Communication

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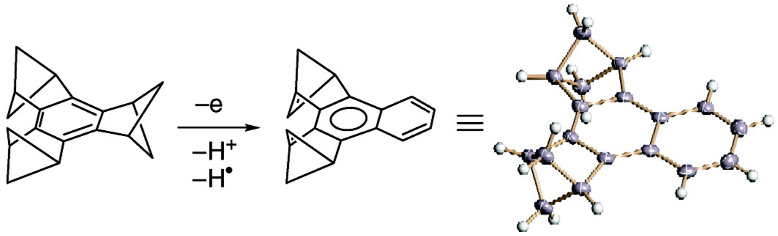
J. Am. Chem. Soc., **2005**, 127 (29), 10162-10163• DOI: 10.1021/ja053769q • Publication Date (Web): 02 July 2005



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A Naphthalene with Unusual Bond Alternation Made by Annelation with Bicyclo[2.1.1]hexene Units: Aromaticity and Reactivity

Takayuki Uto, Tohru Nishinaga, Akira Matsuura, Ryota Inoue, and Koichi Komatsu*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received June 8, 2005; E-mail: komatsu@scl.kyoto-u.ac.jp

The issue of aromaticity of cyclic π-conjugated systems has been the subject of long-lasting discussion from both theoretical and experimental points of view.[1] Naturally, the aromaticity is affected by the extent of bond alternation. Siegel[2] and Stanger[3] showed by theoretical calculations the effect of annelation with strained σ-frameworks to bring about the bond alternation in benzene. In experimental studies, Vollhardt has utilized annelation with benzocyclobutadiene systems,[4] while Siegel[5] has used annelation with highly strained bicyclo[2.1.1]hexene (abbreviated as BCH) units to transform the structure of benzene into cyclohexatriene-like geometry (i.e., **1**). Annelation with strained frameworks tends to elongate the bond endocyclic to the strained system and to give a double bond character to the exocyclic bonds.[6]

It was shown that, despite the presence of large bond alternation ($\Delta R = R_{\text{endo}} - R_{\text{exo}} = 0.089$ Å) in benzene **1**, calculations of nucleus independent chemical shifts (NICS)[7] and magnetic susceptibility exhaltations (MSE), as well as aromatic stabilization energies (ASE), all indicated that **1** retains a considerable degree of aromaticity; values of NICS, MSE, and ASE are −8.0, −8.4, and 34.0 kcal mol^{-1}, respectively, for **1**[5c] compared with −9.7, −16.2, and 34.1 kcal mol^{-1}, respectively, for normal benzene.[5c]

Naphthalene is known to have shorter bonds at α,β- (or 1,2-) positions.[8] Annelation of the BCH units at these positions is expected to decrease bond alternation oppositely to the case of benzene **1**. Here, we report the structure and properties of such a structure-modified naphthalene, which is obtained by one-electron oxidation of benzene **1**.

The HOMO level of benzene **1** is considerably elevated because of a strong $\sigma-\pi$ interaction with the BCH units.[9] Thus, one-electron oxidation of **1** readily proceeded by treatment with 1.5 equiv of $SbCl_5$ in CH_2Cl_2 at 0 °C, causing an immediate color change of the solution to reddish purple. After 20 min, quenching with $Bu_4N^+I^-$ gave a complex mixture of products, out of which was isolated naphthalene **2** as colorless crystals in 29% yield.

A possible mechanism for the formation of **2** is shown in Scheme 1. The HOMO of **1** is delocalized into the bicyclic units owing to the $\sigma-\pi$ interaction[9] (Figure 1a). Therefore, when one electron is removed from the HOMO, methylene−methine σ-bonds are weakened, and a 1,2-shift of this bond takes place with elimination of a hydrogen radical, followed by further rearrangement and elimination of a proton, thus resulting in strain release and aromatization of one of the original BCH units.

The molecular structure of **2** was determined by X-ray crystallography at 100 K (Figure 2). Corresponding bond lengths of parent naphthalene[8] are also shown for comparison. As expected from the BCH annelation, C1−C2 and C3−C4 bonds are elongated and C1−C8a and C2−C3 bonds are shortened. As a result, the extent of bond alternation in the BCH-annelated six-membered ring becomes much smaller than that in the mother compound and that in the nonannelated six-membered ring.

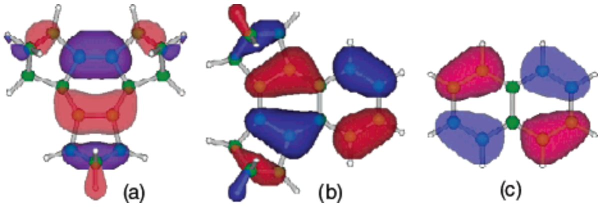


Figure 1. Pictorial presentations of KS HOMO of (a) **1**, (b) **2**, and (c) parent naphthalene (B3LYP/6-31*).

