

Intramolecular Hydrogen Bond in the Hydroxycyclohexadienyl Peroxy Radicals

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ABSTRACT: The hydroxycyclohexadienyl peroxy radicals ($\text{HO}-\text{C}_6\text{H}_6-\text{O}_2$) produced from the reaction of OH-benzene adduct with O_2 were studied with density functional theory (DFT) calculations to determine their characteristics. The optimized geometries, vibrational frequencies, and total energies of 2-hydroxycyclohexadienyl peroxy radical II_s and 4-hydroxycyclohexadienyl peroxy radical III_s were calculated at the following theoretical levels, B3LYP/6-31G(d), B3LYP/6-311G(d,p), and B3LYP/6-311+G(d,p). Both were shown to contain a red-shifted intramolecular hydrogen bond ($\text{O}-\text{H} \cdots \text{O}-\text{H}$ bond). According to atoms-in-molecules (AIM) analysis, the intramolecular hydrogen bond in the 2-hydroxycyclohexadienyl peroxy radical II_s is stronger than that one in 4-hydroxycyclohexadienyl peroxy radical III_s , and the former is the most stable conformation among its isomers. Generally speaking, hydrogen bonding in these radicals plays an important role to make them more stable. Based on natural bond orbital (NBO) analysis, the stabilization energy between orbitals is the main factor to produce red-shifted intramolecular hydrogen bond within these peroxy radicals. The hyperconjugative interactions can promote the transfer of some electron density to the $\text{O}-\text{H}$ antibonding orbital, while the increased electron density in the $\text{O}-\text{H}$ antibonding orbital leads to the elongation of the $\text{O}-\text{H}$ bond and the red shift of the $\text{O}-\text{H}$ stretching frequency.

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Key words: hydroxycyclohexadienyl peroxy radical; intramolecular hydrogen bond; density function theory; AIM topological analysis; NBO analysis

Introduction

Benzene is the simplest among aromatic compounds and is released into the atmosphere by human activities, such as emissions from burn-

ing oil and coal, motor vehicle exhaust, evaporation of solvents, and emission from gasoline stations. Besides the toxicity to humans, conversion of benzene in the atmosphere can play a significant role in the increased ozone concentration in troposphere as well as in the formation of secondary organic aerosols [1]. The reaction of benzene with OH-radicals can occur while it is attacked by OH-radicals in the atmosphere, which has been studied experimentally [2–7] and theoretically [8–11]. In the case of the benzene + OH reaction, the addition, $\text{C}_6\text{H}_6 + \text{OH} \rightarrow \text{C}_6\text{H}_6-\text{OH}$, forming hydroxycyclohexadienyl

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radicals I, C_6H_6-OH , is the major reaction pathway, while the H-atoms abstraction, $C_6H_6 + OH \rightarrow C_6H_5 + H_2O$, is the minor reaction pathway at room temperature [11]. Under atmospheric conditions, the OH-benzene adduct, hydroxycyclohexadienyl radical I, can also react with O_2 by O_2 addition, $C_6H_6-OH + O_2 \rightarrow HO-C_6H_6-O_2$, forming the hydroxycyclohexadienyl peroxy radical ($HO-C_6H_6-O_2$), and this addition can occur at either the *ortho* position or the *para* position with respect to the OH group, to produce 2-hydroxycyclohexadienyl peroxy radical II or 4-hydroxycyclohexadienyl peroxy radical III [12–14]. The fate of the peroxy radicals is governed by competition between the reaction with NO to form alkoxy radicals and the cyclization to form bicyclic radicals. The bicyclic radicals can further undergo unimolecular rearrangement to form epoxide radicals or bimolecular reaction with O_2 to form bicyclic peroxy radicals. Given the steric hindrance problems associated with another cyclization, the bicyclic peroxy radicals react with NO to form a bicyclic oxy radicals and NO_2 . The most suitable reaction path to produce the bicyclic oxy radicals is the fragmentation via favorable β -scission reactions, which can yield an acyclic radical and eventually dicarbonyl products [15, 16]. So, the fragment products are dependent on the hydroxycyclohexadienyl peroxy radical, which are the important intermediates in the reaction of OH-radicals with benzene and consecutive reactions of benzene $-OH$ adducts with O_2 in the gas phase in N_2-O_2 mixtures at atmosphere pressure and room temperature.

