

# Rotation barriers in condensed rings: an extension of Clar's stability rule

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**ABSTRACT:** The rotation barrier for a substituent OH in systems of condensed benzene rings was studied using density functional theory. The barrier height depends on the position of the hydroxy group and the number of independent benzene rings in the condensed ring system, in agreement with Clar's  $\pi$ -electron sextet stability model. Investigating OH-derivatized polycenes with as many as 19 condensed rings showed that increasing the total size of the system does not contribute significantly to the rotation barrier. Copyright © 2005 John Wiley & Sons, Ltd.

**KEYWORDS:** rotation barrier; condensed rings; hydroxy group; Clar's stability rule

## INTRODUCTION

Systems of condensed benzene rings have been the target of intense study with theoretical methods since the early years of computational chemistry. The polycenes were studied theoretically and used for developing and testing both empirical and semi-empirical computational methods. Some of these methods enjoyed renewed popularity after the discovery of fullerenes and nanotubes, which retain many of the properties of the planar polycyclic hydrocarbons. There are several ways to approach the study of interactions within aromatic systems. One is to introduce defects into the carbon lattice either by removing an atom from the conjugated system or by substitution with a  $\pi$ -electron donor. The  $\pi$ -electron approximations, such as the Hückel molecular orbital and Pariser–Parr–Pople methods, perform best for such systems. These methods have been incorporated into the theoretical study of fullerenes and nanotubes, because the latter have relatively small curvature that does not significantly affect the  $\pi$ -electron conjugation.

A second method of exploring these effects is to investigate the behavior of atoms and molecules/clusters adsorbed onto a graphite surface. Often large aromatic hydrocarbons serve as models, so-called cluster calculations, for the graphite surface in the absence of periodic boundary condition methods. Calculations of the atom/cluster interactions with graphite and other surfaces are a broad area of *ab-initio* and DFT computational studies.

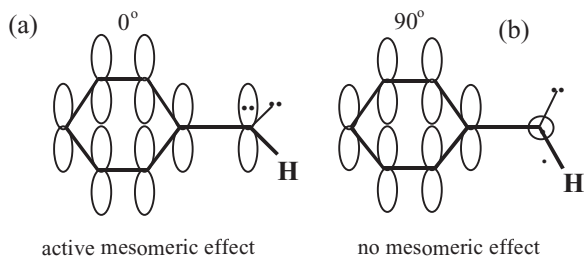
A third approach used to examine interactions in aromatic systems is replacement of a hydrogen atom

with a different atom or group, which will then be in direct contact with the  $\pi$ -electron system. Phenol and hydroxy-substituted polycenes are examples. In these systems, the delocalized  $\pi$ -system of the underivatized molecule is neither destroyed nor seriously modified.

The planar structure of phenol<sup>1</sup> suggests that there is an interaction between the  $\pi$ -electrons from the hydrocarbon and the electrons of the oxygen atom. This interaction, the *mesomeric effect*, is illustrated in Fig. 1. When the OH lies in the molecular plane, the interaction between the electrons of the non-hybridized p-atomic orbital of the oxygen and the  $\pi$ -electrons of the benzene ring is maximized [Fig. 1(a)]. This additional delocalization should lower the total energy. Rotation of the OH around the C–C(OH) bond will decrease this p– $\pi$  alignment and result in an increase in the energy. The interaction is minimal when the oxygen p-orbital becomes coplanar with the benzene ring [Fig. 1(b)]. A similar effect has been discussed to explain the rotation barriers in esters.<sup>2</sup> The amount of p– $\pi$  interaction can be determined from studying the barrier to the latter structure, i.e.  $E_{1b} - E_{1a}$ , in Figure 1; a larger barrier indicates a greater mesomeric effect.

Using a broad range of experimental data, Clar proposed a criterion for the stability of polycyclic hydrocarbons.<sup>3</sup> He suggested that Hückel's rule<sup>4</sup> applied only to monocyclic systems. In polycyclic systems, Clar postulated that the stability criterion is related to the maximum number of aromatic sextets that may be drawn for a given structure. For two related molecules, the structure that has a greater number of compete aromatic rings, a greater Clar number, is expected to be chemically and thermodynamically more stable. Benzene has one aromatic sextet in its single ring. Naphthalene, on the other hand, has two fused rings that share a single sextet

