments, up to M_{12}. For this purpose, multiple linear regression was applied, where the ΔH_f values obtained from the PM7 calculations for 1221 randomly chosen CBHs were used as learning set. Fortunately, the formulas for these spectral moments that depend on molecular structure have already been derived, implying that the model describes ΔH_f in terms of structural details of CBHs. Agreement between the experimental and calculated ΔH_f is satisfactory, with an average relative error of 4.5 %.

It was found that the major part of ΔH_f is determined by **h**, where ΔH_f increases with increasing **h**. Subtle variations in the value of ΔH_f are explained by other structural features of a molecule. ΔH_f decreases with increasing **B**, **C**, and **F**, but increases with increasing $\mathbf{h_{A3}}$. Contribution of each structural property was quantitatively determined. This is the first study that describes ΔH_f of CBHs in terms of structural features that can be straightforwardly obtained.

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1 Introduction

The enthalpy of formation (ΔH_f) is a critical thermodynamic property of compounds that allows a chemist to determine the energy changes of chemical reactions. This fundamental quantity is defined as a change of enthalpy during the formation of 1 mole of a compound in its standard state from its constituent elements in their standard states.

There are numerous experimental data referring to the enthalpy of formation for small molecules. Unfortunately, situation is less favorable for larger molecules. Therefore, much effort has been put into predicting ΔH_f of various compounds. The so-called direct calculation of ΔH_f, which emanates from its definition, requires quantum chemical computations of a certain molecule and the respective constituent atoms. For this purpose several approaches have been developed: Gaussian-3 (G3) [1–5], correlation consistent composite approach (ccCA) [6, 7], complete basis set model chemistries (CBS) [8–10], Weizmann (Wn) methods [11–15], etc. The application of all these approaches is also limited to small molecules. In addition, the ΔH_f predicting methods include the group/bond additivity [16, 17], quantitative structure–property relationships (QSPR) [18, 19], approach based on isodesmic reactions known as high accuracy extrapolated *ab initio* thermochemistry (HEAT) [20, 21], semiempirical methods [22], etc.

Molecules that are deficient in experimental data associated with ΔH_f are polycyclic aromatic compounds (PAHs). PAHs can be released in environment as products of different processes [23–25], and are considered as environmental pollutants [26–29]. Therefore, an important task is to fulfill this gap in scientific literature. Recent study [30] was devoted to the predicting of ΔH_f for 669 PAHs and their derivatives, based on density functional theory and group based correction scheme. The results obtained are comparable to the G3 approach. Even though such methodology yields reasonable results, it is computationally demanding, and requires sophisticated software [31].

Influence of structural features of molecules on the enthalpy of formation has been in focus in our previous studies [32–34]. This paper is concerned with the dependence of ΔH_f of catacondensed benzenoid hydrocarbons (CBHs), a subclass of polycyclic aromatic compounds [35], on molecular features. To achieve this goal, we developed a simple mathematical model, based on spectral graph theory, for predicting ΔH_f of CBHs.

2 Model construction

The k-*th* spectral moment of molecular graph G can be expressed as:

$$M_k = M_k(G) = \sum_{i=1}^{n} (\lambda_i)^k \tag{1}$$

where λ_i denotes the i-*th* eigenvalue of the adjacency matrix spectrum. Spectral moments have been successfully applied in the physical chemistry of solid state [36–38] and theoretical chemistry of conjugated molecules [39–63]. Contemporary applications of spectral moments refer to biochemical systems and drug discovery [64, 65]. Recently, in the article of Hoffmann *et al.* [66] the application of spectral moments in molecular conductance has been reviewed.

In the present work we supposed that ΔH_f of CBHs can be approximated as:

$$\Delta H_\mathrm{f} \approx a_0 M_0 + a_2 M_2 + \cdots + a_{12} M_{12} + const. \tag{2}$$

where a_0, a_2, … a_{12} stand for the fitting parameters.