When O_2 is added to hydroxycyclohexadienyl radical I, two different isomers of a system containing a peroxy and an OH group, facing each other on the scaffold of a phenyl ring, 2-hydroxycyclohexadienyl peroxy radical II_s and 4-hydroxycyclohexadienyl peroxy radical III_s , are formed, respectively. In both isomers mentioned above, when the OH groups are rotated $\sim 180^\circ$, another two kind of isomers, 2-hydroxycyclohexadienyl peroxy radical II_o and 4-hydroxycyclohexadienyl peroxy radical III_o , can be obtained, respectively. In fact, the hydroxycyclohexadienyl peroxy radical can be thought of as a complex of benzene $-OH$ adducts with O_2 . Provided that there exists an intramolecular hydrogen bond with an interaction between the terminal oxygen of the peroxy (O_2) group and the hydrogen of the OH group within 2-hydroxycyclohexadienyl peroxy radical II_s and 4-hydroxycyclohexadienyl peroxy radical III_s , it will have an effect on the stability of this complex, although the hydrogen bond is a

weak interaction between those function groups. Therefore, the stability of the hydroxycyclohexadienyl peroxy will be dependent on whether there is an intramolecular hydrogen bond within these peroxy radicals, and on how strong the intensity of the hydrogen bond is. However, the characteristics of the hydroxycyclohexadienyl peroxy radicals are less known, and the performance of the intramolecular hydrogen bonds within them is not evaluated for the present. The main purpose of this work is to study their characteristics (e.g., optimized geometry, vibrational frequencies, and total energies) of the hydroxycyclohexadienyl peroxy radical ($HO-C_6H_6-O_2$) with density functional theory (DFT), verify the existence of the intramolecular hydrogen bond by atoms-in-molecules (AIM) topological analysis, and discuss the origin of the red-shifted hydrogen bond by natural bond orbital (NBO) analysis.

Computational Methods

All the calculations in the present study were performed using the Gaussian 98 series of programs [17]. The geometries of 2-hydroxycyclohexadienyl peroxy radical II_s , 2-hydroxycyclohexadienyl peroxy radical II_o , 4-hydroxycyclohexadienyl peroxy radical III_s , and 4-hydroxycyclohexadienyl peroxy radical III_o were optimized at the B3LYP/6-311G(*d,p*) level, 2-hydroxycyclohexadienyl peroxy radical II_s and 4-hydroxycyclohexadienyl peroxy radical III_s were also studied at the B3LYP level with the 6-31G(*d*), 6-311G(*d,p*), and 6-311+G(*d,p*) basis sets, respectively. The structures and vibration frequencies of the hydroxycyclohexadienyl radical I and O_2 were studied at the same levels. The basis set superposition error (BSSE) was calculated according to the counterpoise method proposed by Boys and Bernardi [18]. Hydrogen bonding energy (ΔE^{BSSE}) was computed as the difference between the total energy of the complex [$E(A-B)_{AB}$] and the sum of the subsystem energy [$E(A)_{AB}$, $E(B)_{AB}$]:

$$\Delta E^{BSSE} = E(A-B)_{AB} - E(A)_{AB} - E(B)_{AB}.$$

The nature of the strong intramolecular hydrogen bond in most stable conformers for the hydroxycyclohexadienyl peroxy radicals was studied by using the AIM theory of Bader [19] at the B3LYP/6-311G(*d,p*) level. NBO [20] analysis is also carried out at the B3LYP/6-311G(*d,p*) level.