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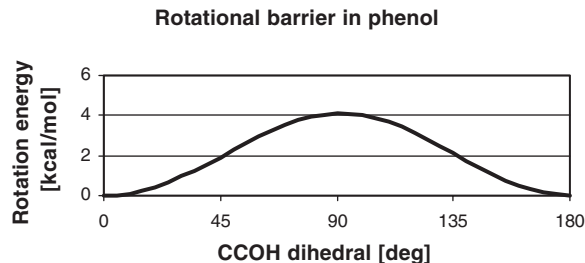
**Figure 1.** Schematic representation of the p- $\pi$  overlap between the electron donating hydroxy group and the benzene ring in phenol

in each of the two possible resonance structures. This indicates, according to Clar's rule, increasing reactivity in comparison with benzene. Continuing with the acene series, all of these systems have a single  $\pi$ -electron sextet and an increasing number of fused rings. For example, pentacene, which has 22 atoms and 22  $\pi$ -electrons, has a single  $\pi$ -electron sextet and is known to be more reactive than benzene, naphthalene or anthracene. Heptacene has seven fused rings with a single  $\pi$ -electron sextet and, although the parent structure has been reported,<sup>5</sup> it is unstable. Within a given polycene, we may compare structural isomers. For example, consider the three-fused-ring (catacondensed) systems anthracene and phenanthrene. The latter has two  $\pi$ -electron sextets, on the terminal rings, whereas anthracene has only one such sextet. The phenanthrene system is more stable to reaction.

Studying the rotational barrier of the hydroxy group in aromatic compounds will provide insight into two fundamental questions: (1) does the barrier height depend on the size of the system, so that an extrapolation from condensed rings to a substituted graphite layer may be made?; and (2) does varying the position of the substitution provide trends in agreement with Clar's rule in cases where electrons from *outside* the ring system participate in  $\pi$ -electron conjugation? Can we propose an extension of Clar's rule? These questions were addressed in this work.

## COMPUTATIONAL DETAILS

All calculations were carried out with the Gaussian 98 suite of programs.<sup>6</sup> The B3LYP density functional was combined with the 6-31G\* basis set for all molecules.<sup>7</sup> The more extensive 6-311G\*\* basis set was also used to study molecules containing up to four rings, but energy differences among a particular set of isomers were essentially constant within a basis set. Each structure was fully optimized to obtain a starting point for a potential surface scan. In all cases, the energy minimum was found to be that in which the hydroxy group sits in the molecular plane so that the atomic p-orbital lies perpendicular to the plane of the ring. The relaxed potential surface scan was performed over the C—C—O—H dihedral angle, which was varied from 0 to 180°,