To build a mathematical model capable to reproduce ΔH_f of CBHs, experimental data and dependence of spectral moments on structural features are needed. Fortunately, the formulas for spectral moments of CBHs up to M_{12} have already been derived (Eqs. 3–9) [67, 46, 42, 43, 68, 53, 54].

$$M_0 = 4\mathbf{h} + 2 \tag{3}$$

$$M_2 = 10\mathbf{h} + 2 \tag{4}$$

$$M_4 = 42\mathbf{h} - 6 \tag{5}$$

$$M_6 = 214\mathbf{h} + 6\mathbf{B} + 12\mathbf{C} + 18\mathbf{F} - 82 \tag{6}$$

$$M_8 = 1194\mathbf{h} + 80\mathbf{B} + 168\mathbf{C} + 256\mathbf{F} + 16\mathbf{h}_{\mathbf{A_3}} - 694 \tag{7}$$

$$\begin{aligned} M_{10} = {} & 6970\mathbf{h} + 770\mathbf{B} + 1700\mathbf{C} + 2640\mathbf{F} + 410\mathbf{h}_{\mathbf{A_3}} \\ & - 50\mathbf{h}_{\mathbf{L_1}} + 10(\mathbf{P_1} + \mathbf{P_2}) - 5178 \end{aligned} \tag{8}$$

$$\begin{aligned} M_{12} = {} & 41718\mathbf{h} + 6366\mathbf{B} + 14868\mathbf{C} + 23610\mathbf{F} + 5040\mathbf{h}_{\mathbf{A_3}} \\ & +252\mathbf{P_3} + 336\mathbf{P_4} + 12(\mathbf{P_5} + \mathbf{P_6} + \mathbf{P_7}) + 24(\mathbf{P_8} + \mathbf{P_9} - \mathbf{P_{10}}) - 38298 \end{aligned} \tag{9}$$

In Eqs. 3–9 **h**, **B**, **C**, **F**, $\mathbf{h_{A3}}$, and $\mathbf{h_{L1}}$ denote the number of hexagons, number of bays, number of coves, number of fjords, number of the A_3-type hexagons, and number of the L_1-type hexagons, whereas **P_1–P_{10}** stand for the number of specific structural features of the perimeter (Fig. 1).

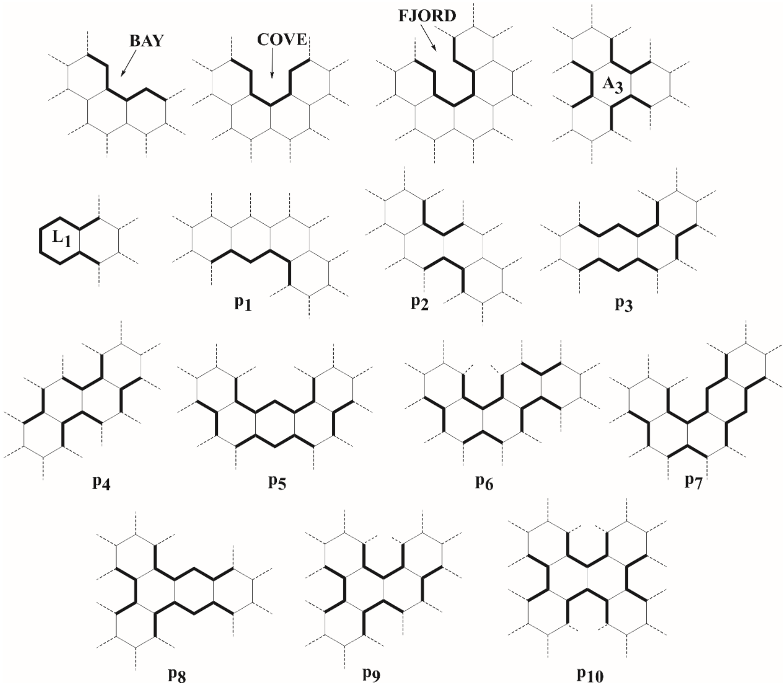

Fig. 1. Structural properties of CBHs.