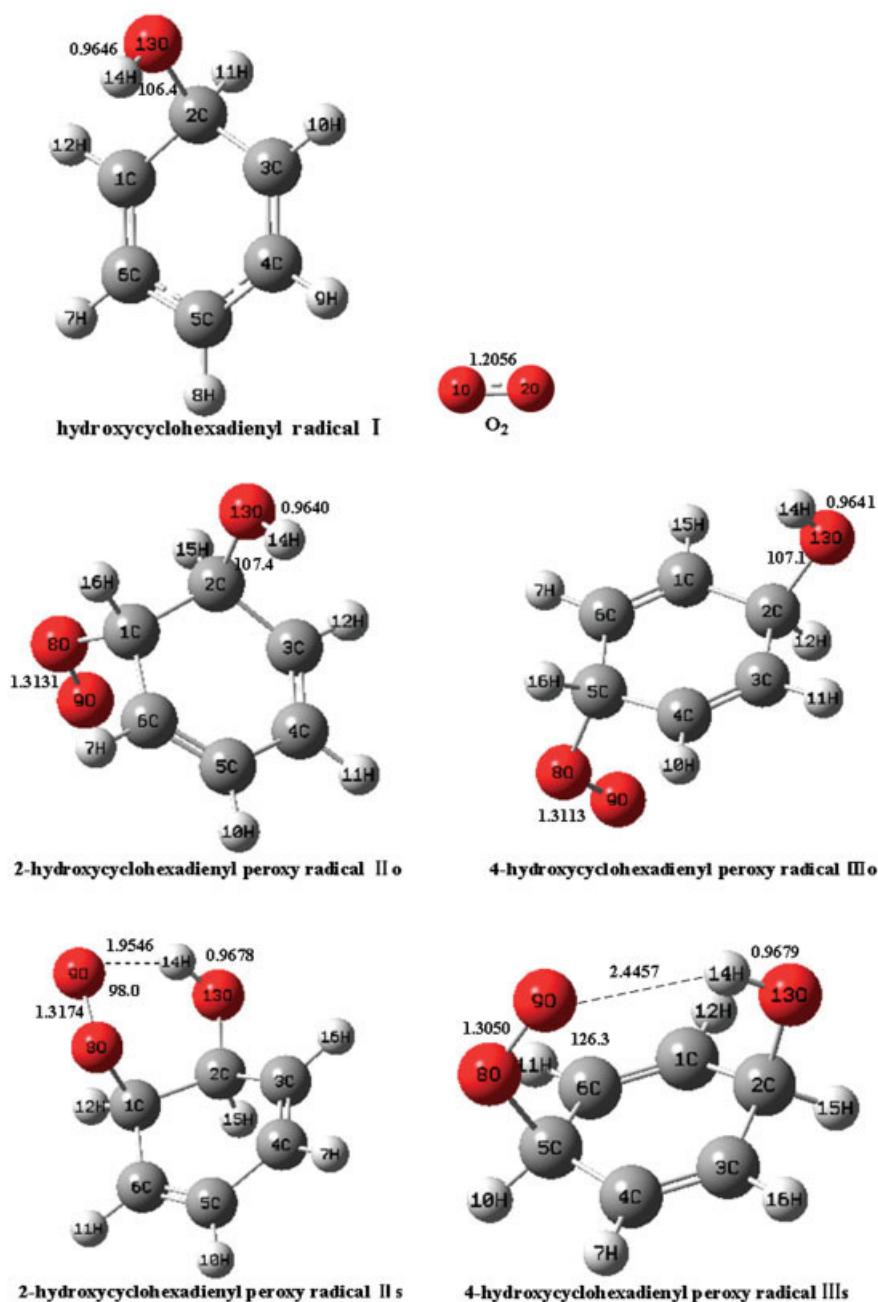


FIGURE 1. Optimized geometries of the hydroxycyclohexadienyl radical I, O₂, 2-hydroxycyclohexadienyl peroxy radical II_o and II_s and 4-hydroxycyclohexadienyl peroxy radical III_o and III_s at the B3LYP/6-311G(*d,p*) level. Bond lengths in Ångstroms (Å), bond angles in degrees (°).

Results and Discussion

GEOMETRIES, FREQUENCIES, AND ENERGIES

The structures of the hydroxycyclohexadienyl radical I, O₂, 2-hydroxycyclohexadienyl peroxy

radical II_s, 2-hydroxycyclohexadienyl peroxy radical II_o, 4-hydroxycyclohexadienyl peroxy III_s, and 4-hydroxycyclohexadienyl peroxy III_o are optimized with the B3LYP/6-311G(*d,p*) level and are shown in Figure 1. The geometric parameters calculated using the B3LYP/6-31G(*d*), B3LYP/6-311G(*d,p*), and B3LYP/6-311+G(*d,p*) levels are

TABLE I

Change in bond length, change in bond stretching frequency, and interaction energy with BSSE correction at the B3LYP/6-31G(d), B3LYP/6-311G(d,p), and B3LYP/6-311+G(d,p) levels.