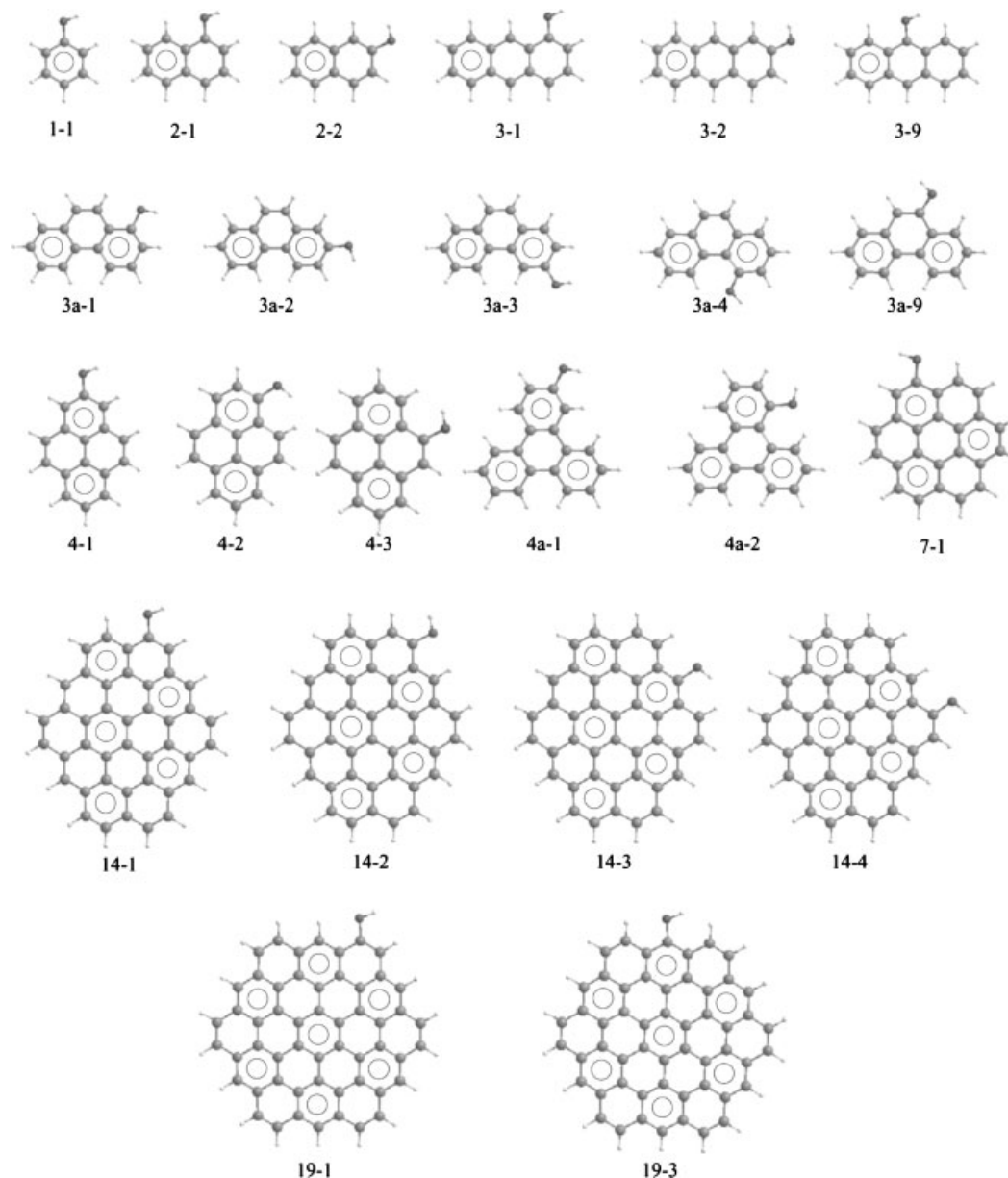


**Figure 2.** Potential energy scan over the rotation of the OH about the C—C bond in phenol

using a step size of 10°. The symmetric potential energy curve for phenol at the B3LYP/6-31G\* level of theory is shown in Fig. 2. The  $C_s$  symmetry of phenol ensures that the potential surface between 180 and 360° is identical with the segment shown here. Since the energy change between adjacent steps near the maximum was found to be less than 0.02 kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ), steps of smaller size in the potential scan were deemed unnecessary. Monohydroxy derivatives of benzene (**1**), naphthalene (**2**), anthracene and phenanthrene (**3**), pyrene and triphenylene (**4**), coronene (**7**), circumpyrene (**14**) and circumcoronene (**19**) were studied; see Fig. 3 and Tables 1 and 2. No experimental data are known for the rotational barriers of any of these molecules, except phenol. All positional isomers were considered and, in the case of a non-symmetric environment around the hydroxy group, both planar conformers were taken into account. For more convenient notation, the structures are denoted by the number of rings, followed by the position of the substituent, as indicated in Fig. 3. Note in Table 1 the slight difference in the parameters for phenol and **3–9** at 0 and 180°. These should be identical and the insignificant difference represents computational error.

## RESULTS AND DISCUSSION

Two effects of opposite sign compete in establishing the magnitude of the rotational barrier: the mesomeric effect of the OH and hydrogen–hydrogen steric repulsion. As the C—C—O—H dihedral angle increases from 0 to 90°, the lone electron pair on the oxygen atom becomes localized, the mesomeric effect is substantially reduced and the energy increases. Concurrently, the distance between the hydrogen atom from the OH group and its nearest neighbor hydrogen atom typically reaches a maximum at 90°, resulting in reduced hydrogen–hydrogen steric repulsion. Generally, the increase in the energy due to the removal of the electrons from the extended, delocalized  $\pi$ -system exceeds the steric stabilization as the angle approaches 90°. As a result, the calculations indicate that the minimum energy in all cases corresponds to a planar structure. There is no possibility of directly separating the magnitude of the two competing effects in these calculations. One way to circumvent this



**Figure 3.** The monohydroxy-derivatives are shown only with complete  $n$ -electron sextets, the Clar formulae. For many of these ring systems, other Kekulé structures may be drawn, but the Clar number is unchanged. The numbering system is described in the text

issue is to compare the energy barriers for species in which the lowest lying conformer has approximately the same  $\text{—OH—H}$  distance, so that the steric effect is essentially constant. In this case, variations in the rotational barrier may be attributed to the mesomeric effect. Below, we discuss each of the ring systems separately and then combine the results to provide some general conclusions. Absolute energies are presented in Table 2 and barrier energies in Table 3.

Phenol [Fig. 4(a)] is the first member of the series and its properties may be used as a reference. In the following discussion, results from the 6-31G\* basis set calculations will be used for the comparisons. Comparison of the available experimental data<sup>8-10</sup> with our DFT results

indicates that the bond lengths are within 0.01 Å of the experimental values. The experimentally obtained values for the barrier in phenol are in the 3.37–3.55 kcal mol<sup>-1</sup> range.<sup>11,12</sup> However, an error of at least 0.1 kcal mol<sup>-1</sup> has been reported for the value obtained using the rigid rotor approximation<sup>13</sup>. In the present work, the barrier height is 4.08 kcal mol<sup>-1</sup>. Zierkiewicz *et al.* used the larger 6-311++G\*\* basis set to obtain 3.67 kcal mol<sup>-1</sup> for the phenol rotation barrier.<sup>13</sup> The difference between that barrier height and the current estimate reflects the difference in basis set size; note the decrease in barrier height for phenol using the 6-311G\*\* basis set in Table 3. The size of the molecules in the current work precludes use of such large basis sets. Provided that we rely on