On the other hand, there are only few experimental data on ΔH_f of CBHs (Table 1). For this reason the ΔH_f values from the PM7 calculations [69] were used instead of experimental results. The learning set was created in the following manner: For **h**=2–7 all possible isomers were constructed. For **h**=8–17 around 100 representatives were randomly selected for each molecular formula. For these purposes the CaGe computer program [70] was applied. The so–obtained learning set consists of 1221 CBHs. Spectral moments for all 1221 CBHs were calculated using the in–house Python program, and the fitting parameters in Eq. 2 were determined by the least square method. This huge amount of work was significantly facilitated using cheminformatics tools. The above described procedure led to the approximative formula 10. In Fig. 2 correlation between ΔH_f obtained by the PM7 calculations and by Eq. 10 is depicted. More information on the calculated Δ*H*f values can be obtained from the authors (I. R.) upon request.

$$\Delta H_\mathrm{f} \approx 3.4496M_0 + 8.6241M_2 + 36.2212M_4 + 0.0067M_6 - 4.1052M_8 + 0.6619M_{10} - 0.0303M_{12} - 305.6799\ \mathrm{kJ\ mol^{-1}} \tag{10}$$

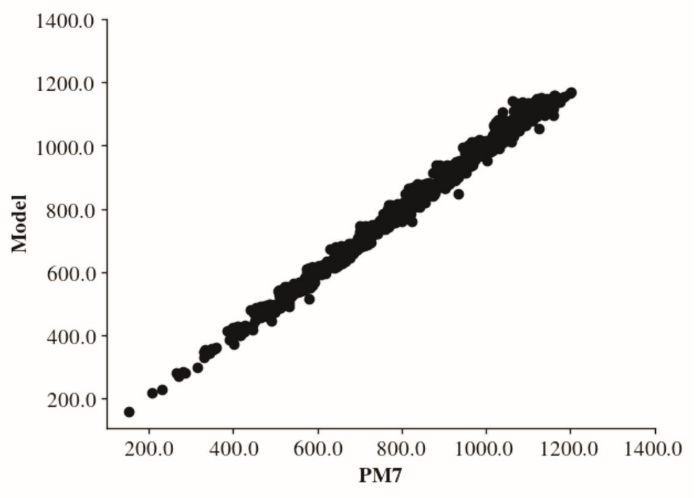

Fig. 2. Correlation between Δ*H*f values (kJ mol^{-1}) for 1221 CBHs obtained by the PM7 calculations and Eq. 10 (model), with the correlation coefficient R=0.996.

Then, the formulas for spectral moments (Eqs. 3–9) were inserted into Eq. 10, and the following approximative formula for Δ*H*f of CBHs was obtained:

$$\Delta H_\mathrm{f} \approx 71.38\mathbf{h} - 11.46\mathbf{B} - 14.53\mathbf{C} - 18.25\mathbf{F} + 53.10\mathbf{h}_{\mathbf{A_3}} - 33.09\mathbf{h}_{\mathbf{L_1}} + 6.62(\mathbf{P_1} + \mathbf{P_2}) - 7.63\mathbf{P_3} - 10.17\mathbf{P_4} - 0.36(\mathbf{P_5} + \mathbf{P_6} + \mathbf{P_7}) - 0.73(\mathbf{P_8} + \mathbf{P_9} + \mathbf{P_{10}}) + 81.89\ \mathrm{kJ\ mol^{-1}} \tag{11}$$

To illustrate how one can obtain Δ*H*f of CBHs by using Eq. 11, we now demonstrate calculation of Δ*H*f for an arbitrary molecular graph depicted in Fig. 3:

$$\Delta H_\mathrm{f} = 71.38 \times 6 - 11.46 \times 2 - 18.25 \times 1 + 53.10 \times 1 - 33.09 \times 3 + 6.62 \times 1 - 10.17 \times 1 - 0.36 \times 1 - 0.73 \times 1 + 81.89 = 418.2\ \mathrm{kJ\ mol^{-1}} \tag{12}$$

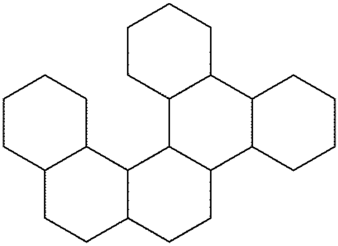

Fig 3. Benzenoid graph used in Eq. 12.

