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Synthesis, Structure and Properties of Naphthalene Fully Annelated with Bicyclo[2.2.2]octene Frameworks

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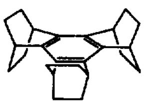
Abstract: Novel naphthalene derivative **4** annelated with four bicyclo[2.2.2]octene frameworks was synthesized. X-ray analysis showed that the acene core of **4** deviates from planarity. The remarkable effect of annelation was observed in its oxidizability as revealed by cyclic voltammetry, and **4** was readily converted to highly stable radical cation $\mathbf{4}^{+\bullet}$ and to the dication $\mathbf{4}^{2+}$. © 1998 Elsevier Science Ltd. All rights reserved.

Although the readiness of polycyclic aromatic hydrocarbons toward oxidation is well recognized, naphthalene, which is the simplest member of the condensed benzenoid aromatics, is less oxidizable to the cationic species than other higher homologues due to its lower HOMO level.[1] So far, studies of the naphthalene radical cation have been mainly focused on the transannular interaction in the *dimer* radical cation, and the structure of the *monomer* radical cation has been investigated only by spectroscopic methods such as ESR and electronic absorption spectroscopy.[2] This is in contrast to the ready accessibility of the corresponding anionic species: the naphthalene radical anion has been widely used as a reducing agent in organic synthesis, and even the dilithium salt of the dianion has been isolated and its structure determined by X-ray crystallography in spite of the inherent instability due to its antiaromatic character.[3]

In the previous studies, we have synthesized several monocyclic conjugated π-systems annelated with bicyclo[2.2.2]octene (abbreviated as BCO) as exemplified by benzene **1**,[4] and it has been found that such structural modification with bicycloalkane frameworks exerts remarkable stabilization effect upon positively charged π-systems.[5] Similar stabilization has also been demonstrated by the high stability of radical cations derived from anthracene **2**[6] and biphenylene **3**[7]. Our interest is now focused on novel naphthalene **4**, which can be regarded as a link between the benezene and the higher homologues, **2** and **3**. In this paper, we report the synthesis, structure, and facile trasformation into the cationic species of **4** fully annelated with BCO units.



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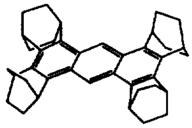

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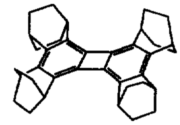

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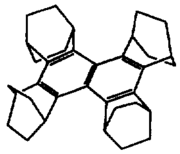

4

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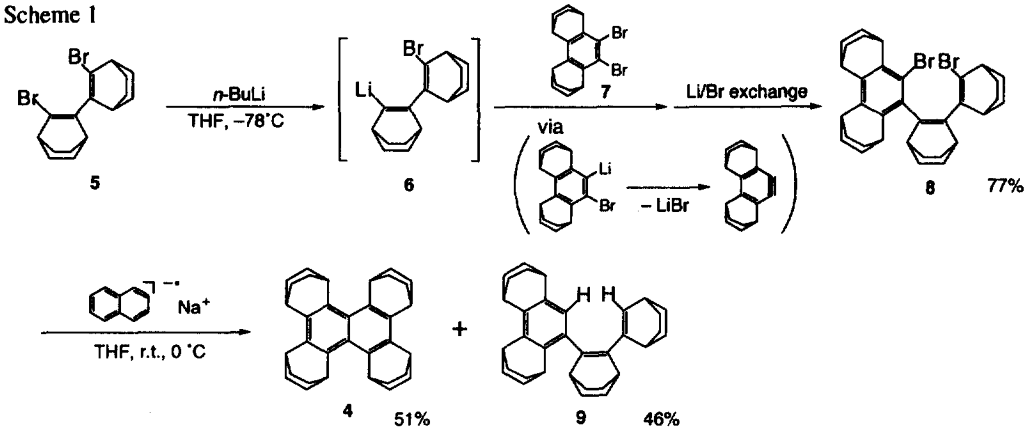
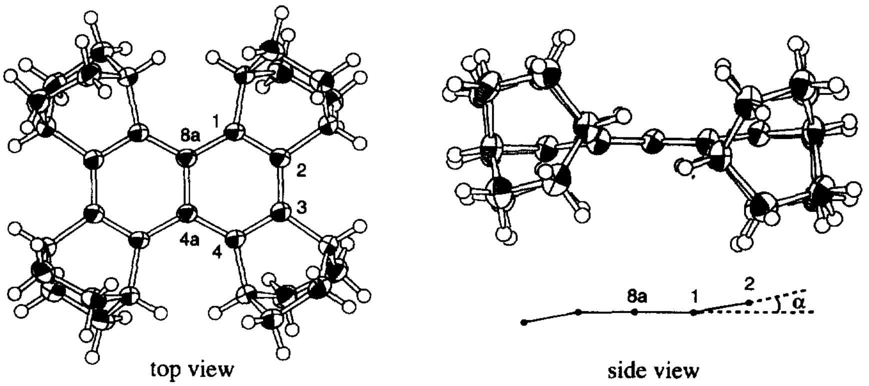
The synthesis of naphthalene **4** was achieved by a rather unique method (Scheme 1). Treatment of the dibromide of BCO-dimer **5** with a slight excess of *n*-butyllithium followed by the addition of dibromobenzene **7**[7] gave coupling product **8** in good yield. The reaction presumably proceeds in the following manner. First, metal–halogen exchange between lithiated species **6** and dibromobenzene **7** occurs and benzyne is generated via elimination of lithium bromide. Then, it inserts into the C–Li bond of another molecule of **6** followed by the metal–halogen exchange to give **8**. Reductive cyclization[4b] of the dibromide **8** by the use of excess sodium naphthalenide in THF gave the desired naphthalene **4**[8] along with **9** which resulted from hydrogen abstraction of the intermediate σ–radical species.