**Table 1.** Selected structural parameters (bond lengths, Å) obtained at the B3LYP/6–31G\* level of theory: the structure number in bold (see Fig. 3) is followed by the angle of the OH rotation

Structure	$r_{C-C1}$	$r_{C-C2}$	$r_{C-O}$	$r_{H-H}$	Structure	$r_{C-C1}$	$r_{C-C2}$	$r_{C-O}$	$r_{H-H}$
<b>Phenol-00</b>	1.399	1.399	1.369	2.291	<b>4-1-00</b>	1.396	1.397	1.368	2.280
<b>Phenol-90</b>	1.397	1.397	1.390	2.956	<b>4-1-90</b>	1.394	1.394	1.390	2.950
<b>Phenol-180</b>	1.400	1.399	1.369	2.292	<b>4-1-180</b>	1.397	1.396	1.368	2.280
<b>2-1-00</b>	1.380	1.428	1.368	2.276	<b>4-2-00</b>	1.397	1.411	1.368	2.263
<b>2-1-90</b>	1.377	1.426	1.390	2.747	<b>4-2-90</b>	1.394	1.409	1.390	2.723
<b>2-1-180</b>	1.381	1.431	1.367	1.892	<b>4-2-180</b>	1.398	1.413	1.366	1.904
<b>2-2-00</b>	1.379	1.420	1.367	2.304	<b>4-3-00</b>	1.365	1.445	1.367	2.279
<b>2-2-90</b>	1.376	1.418	1.389	2.959	<b>4-3-90</b>	1.362	1.444	1.389	2.705
<b>2-2-180</b>	1.380	1.419	1.369	2.269	<b>4-3-180</b>	1.365	1.449	1.367	1.869
<b>3-1-00</b>	1.373	1.437	1.367	2.283	<b>4a-1-00</b>	1.386	1.403	1.368	2.303
<b>3-1-90</b>	1.370	1.436	1.389	2.736	<b>4a-1-90</b>	1.383	1.401	1.389	2.913
<b>3-1-180</b>	1.374	1.441	1.367	1.876	<b>4a-1-180</b>	1.386	1.404	1.367	2.254
<b>3-2-00</b>	1.373	1.429	1.367	2.309	<b>4a-2-00</b>	1.390	1.429	1.372	2.115
<b>3-2-90</b>	1.370	1.428	1.389	2.960	<b>4a-2-80</b>	1.387	1.426	1.394	2.476
<b>3-2-180</b>	1.373	1.428	1.368	2.257	<b>4a-2-180</b>	1.391	1.424	1.368	1.755
<b>3-9-00</b>	1.411	1.410	1.366	1.873	<b>7-1-00</b>	1.376	1.431	1.368	2.272
<b>3-9-90</b>	1.406	1.406	1.391	2.717	<b>7-1-90</b>	1.373	1.430	1.390	2.749
<b>3-9-180</b>	1.410	1.401	1.367	1.875	<b>7-1-180</b>	1.376	1.434	1.367	1.885
<b>3a-1-00</b>	1.384	1.422	1.369	2.273	<b>14-1-00</b>	1.374	1.432	1.367	2.271
<b>3a-1-90</b>	1.381	1.420	1.391	2.700	<b>14-1-90</b>	1.371	1.431	1.390	2.758
<b>3a-1-180</b>	1.385	1.425	1.368	1.851	<b>14-1-180</b>	1.375	1.435	1.367	1.880
<b>3a-2-00</b>	1.383	1.410	1.367	2.304	<b>14-2-00</b>	1.375	1.435	1.367	2.272
<b>3a-2-90</b>	1.381	1.408	1.389	2.960	<b>14-2-90</b>	1.371	1.434	1.388	2.742
<b>3a-2-180</b>	1.384	1.410	1.368	2.285	<b>14-2-180</b>	1.375	1.438	1.366	1.876
<b>3a-3-00</b>	1.386	1.400	1.369	2.286	<b>14-3-00</b>	1.402	1.420	1.365	1.881
<b>3a-3-90</b>	1.383	1.408	1.389	2.952	<b>14-3-90</b>	1.397	1.417	1.389	2.708
<b>3a-3-180</b>	1.385	1.410	1.367	2.260	<b>14-3-180</b>	1.400	1.422	1.366	1.866
<b>3a-4-00</b>	1.389	1.428	1.371	2.148	<b>14-4-00</b>	1.363	1.449	1.366	2.287
<b>3a-4-90</b>	1.386	1.426	1.394	2.346	<b>14-4-90</b>	1.360	1.449	1.388	2.732
<b>3a-4-180</b>	1.390	1.427	1.367	1.687	<b>14-4-180</b>	1.363	1.453	1.366	1.859
<b>3a-9-00</b>	1.363	1.442	1.368	2.277	<b>19-1-00</b>	1.367	1.444	1.366	2.276
<b>3a-9-90</b>	1.360	1.442	1.390	2.689	<b>19-1-90</b>	1.364	1.444	1.388	2.736
<b>3a-9-180</b>	1.363	1.447	1.367	1.834	<b>19-1-180</b>	1.367	1.448	1.366	1.865
					<b>19-3-00</b>	1.411	1.410	1.366	1.874
					<b>19-3-90</b>	1.406	1.407	1.389	2.704
					<b>19-3-180</b>	1.410	1.411	1.366	1.873