The quality of the obtained approximation for ΔH_f was examined by comparison between the experimental and calculated ΔH_f values, where correlation coefficient (R) and average relative error (ARE) were used as descriptors (Table 1). Obviously, the best agreement with the experimental values was achieved with the PM7 method. This fact justifies our choice of the auxiliary method for calculating ΔH_f for numerous CBHs whose experimental values are not available. Our model shows reasonably good agreement with the experimental results. An improvement of the model can be achieved by inclusion of much more reliable experimental values, and increased number of terms in Eq. 11. Unfortunately, none of the two conditions can be fulfilled so far.

We wish to point out that Eq. 11 is the first formula for approximating ΔH_f of CBHs that depends only on structural features that can be easily recognized. The formula itself describes how ΔH_f of CBHs depends on molecular structure, and allows one to quantitatively determine contributions of key structural properties.

Table 1. Comparison between experimental and calculated ΔH_f of CBHs.

	Exp. [71]	**Ref.** [30]	**PM7**	**Model**
naphthalene	150.0	141.0	151.2	158.5
anthracene	223.0	222.6	229.9	229.9
phenathrene	202.2	202.7	207.8	218.4
benz[a]anthracene	290.3	277.1	279.7	284.6
chrysene	268.7	271.1	270.1	270.6
benzo[c]phenathrene	291.2	295.3	285.5	282.5
triphenylene	270.1	275.1	266.0	282.7
dibenz[a,c]anthracene	331.1	348.0	333.9	355.5
dibenz[a,h]anthracene	328.1	335.0	331.5	347.7
R		**0.994**	**0.996**	**0.984**
ARE, %		**2.5**	**1.8**	**4.5**

3 Dependence of ΔH_f on molecular structure of CBHs

We examined the dependence of ΔH_f of CBHs on the following structural properties: **h**, **B**, **C**, **F**, and $\mathbf{h_{A3}}$. For this purpose the necessary ΔH_f values were calculated by means of Eq. 11. As such investigation requires, when the impact of a certain structural property on ΔH_f was inspected, the other four were kept constant to prevent possible shading of some weak effects by much stronger ones. The size of all examined molecules was **h**=20, except in the case of examining the dependence of ΔH_f on molecular size where **h** was gradually increased up to **h**=20. The variation of the **B**, **C**, **F**, and $\mathbf{h_{A3}}$ values within this molecular size was realized by forcing necessary number of hexagons to form linear polyacene–like fragments.

3.1 Dependence of ΔH_f on molecular size

To examine the dependence of ΔH_f on **h** a series of molecules was constructed (Fig. 4). Fig. 5 shows that this dependence is linear. The correlation coefficient for the formed straight line is very large: 0.9999996. ΔH_f increases with increasing **h** by around 72 kJ mol^{-1}. This finding reveals that ΔH_f of CBHs is strongly dependent on molecular size.

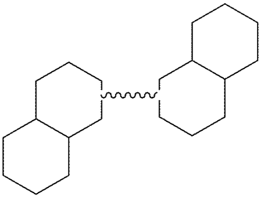

Fig. 4. Model molecule for examining the dependence of ΔH_f on **h**.

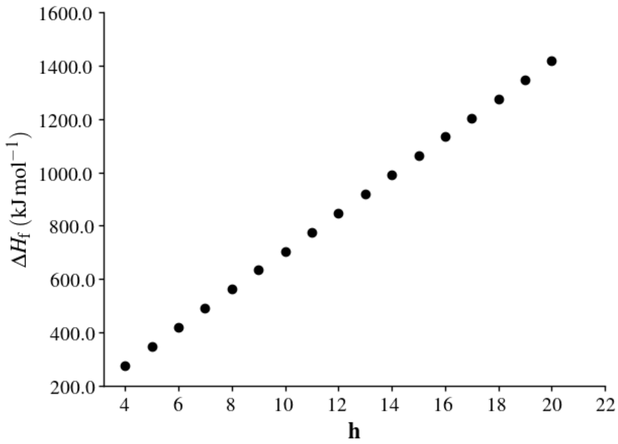

Fig. 5. Dependence of ΔH_f of CBHs on **h**.