	B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3LYP/6-311+G(d,p)
Peroxy radical II _s			
$\Delta r(\text{O13—H14}) (\text{\AA})$	+0.0031	+0.0032	+0.0027
$\Delta \nu(\text{O13—H14}) (\text{cm}^{-1})$	−66	−72	−67
$\Delta E^{\text{BSSE}} (\text{kJ mol}^{-1})$	−18.74	−9.80	−13.77
Peroxy radical III _s			
$\Delta r(\text{O13—H14}) (\text{\AA})$	+0.0033	+0.0033	+0.0028
$\Delta \nu(\text{O13—H14}) (\text{cm}^{-1})$	−38	−45	−40
$\Delta E^{\text{BSSE}} (\text{kJ mol}^{-1})$	−15.97	−8.98	−12.74

listed in Table I. The zero-point energy (ZPE)-corrected relative energies and H-bond strength for peroxy radicals at the B3LYP/6-311G(d,p) level are also listed in Table II. As shown in Figure 1, in the 2-hydroxycyclohexadienyl peroxy radical II_o and 4-hydroxy-cyclohexadienyl peroxy III_o, the intramolecular hydrogen bond cannot be formed through OH group and peroxy group. In contrast, there is an intramolecular hydrogen bond with an interaction between the terminal oxygen of the peroxy (O₂) group and the hydrogen of the OH group within 2-hydroxycyclohexadienyl peroxy radical II_s and 4-hydroxycyclohexadienyl peroxy III_s.

As shown in Table I, the results indicate good agreement between various levels. For peroxy radicals II_s, the calculated distance for O9...H14 is 1.9546 Å. It is worth mentioning that there is a C1—O8—O9—H14—O13—C2 six-membered ring in the peroxy radicals II_s. In the cyclic structure, O8—O9—H14 is not linear, and their bond angle is 98.0°. From the Table I, it can be seen that, by comparison with O13—H14 in the hydroxycyclohexadienyl radical I, there is a large red shift (72 cm^{−1}) of the O13—H14 stretching frequency in the

peroxy radicals II_s, which is correlated with the bond elongation (0.0032 Å) of the O13—H14 bond.

The structure of the peroxy radicals III_s is similar to that of peroxy radicals II_s. The corresponding length for O9...H14 is 2.4457 Å in the peroxy radicals III_s at the B3LYP/6-311G(d,p) level. By comparison with O13—H14 in hydroxycyclohexadienyl radical I, peroxy radicals III_s exhibits a red shift (45 cm^{−1}) of the O13—H14 stretching frequency, and this frequency shift is also correlated with the bond elongation (0.0033 Å) of the O13—H14 bond.

As shown in the Table I, the interaction energies with BSSE correction for the peroxy radicals II_s and III_s are −9.80 and −8.98 kJ mol^{−1} at the B3LYP/6-311G(d,p) level, respectively. The results show that the peroxy radicals II_s is slightly more stable than the peroxy radical III_s.

From Table II, we can see that, as contrasted with the peroxy radicals II_s and III_s, peroxy radicals III_o is slightly more stable than peroxy radicals II_o (only about −0.48 kJ mol^{−1}). For the 2-hydroxycyclohexadienyl peroxy radical, peroxy radical II_s is more stable than peroxy radical II_o (about −5.78 kJ

TABLE II

ZPE-corrected relative energies and H-bond strength for peroxy radicals at the B3LYP/6-311G(d,p) level of theory.

	Energy (hartree)	ZPE (hartree)	Relative energy (kJ mol ^{−1})	H-bond strength (kJ mol ^{−1})
Radical I + O ₂	−458.456097305	0.117275	0.0	—
Peroxy radicals II _o	−458.463583921	0.122517	−5.89	—
Peroxy radicals II _s	−458.465634421	0.122368	−11.67	−9.80
Peroxy radicals III _o	−458.463679022	0.122430	−6.37	—
Peroxy radicals III _s	−458.464705614	0.122891	−7.85	−8.98

TABLE III

Topological parameters of the O9—H14 bond critical point at the B3LYP/6-311G(*d,p*) level.