relative values of barrier height, the smaller basis set used throughout should be sufficient. The agreement between the previously obtained experimental and computational data provides confidence in the data that we obtained for the larger ring systems. We also calculated the entropy change associated with the barrier. This is, on average,  $\sim 1 \text{ kcal mol}^{-1} \text{ K}^{-1}$  (entropy is reduced at the barrier), so that even at 300 K, the entropic term,  $-T\Delta S$ , is less than  $0.35 \text{ kcal mol}^{-1}$ . Since the entropic change is essentially a constant value and significantly less than the barrier enthalpy, it does not influence the conclusions in this report and we have chosen to report only the energy terms.

The hydroxy derivatives of naphthalene, **2-1** and **2-2**, display differences in the hydrogen–hydrogen steric repulsion depending on the orientation of the OH in the planar configuration [Fig. 4(b) and (c)]. The absolute energies of the two conformers of **2-1**, corresponding to C–C–O–H dihedral angle values of 0 and 180°, differ by  $1.68 \text{ kcal mol}^{-1}$ ; bond lengths in Table 1 are identical

in the two configurations. The parameter that does significantly change is the hydrogen–hydrogen distance, from  $2.276 \text{ Å}$  in the lower lying, 0°, isomer to  $1.892 \text{ Å}$  in the hindered, 180°, structure. Focusing on the lower energy conformer of **2-1**, the energy barrier of  $4.04 \text{ kcal mol}^{-1}$  is reached when the C–C–O–H dihedral angle becomes 90°. The carbon–carbon bond lengths at this point decrease by 0.14%, whereas the C–O bond length increases by 1.61% to  $1.390 \text{ Å}$ . The direction of the changes in these parameters indicates a decrease in electron delocalization as a result of the OH rotation. Structure **2-2** has more symmetric hydrogen–hydrogen distances in the two (0° and 180°) conformers, which result in an absolute energy difference between the two structures of only  $0.69 \text{ kcal mol}^{-1}$ . The energy barrier for 90° rotation, however, is  $4.50 \text{ kcal mol}^{-1}$ , 10% higher than for **2-1**. The explanation for this barrier energy increase may be found by comparing the hydrogen steric repulsion in **2-1** and **2-2**. Isomer **2-1** has its shortest hydrogen–hydrogen distance when it is in its



**Table 2.** Absolute energies of the lowest conformers at the 6–31G\* level of theory

Structure	Energy (a.u.)	E <sub>rel</sub> (kcal mol <sup>-1</sup> )
<b>Phenol</b>	-307.46487	0
<b>2-1</b>	-461.10909	0.21
<b>2-2</b>	-461.10942	0
<b>3-1</b>	-614.74727	0.18
<b>3-2</b>	-614.74757	0
<b>3-9</b>	-614.74427	2.08
<b>3a-1</b>	-614.75459	0.39
<b>3a-2</b>	-614.75454	0.44
<b>3a-3</b>	-614.75468	0.35
<b>3a-4</b>	-614.75093	2.70
<b>3a-9</b>	-614.75522	0
<b>4-1</b>	-690.98915	0.51
<b>4-2</b>	-690.98911	0.53
<b>4-3</b>	-690.98995	0
<b>4a-1</b>	-768.39771	0
<b>4a-2</b>	-768.39103	4.20
<b>7-1</b>	-997.11441	0
<b>14-1</b>	-1685.57486	0.28
<b>14-2</b>	-1685.57490	0.25
<b>14-3</b>	-1685.57217	1.98
<b>14-4</b>	-1685.57532	0
<b>19-1</b>	-2144.16514	0
<b>19-3</b>	-2144.16188	2.05

lowest energy conformation, 0° dihedral. This distance increases as the rotation proceeds to 90°, reducing the steric repulsion. The hydrogen–hydrogen distance is only ~1% less than that in phenol. Therefore, one expects that **2-1** will benefit to a similar extent as phenol from the rotation of the OH to alleviate the steric repulsion. This is