3.2 Dependence of ΔH_f on bays, coves, and fjords

The influences of **B**, **C**, and **F** on ΔH_f of CBHs were investigated for the suitable series of the molecules depicted in Fig. 6. Note that the graphs in the *b* and *c* series were constructed in a manner that each edge belongs to a single cove or fjord. Thus, **B**, **C**, and **F** values ranged from 1 up to 18, 9, and 4, respectively. All three dependences are linear, and the R values are very close to -1 (Fig. 7). It turned out that with increasing **B**, **C**, and **F** ΔH_f decreases by around 15, 18, and 20 kJ mol^{-1}, respectively. The influences of all three structural properties are mutually very similar, and much weaker than that of the molecular size.

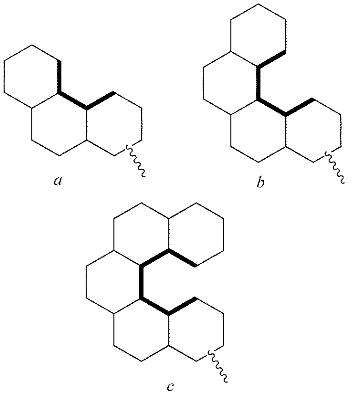

Fig. 6. Model molecules for examining the dependence of ΔH_f on **B** (*a*), **C** (*b*), and **F** (*c*).

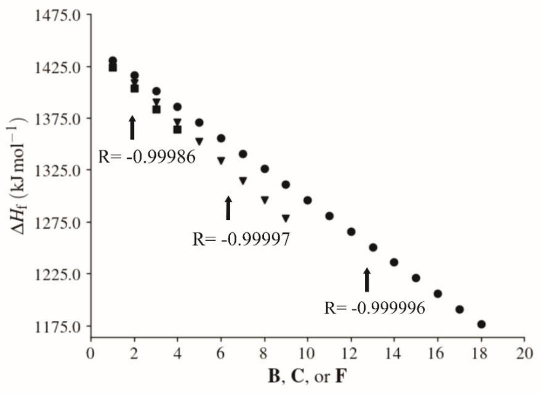

Fig. 7. Dependence of ΔH_f of CBHs on **B** (circles), **C** (triangles), and **F** (squares).

3.3 Dependence of ΔH_f on branching

Introduction of each A_3-type hexagon necessarily induces formation of 3 bays. In addition, $\mathbf{h}_{L1}=\mathbf{h}_{A3}+2$. Therefore, it is difficult to distinguish among the influences of these three structural properties. We tried to estimate the influence of molecular branching in the following way. Two series of molecules (*a* and *b*) were constructed (Fig. 8). The construction of the members in the *b* series is self-explanatory from Fig. 8. As for the *a* series, the following construction pattern was applied: a single hexagon was attached at one attaching site, and linear polyacene–like fragment was attached at the other site (Fig. 8). Thus, in the *a* series $\mathbf{h}_{A3}$ was increased from 1 up to 6 (and $\mathbf{h}_{L1}$ was increased from 1 up to 8), whereas in the *b* series **B** was gradually increased by 3, up to 18 ($\mathbf{h}_{L1}=2$). In this way, the **B** values for all the corresponding pairs of molecules are identical and planarity of the members in the *a* series is preserved, but the $\mathbf{h}_{L1}$ values are not equal. The graphs in Fig. 9 show that the ΔH_f values for the *a* series are larger than those for the *b* series. The difference in ΔH_f between each two corresponding molecules is equal to around $\mathbf{h}_{A3}\times 25$ kJ mol^{-1}. Taking this fact into account, as well as the finding that the L_1-type rings decrease ΔH_f (Eq. 11), one can conclude that molecular branching increases ΔH_f of CBHs. It should not be concluded that ΔH_f increases with increasing $\mathbf{h}_{A3}$ by 25 kJ mol^{-1}, because this portion of energy also includes the influence of $\mathbf{h}_{L1}$. One may suppose that the influence of $\mathbf{h}_{A3}$ is also weaker than that of **h**.