Scheme 1



peri-Substituted naphthalenes, including octasubsutituted derivatives, have attracted considerable attention and have been the subject of X-ray structural investigations as examples of the substantially strained aromatic compound.[9] The molecular structure of **4** was determined by X-ray crystallography[10] (Fig. 1). The acene core was found to be non-planar but to adopt an undulating conformation composed of two shallow boats due to the steric repulsion between bridgehead hydrogens at the *peri* positions, and the bending angle of each benzene ring (defined as α in Fig. 1) is 9.82 °. Interestingly, the molecule has approximate C_{2h} symmetry unlike D_2 symmetric octamethylnaphthalene with a twisted acene core.[11] PM3 calculations indicated, however, that com-



top view

side view

Fig. 1. ORTEP drawing of the X-ray structure of **4**.

pound **4** has two potential minima with C_{2h} and D_2 symmetry with the former being 2.1 kcal/mol less stable than the latter. The observation of C_{2h} geometry in the X-ray structure may be ascribed to the influence of the crystal packing forces. In this regard, some octasubsututited naphthalenes have been reported to exist in two crystal forms with C_2 and Ci geometries.[12] In the present study, however, no second crystal form has been observed for **4**. The averaged bond lengths (Å) of the aromatic core in **4** are 1.381 (C1–C2), 1.405 (C2–C3), 1.431 (C1–C8a), and 1.449 (C4a–C8a), whereas the values for the corresponding bonds in octamethylnaphthalene are 1.370, 1.411, 1.433, and 1.423, respectively.[11] Therefore, it can be concluded that the annelation of four BCO frameworks does not cause significant changes in the peripheral bond lengths of the naphthalene nucleus. On the other hand, the bond at the central ring fusion is substantially longer than those in the usual octasubstituted derivatives.[13]

The UV spectrum of **4** showed further bathochromic shift of the E_2 absorption band by approximately 10 nm relative to that in octamethylnaphthalene,[9a,14] as expected from the enhanced hyperconjugative ability of the BCO units. The characteristic vibrational fine structure is unresolved like some polymethylnaphthalenes,[15] which is presumably due to the loss of planarity. The ^{13}C NMR spectrum of **4**, however, indicates that the conformational flexibility is great enough in solution to afford it time-averaged planar D_{2h} symmetry on the NMR time scale.