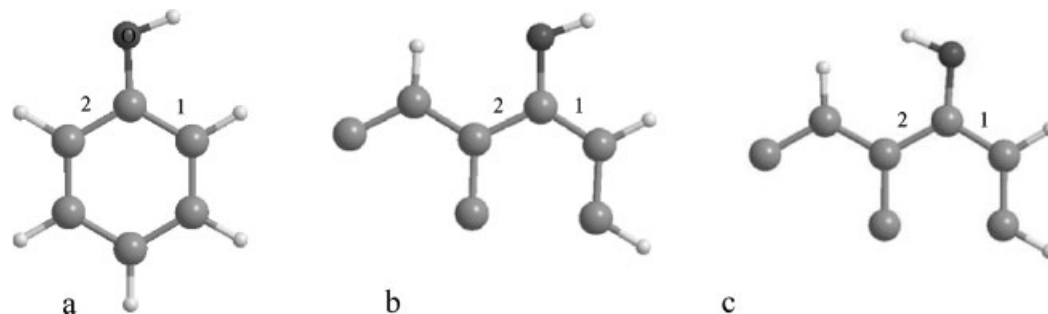
**Table 3.** Hydroxy group rotation barriers (kcal mol<sup>-1</sup>)

Structure	6–31G*	6–311G**
<b>Phenol</b>	4.08	3.87
<b>2-1</b>	4.04	3.78
<b>2-2</b>	4.50	4.22
<b>3-1</b>	4.15	3.87
<b>3-2</b>	4.73	4.45
<b>3-9</b>	2.31	2.19
<b>3a-1</b>	3.90	3.64
<b>3a-2</b>	3.99	3.69
<b>3a-3</b>	3.97	3.67
<b>3a-4</b>	3.78	3.64
<b>3a-9</b>	4.22	3.92
<b>4-1</b>	4.15	3.83
<b>4-2</b>	3.87	3.60
<b>4-3</b>	4.29	3.94
<b>4a-1</b>	4.24	3.90
<b>4a-2</b>	3.46	3.30
<b>7-1</b>	4.15	
<b>14-1</b>	4.22	
<b>14-2</b>	4.22	
<b>14-3</b>	2.49	
<b>14-4</b>	4.38	
<b>19-1</b>	4.34	
<b>19-3</b>	2.31	

what we observe in comparing the barrier energy for **2-1** and phenol. The hydrogen–hydrogen distance in **2-2** is similar to that in phenol and slightly greater than that in **2-1**, so that relief of steric repulsion is not a critical factor in any energy barrier difference. The rotation barrier for **2-2** is 0.46 kcal mol<sup>-1</sup> greater than that for **2-1** and 0.62 kcal mol<sup>-1</sup> greater than for phenol. This higher value arises predominately from perturbation of the p–π delocalization, indicating that **2-2** experiences a greater mesomeric effect than phenol or **2-1**.

The hydroxy derivatives of anthracene, **3-1** and **3-2**, show the same barrier trends as naphthol. This is not unexpected, since the local environment is identical for the two sets of structures and other structurally related polycenes. The barrier in **3-1**, which has a 2.283 Å hydrogen–hydrogen distance, is 4.15 kcal mol<sup>-1</sup>. Since the hydrogen atom experiences slightly greater steric repulsion, at both 0° and 90°, than does phenol, one expects that the barrier, relative to phenol, would decrease. The calculated barrier is actually higher and indicates a greater extent of stabilization from the p–π overlap. In the less sterically hindered isomer, **3-2**, the energy of rotation increases to 4.73 kcal mol<sup>-1</sup>. The increase is indicative of the larger contribution of the mesomeric effect. An interesting case is the **3-9** isomer, which has identical conformations at dihedral angles of 0° or 180°, both with severe steric hindrance. The nearby hydrogen atom is located only 1.873 Å from the hydroxy group hydrogen. The significant hydrogen–hydrogen steric repulsion is responsible for lowering the rotational barrier to 2.31 kcal mol<sup>-1</sup>. Notario *et al.*<sup>14</sup> used the MP2/6–31G\* level of theory to calculate the difference in barrier height for these three anthrol isomers. They found, including the zero point vibrational energy and thermal corrections, that 1-anthrol and 2-anthrol show almost no change in the barrier energy (1-anthrol is ~0.05 kcal mol<sup>-1</sup> higher) and that the **3-9** barrier is ~1.5 kcal mol<sup>-1</sup>. Although the corrections play a role in the discrepancy with the current work, they are small and are not required to make the relative assignments with which we are concerned. The difference between the two calculations is almost certainly a reflection of the different level of theory employed. It is interesting to note that tautomerism occurs for **3-9** and the keto form dominates in a 9:1 ratio over the hydroxy compound. The computational value for the rotational barrier in this isomer suggests that the hydroxy group will more easily rotate and, perhaps, have some effect on the tautomerization.