	ρ	$\nabla^2\rho$	λ_1	λ_2	λ_3
Peroxy radical II	0.02640	0.0936	−0.0359	−0.0341	0.164
Peroxy radical III	0.00905	0.0285	−0.00886	−0.00858	0.0460

mol^{−1}). Quite the same as the 2-hydroxycyclohexadienyl peroxy radical, in the 4-hydroxycyclohexadienyl peroxy radical, peroxy radical III_s is slightly more stable than peroxy radical III_o (about −1.48 kJ mol^{−1}). Although the H-bond energy difference between the peroxy radicals II_s and III_s is small, the intramolecular hydrogen bond in the 2-hydroxycyclohexadienyl peroxy radical has a stronger interaction than that in 4-hydroxycyclohexadienyl peroxy radical.

AIM TOPOLOGICAL ANALYSIS

To confirm the existence of the red-shifted intramolecular H-bond, AIM topological analysis should be performed. According to the AIM theory proposed by Bader [19], the topological characteristics of electron density depend on the grads vector of electron density [$\nabla\rho(r)$] and Laplacian of electron density [$\nabla^2\rho(r)$] values. In general, ρ is used to describe the strength of a bond, and the larger the value of ρ , the stronger the bond. The $\nabla^2\rho$ is used to describe the characteristic of the bond and $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$, where λ_i is an eigenvalue of the Hessian matrix of ρ . If one of the three λ_i is positive and the other two are negative, we can denote it by (3, −1) and call it the bond critical point (BCP). While $\nabla^2\rho < 0$, the bond is covalent bond; as $\nabla^2\rho > 0$, the bond belongs to the ionic bond, hydrogen bond, and van der Waals interactions. Koch and Popelier [21, 22] proposed eight topological criteria for the existence of hydrogen bonding interactions, and among them, three are most often applied [23]. In the opinion of Koch and Popelier, the electron density and its Laplacian for the H...Y contact within the X—H...Y H-bond should have a relatively high value. Both parameters for open-shell interactions as H-bonds are positive and should be within the following ranges: 0.002–0.035 a.u. for the electron density and 0.024–0.139 a.u. for its Laplacian [23].

The topological parameters of the BCP at the B3LYP/6-311G(*d,p*) level are listed in Table III. The value of the electron density ρ for O9...H14 in the

peroxy radicals II_s and III_s are 0.0264 and 0.00905 a.u. These values do fall within the proposed typical range of the H-bond. Since the $\rho(\text{O9...H14})$ in the peroxy radical II_s is larger than the $\rho(\text{O9...H14})$ in the peroxy radical III_s, we expect the former bond to be stronger than the latter. This demonstrates that the 2-hydroxycyclohexadienyl peroxy radical II_s is the more stable isomer. It is clear that hydrogen bonding plays a role in stabilizing the peroxy radicals: the hydrogen bond lengths are 1.9546 and 2.4457 Å for II_s and III_s, respectively, correlating with their relative stability. The values of the $\nabla^2\rho$ for O9...H14 in the peroxy radicals II_s and III_s are 0.0936 and 0.0285 a.u., respectively. These values are also in the range of the H-bond.

On the basis of AIM topological analysis, the O—H...O bond can be classified as H-bonds in the peroxy radicals II_s and III_s. It should be pointed out that the O—H bond in the peroxy radicals II_s and III_s exhibits red shift. However, the AIM analysis can not determine the origin of the red-shifted H-bonds, which will be done by performing NBO analysis.

NBO ANALYSIS

The H-bonds are complicated in the peroxy radicals II_s and III_s that exhibit a red-shifted O—H...O (shown in Fig. 1). NBO analysis of the peroxy radicals II_s and III_s was performed to investigate the nature of the so-called red-shifted H-bonds within them. The corresponding results are given in Table IV. In NBO analysis, the importance of hyperconjugative interaction and electron density transfer (EDT) from lone electron pairs of the Y atom to the X—H antibonding orbital in the X—H...Y system is well discussed [20]. In general, hyperconjugative interactions lead to an increase in the population of X—H antibonding orbital. The increase of the electron density in X—H antibonding orbital weakens the X—H bond and leads to its elongation and concomitant red shift of the X—H stretching frequency.