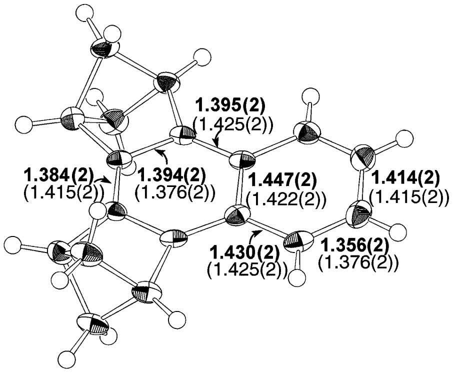
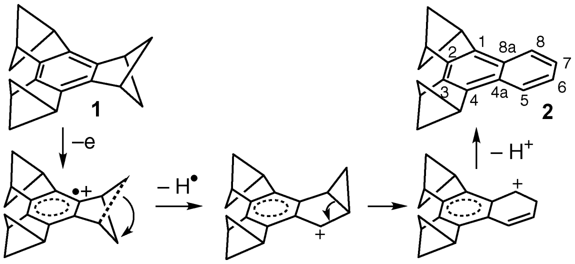


Figure 2. ORTEP drawing and bond lengths (Å) of **2** together with those for parent naphthalene shown in parentheses (ref 8). Estimated standard deviations of mean values are calculated by the following equation: $\sigma(l) = 1/(\Sigma(1/\sigma_i^2))^{1/2}$.

Scheme 1



The HOMOs of **2** and parent naphthalene are shown in Figure 1b,c. Despite such a structural change, the shape of the HOMO of the π-system in **2** is quite similar to that of parent naphthalene, except that the lobes of the HOMO extend to C4a and C8a in **2**.

To examine the degree of aromaticity of the two six-membered rings in naphthalene **2**, two different indexes were calculated. The Harmonic Oscillator Model of Aromaticity (HOMA),[10] which is a geometry-based aromaticity index, was calculated based on the X-ray crystal structure. The value for the BCH-annelated ring of **2** was 0.843, which is larger and closer to the value of benzene (0.979)[10b] than that of parent naphthalene (0.789). In contrast, that of the nonannelated ring is considerably reduced to 0.582.

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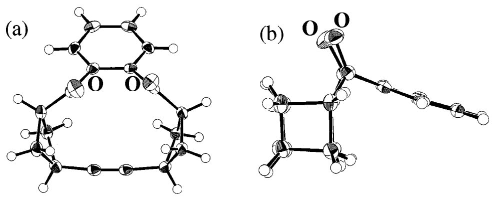
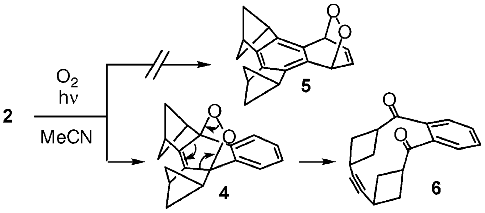


Figure 3. ORTEP drawings of **6**: (a) top and (b) side views.

Scheme 2



The NICS,[7] an aromaticity index based on magnetic property, also showed the same tendency despite the difference in theoretical basis of calculations. The value of NICS of the BCH-annelated ring of **2** was calculated as −11.8, which is even more negative (i.e., more aromatic) than that of parent naphthalene (−9.9), while that for the nonannelated ring was calculated as −7.5. Apparently, the BCH-annelated ring with less bond alternation is more aromatic than the other ring. The result of NICS calculations was experimentally confirmed by the ^{1}H NMR chemical shift of a β-proton of the nonannelated ring, which should be hardly affected by the effect of the other ring. The chemical shift of the β-proton of **2** was 7.17 ppm and less downfield shifted than that of parent naphthalene (7.48 ppm),[11] apparently due to a weakened diatropic ring-current effect.

The calculated energy level of the HOMO of **2** is 0.41 eV higher than that of 1,2,3,4-tetramethylnaphthalene (**3**), again due to the $\sigma-\pi$ conjugation effect.[9] This is reflected in 0.35 V lowering of the oxidation wave, as compared with **3**,[12] in the cyclic voltammogram of **2**, which is totally reversible, suggesting the stability of radical cation **2**$^{\bullet+}$. Since the LUMO levels are not much affected by these substitutions, the HOMO−LUMO gap in **2** becomes small, resulting in considerable bathochromic shift of the longest wavelength absorption (329 nm) as compared with that of **3** (293 nm).[13]

Naphthalenes are known to react at 1,4-positions with singlet oxygen to yield endoperoxides.[14] Accordingly, **2** underwent a smooth reaction with oxygen in acetonitrile under irradiation of visible light to give an oxidation product quantitatively. However, X-ray crystallography demonstrated that the product is not an endoperoxide but an acetylene-containing macrocyclic diketone **6** (Figure 3), possibly produced from endoperoxide **4**, as shown in Scheme 2. The singlet oxygen formed by photoexcited naphthalene **2** preferentially reacts with 1,4-carbons rather than with 5,8-carbons because of larger HOMO coefficients on the former carbons (0.497) than the latter (0.362) (B3LYP/6-31G*). Furthermore, DFT calculations indicate that **4** is 13.4 kcal mol^{-1} more stable than **5**.[15] While the cycloreversion of **5** can only give back **2**, a [2 + 2 + 2]-cycloreversion of **4** involving cleavages of BCH's endocyclic bonds and an O−O bond irreversibly gives macrocyclic compound **6**.[16] DFT calculations indicate an exothermicity of −64.6 kcal mol^{-1} for the process of **4** to **6** with release of strain. Here, the strain factor is apparently more significant than the loss of aromaticity in the original BCH-annelated ring.[17]

In conclusion, although the six-membered ring of **2** annelated with BCH units has been made more aromatic by the bond-length equalization, it has become more reactive than the other ring because of increased strain.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research (B) (No. 14340196) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Detailed experimental procedures, including spectral, electrochemical, and calculated data (B3LYP/6-31G(d)), and CIF data of **2** and **5**. This material is available free of charge via the Internet at http://pub.acs.org.

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JA053769Q