Phenanthrene has five monohydroxy derivatives. Unlike anthracene, which belongs to the linear acene series and has only a single benzoid ring in any resonance structure, the catacondensed phenanthrene has two independent π-electron sextets located at the terminal rings. There are two distinct choices for the OH substituent: the terminal rings (structure **3a-1** through **3a-4**) or the central double bond (structure **3a-9**). In the first case, one of the



**Figure 4.** The geometry parameters for phenol and generalized larger hydroxy-polycene derivatives are shown. In (a), the phenol structure, the configuration shown and one in which the OH is rotated  $180^\circ$  are in equivalent environments. The structures (b) and (c) represent two different planar forms of the same structural isomer. They differ by a  $180^\circ$  rotation of the OH. The environment of the hydroxy group hydrogen atom is different in these two cases. The lower energy structure is (b), the  $0^\circ$  form, with less hydrogen–hydrogen steric repulsion

$\pi$ -electron sextets will be perturbed, whereas in the second, the central double bond interacts with the lone pair of electrons on the oxygen atom. The rotation barriers for the first four structures in Fig. 3, 3.90, 3.99, 3.97 and 3.78 kcal mol $^{-1}$ , respectively, correlate with the hydrogen–hydrogen distances in the isomers, 2.273, 2.304, 2.286 and 2.148 Å; these exhibit similar mesomeric effects and the barrier value is controlled by steric effects. The fifth isomer, **3a-9**, has a hydrogen–hydrogen distance of 2.277 Å, so that a barrier similar to **3a-1** might be expected. However, the energy required to reach a  $90^\circ$  dihedral angle is 4.22 kcal mol $^{-1}$ , 10% greater than for the **3a-1** isomer. In **3a-9**, rotation of the OH group results in a 0.2% change in the length of the carbon–carbon double bond, while the length of the neighboring single bond remains unchanged, indicating that any additional delocalization occurs outside of the terminal (aromatic) rings. Clearly, the position of the OH plays a major role in the mesomeric effect and the resulting rotational barrier values. In both cases, substitution at the terminal ring or the double bond, there is stabilization due to the mesomeric effect. However, substitution at carbon atoms that are not components of independent sextets appears to provide greater mesomeric stabilization.

Pyrene has three monohydroxy derivatives, as shown in Fig. 3. If the position of the OH group were not a factor, then the barrier to rotation for **4-1** would be approximately equal to that of **4-3** because steric effects are identical. In contrast, isomer **4-3** has the higher barrier energy, 4.29 kcal mol $^{-1}$ . This barrier is greater than that for phenol, even though the hydrogen–hydrogen distance is approximately 1% shorter than in phenol. Clearly, the mesomeric effect is greater in **4-3** than in **4-1** or phenol. Pyrene may be represented as having two independent sextets in opposite rings, analogous in that respect to biphenyl (Fig. 3). This creates two double bonds in the two opposing rings, which are perpendicular to the  $\pi$ -electron sextets. When the OH substituent is located at these double bonds, the interaction with the lone pair of the oxygen atom is significant. The stability imparted by this mesomeric interaction is reflected in the larger than

expected barrier for **4-3**. Isomer **4-2** is subject to greater hydrogen–hydrogen repulsion and its alleviation makes the OH rotation occur more readily; this isomer has the lowest energy barrier among these derivatives.

Triphenylene is an interesting case with three  $\pi$ -electron sextets in the rings that surround the central ring. Any substituent will be positioned on a  $\pi$ -electron sextet. This observation leads one to predict that triphenylene will benefit from the mesomeric effect to a lesser extent than pyrene. The barrier for **4a-1**, 4.24 kcal mol $^{-1}$ , is very slightly greater than that for **4-1**. The hydrogen–hydrogen distance, 2.303 Å, in **4a-1** is greater (2.280 Å in structure **4-1**) and the basis for the slight increase. Isomer **4a-2** is sterically hindered and is the only isomer having a non-planar second form. This is reflected in the barrier energy, which reaches 3.50 kcal mol $^{-1}$  at  $80^\circ$ .

Coronene can be represented by two resonance structures, each with three independent benzene rings. —OH rotation in coronenol must surmount a relatively high barrier, 4.15 kcal mol $^{-1}$ , given the relatively short hydrogen–hydrogen distance, 2.272 Å (compare with the phenol distance of 2.291 Å and barrier of 4.08 kcal mol $^{-1}$ ). The OH interacts with a ring in **7-1** and with a double bond in its second resonance form. In this aspect, coronenol resembles naphthol, where the substitution affects a  $\pi$ -electron sextet in only one of the two resonance forms. The barrier height is similar to that for **2-1**.