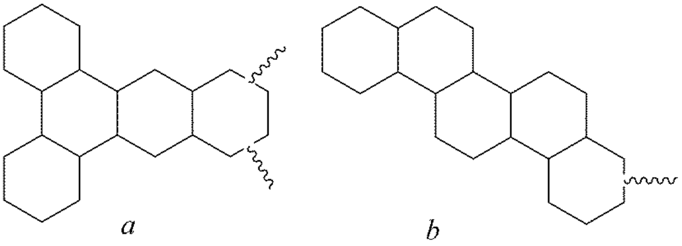

Fig. 8. Model molecules for examining the dependence of ΔH_f on $\mathbf{h}_{A3}$.

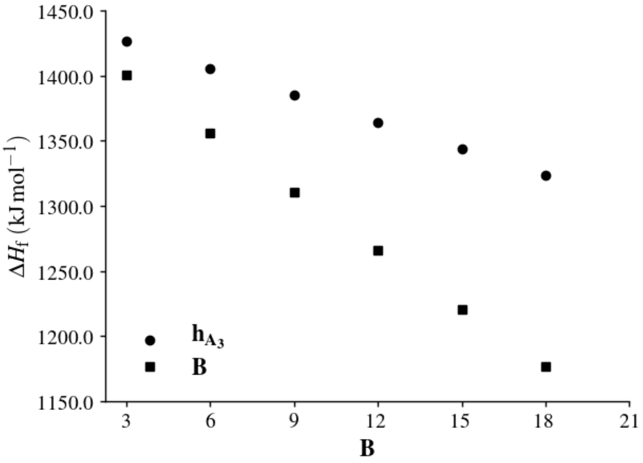

Fig. 9. Dependence of ΔH_f of CBHs on $\mathbf{h}_{A3}$.

Conclusion

Eq. 11 presents a simple mathematical model that describes ΔH_f of CBHs in terms of structural features that can be easily recognized from the corresponding molecular graphs. The model shows that ΔH_f increases with increasing **h** and $\mathbf{h}_{A3}$, as well as with the increasing number of the p_1 and p_2 details of the perimeter. ΔH_f decreases with the increasing counts of all other structural properties: **B**, **C**, **F**, $\mathbf{h}_{L1}$, and **P3**–**P10**. Furthermore, the model enables one to quantitatively determine the contribution of each structural property to ΔH_f. As expected, the major part of ΔH_f is determined by **h**, whereas the fine structure of ΔH_f is explained by other structural properties figuring in Eq. 11. The subtle influences of the key features: bays, coves, fjords, and molecular branching were here examined. This work is the first attempt of describing the ΔH_f of CBHs in terms of the counts of structural features.

Agreement between the experimental and calculated ΔH_f is relatively good, with an average relative error of 4.5 %. We need to emphasize that there are only few experimental results on ΔH_f of CBHs. It is expected that inclusion of much more reliable experimental values would improve the model accuracy.

Finally, we need to share with the readership our impression that appeared during this work: Big is really beautiful! [72] (Fig. 10).

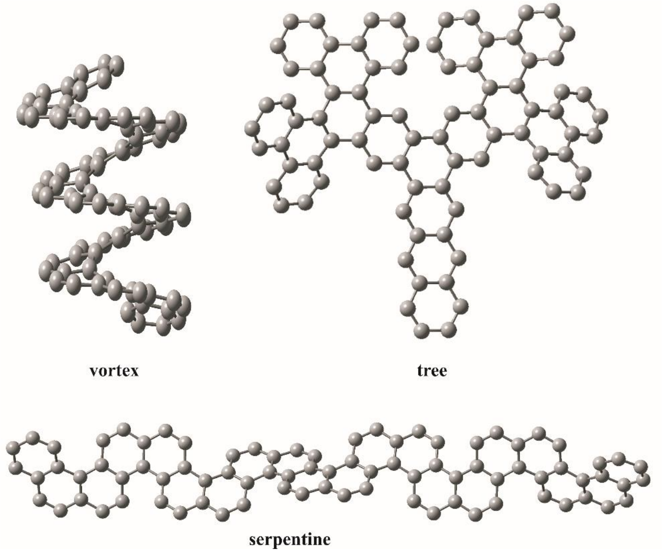

Fig. 10. Molecular graphs of some big, beautiful benzenoid hydrocarbons.

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