TABLE IV

Energy of hyperconjugative interaction (kJ/mol) and occupancy (e) at the B3LYP/6-311G(d,p) level.

$E^{(2)}$	Radical I/O ₂	Peroxy radicals II	Peroxy radicals III
$n_1(\text{O9}) \rightarrow \sigma^*(\text{O13—H14})$	—	4.28	1.34
$n_2(\text{O9}) \rightarrow \sigma^*(\text{O13—H14})$	—	6.89	—
Occupancy			
$\sigma^*(\text{O13—H14})$	0.00356	0.01294	0.00671
$n_1(\text{O9})$	0.99961	0.99322	0.99675
$n_2(\text{O9})$	0.99961	0.97851	0.96939

As shown in Table IV, in the peroxy radicals II_s, two lone electron pairs, n_1 and n_2 , of the O9 atom have the stabilization energy on the O13—H14 antibonding orbital, and the hyperconjugative $n_1(\text{O9}) \rightarrow \sigma^*(\text{O13—H14})$ and $n_2(\text{O9}) \rightarrow \sigma^*(\text{O13—H14})$ interactions are 4.28 and 6.89 kJ/mol, respectively. However, in the peroxy radicals III_s, only one lone electron pair, n_1 of the O9 atom, has the stabilization energy on the O13—H14 antibonding orbital, the corresponding hyperconjugative $n_1(\text{O9}) \rightarrow \sigma^*(\text{O13—H14})$ interactions are 1.34 kJ/mol. Hyperconjugative $n(\text{O9}) \rightarrow \sigma^*(\text{O13—H14})$ interactions lead to an increase in the population of O13—H14 antibonding orbital within the peroxy radicals II_s and III_s. For the peroxy radicals II_s and III_s, the electron density in the $\sigma^*(\text{O13—H14})$ was increased from 0.00356e of hydroxycyclohexadienyl radical I to 0.01294e and 0.00671e, respectively. The increased electron density in O13—H14 antibonding orbital weakens the O13—H14 bond, which leads to its elongation and concomitant red shift of the O13—H14 stretching frequency. Because the increase of the electron density in the $\sigma^*(\text{O13—H14})$ in the 2-hydroxycyclohexadienyl peroxy radical II_s is stronger than that one in 4-hydroxycyclohexadienyl peroxy radical III_s, the corresponding red shift of the O7—H15 stretching frequency in the 2-hydroxycyclohexadienyl peroxy radical II_s is larger than that one in 4-hydroxycyclohexadienyl peroxy radical III_s. Up to this point, the NBO results discussed the origin of the red-shifted H-bonds and provided a reasonable explanation on the theoretical prediction of the red shift of the O13—H14 stretching frequency in peroxy radicals II_s and III_s.

Conclusions

In the present theoretical study, DFT, AIM, and NBO analysis are used to determine the character-

istics of hydroxycyclohexadienyl peroxy radicals and investigate the intramolecular hydrogen bonds within them. From this study, we can draw the following conclusions:

1. 2-hydroxycyclohexadienyl peroxy radical II_s and 4-hydroxycyclohexadienyl peroxy radical III_s all exhibit a red-shifted O—H...O H-bond. The intramolecular hydrogen bond in the 2-hydroxycyclohexadienyl peroxy radical II_s is stronger than that in 4-hydroxycyclohexadienyl peroxy radical III_s, and the former is the most stable conformation among its isomers.
2. The stabilization energy between orbitals is the main factor to produce red-shifted intramolecular hydrogen bond within hydroxycyclohexadienyl peroxy radical. The hyperconjugative interactions can promote some transfer of electron density to the O—H antibonding orbital, while the increase of the electron density in O—H antibonding orbital leads to the elongation of the O—H bond and the red shift of the O—H stretching frequency.
3. The intramolecular hydrogen bond plays a role in stabilizing the hydroxycyclohexadienyl peroxy radicals.

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