The four derivatives of circumpylene are an excellent set to explore the role of the hydroxy group position. The parent molecule has two resonance structures with five  $\pi$ -electron sextets. Structures **14-1** and **14-2**, functionalized on the same ring (having a  $\pi$ -electron sextet in one resonance form, but not the second), have identical hydrogen environments and identical 4.22 kcal mol $^{-1}$  rotation barriers. The third isomer, **14-3**, is sterically hindered, as was **3-9**; the hydrogen–hydrogen bond distance is only 1.881 Å. This lowers the barrier to 2.49 kcal mol $^{-1}$ . Isomer **14-4** is different from all of the others; the OH is bound to a ring that lacks a sextet in either Kekulé structure. Substitution at such a site leads to greater stabilization by the electron-donating substituent

owing to the mesomeric effect and the energy barrier to rotation is  $4.38 \text{ kcal mol}^{-1}$ , larger than for either **14-1** and **14-2**.

The largest molecules studied in this work are the isomers of circumcoronenol. This molecule has only a single Kekulé structure with seven  $\pi$ -electron sextets, leaving double bonds with bond lengths of  $1.363 \text{ \AA}$  on each of the six corners (Fig. 3). The barrier in **19-1** is  $4.34 \text{ kcal mol}^{-1}$ , similar to that for the previous non-benzoid example, **14-4**. The hydroxy group hydrogen atom in **19-3** is hindered by hydrogen atoms from either side. The short hydrogen–hydrogen distance,  $1.874 \text{ \AA}$ , provides significant steric repulsion and lowers the rotation barrier to  $2.31 \text{ kcal mol}^{-1}$  as in **14-3**.

Examining the series phenol, coronenol and circumcoronenol, the rotation of the OH requires 4.08, 4.15 and  $4.34 \text{ kcal mol}^{-1}$ , respectively. Two features vary across this series: the size of the ring system and the position of the substituent. Size cannot be the sole basis for the energy barrier variation, since the barriers for **2-2** and **3-2** are greater than that for circumcoronenol. If we consider structure, the picture is as follows. Phenol has a single  $\pi$ -electron sextet and the OH interacts with the ring by default. Coronenol has two Kekulé structures, each with three independent  $\pi$ -electron rings. The hydroxy group is bound to such a ring in only one of the two resonance structures. In circumcoronenol, **19-1**, the substituent does not interact with a ring at all. The percentage of resonance structures in which  $\pi$ -electron sextets are influenced by the hydroxy group substitution decreases from 100% in phenol to 50% in coronenol and 0% in circumcoronenol and the barrier increases. The energy barriers for structures with 0%  $\pi$ -sextet interaction, **3a-9**, **4-3**, **14-4** and **19-1**, are the highest among their corresponding isomers. The results indicate a greater mesomeric effect in molecules where the OH is not bound to a  $\pi$ -electron sextet. This is in agreement with Clar's stability rule, which may be paraphrased as 'the stability of a polycyclic hydrocarbon is proportional to the maximum number of independent benzene rings that can be formed'. Extending this statement to the derivatives studied here, we postulate that 'in structures with independent sextets, regions in which the atoms do not contribute orbitals to such an independent  $\pi$ -electronic sextet will be more stabilized by substitution, compared with those regions in which atoms do contribute to such rings'. The mesomeric effect may be operative in all cases, but its magnitude is greater when the lone electron pair from the substituent interacts with a non-benzoid region. Note that this does not characterize the ease of a substitution reaction. The effect in this work occurs in molecules for which the integrity of the  $\pi$ -electronic structure is preserved *after* substitution. The mesomeric effect is a special case of electron delocalization, where the lone pair is in partial conjugation with a double bond or a system of double bonds. A typical example is the relationship between the amino group and the carbonyl

oxygen, when bonded to the same carbon atom. The lone pair of the amino group is conjugated with the  $\pi$ -electrons of the carbonyl group. The rationale for the new Clar's rule postulate in our case may be seen by studying the resonance structures for the substituted ring systems. Substitution on a  $\pi$ -electron sextet destroys the integrity of that sextet. Examples of this effect include **3a-1** through **3a-4**. In **3a-9**, where the substitution occurs at a carbon that is not part of a sextet, we create a more extended delocalized system. Preservation of the sextets is the controlling factor. Since the differences being discussed are small and there is a contribution to the rotation barrier that is inherent to the structure, it is not possible to predict *a priori* the magnitude of the rotational barrier of a particular molecule. What is feasible is a prediction of which derivative for a given polycyclic hydrocarbon will benefit to a greater extent from the mesomeric effect and, subsequently, will have a higher rotational barrier.

## CONCLUSIONS

From the energies of rotation, the absolute energies and accounting for the hydrogen–hydrogen steric repulsion, one may conclude that for substituted polycyclic hydrocarbons, the  $p$ – $\pi$  interaction is greater when the substituent is bound to a region that does not participate in a  $\pi$ -electronic sextet. These calculations are in agreement with an extension of Clar's stability rule.

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