The remarkable effect of BCO annelation upon the HOMO level of **4** was observed in its redox behavior. As shown in Fig. 2, compound **4** exhibited a well-defined reversible oxidation wave at $E_{1/2}$ = +0.33 V and an irreversible one at +1.17 V *vs* ferrocene/ferrocenium upon cyclic voltammetry in 1,1,2,2-tetrachloroethane at room temperature. This result indicates that **4** can yield a stable radical cation and a less stable dication upon consecutive oxidation. In sharp contrast, unsubstituted naphthalene showed no well-defined oxidation peak under the same conditions, and even octamethylnaphthalene has been reported to show only one reversible oxidation wave at $E_{1/2}$ = +0.90 V *vs* NHE (calibrated to 0.5 V vs Fc/Fc$^+$) in dichloromethane.[2a]

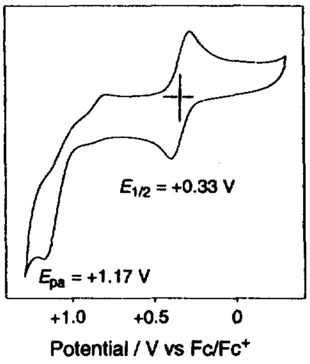


Fig. 2. Cyclic voltammogram of **4** in 1,1,2,2-tetrachloroethane with Bu_4ClO_4 as a supporting electrolyte; scan rate. 20 mV s^{-1}

The radical cation salt $4^{+\bullet}SbCl_6^-$ can be isolated as a deep–green solid by the treatment of **4** with 1.5 equivalent of $SbCl_5$ in carbon disulfide and it exhibited a broad single-line signal in ESR spectrum (g = 2.003) in dichloromethane. This radical cation salt is quite robust at room temperature even under air in the solid state, and shows no color decay in dichloromethane under vacuum.

When compound **4** was treated with a large excess of a stronger oxidant, SbF_5, in CD_2Cl_2 at –78 °C in a vacuum-sealed tube, the solution was immediately colored purple. The ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra of this solution clearly indicated the generation of dication 4^{2+}. In ^{1}H NMR, signals of the bridgehead protons are up-field shifted from 3.78 and 3.46 to 2.98 and 2.88 on going from **4** to 4^{2+} due to the effect of the paramagnetic ring current. In ^{13}C NMR, the peaks of the aromatic ring carbons are all deshielded (210.8, 160.7 and 154.0), and the averaged chemical shift of sp^2-carbons (δ_{av} 179.4) is in good agreement with that of the octamethylnaphthalene dication (δ_{av} 181.4).[1c]

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REFERENCES AND NOTES

1. (a) Streitwieser, A. Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961. (b) Herndon, W. C. *J. Am. Chem. Soc.* **1976**, *98*, 887. (c) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086. (d) Lammertsma, K.; Olah, G. A.; Berke, C. M.; Streitwieser, A. Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6658.
2. (a) Terahara, A.; Ohya–Nishiguchi, H.; Hirota, N.; Oku, A. *J. Phys. Chem.* **1986**, *90*, 1564. and references cited therein. (b) Bakker, M. G.; Claridge, R. F. C.; Kirk, C. M. *J. Chem. Soc., Perkin Trans. II.* **1986**, 1735.
3. Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7346.
4. (a) Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirosawa, C.; Takeuchi, K. *J. Org. Chem.* **1991**, *56*, 195. (b) Komatsu, K. *Pure & Appl. Chem.* **1993**, *65*, 73.
5. (a) Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633. (b) Nishinaga, T.; Komatsu, K.; Sugita, N. *J. Am. Chem. Soc.* **1993**, *115*, 11642. (c) Nishinaga, T.; Komatsu, K.; Sugita, N. *J. Chem. Soc., Chem. Commun.*, **1994**, 2319.
6. Matsuura, A.; Nishinaga, T.; Komatsu, K. *Tetrahedron Lett.* **1997**, *38*, 3427.
7. Matsuura, A.; Nishinaga, T.; Komatsu, K. *Tetrahedron Lett.* **1997**, *38*, 4125.
8. **4**; colorless prisms from CS_2/hexane; mp > 400 °C ; UV (CH_2Cl_2) λ_{max} 247 (log ε 4.56), 320 nm (3.81); ^1H NMR (300 MHz, CS_2–$CDCl_3$ 1:1) δ 3.78 (br s, 4H, CH), 3.46 (br s, 4H, CH), 1.82 (br s, 8H, CH_2), 1.79 (br s, 8H, CH_2), 1.41 (br s, 8H, CH_2), 1.38 (br s, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.32, 135.29, 125.1, 32.7, 28.8, 26.6, 26.4; Anal Calcd for $C_{34}H_{40}$: C, 91.01; H, 8.99. Found: C, 90.77; H, 9.05.; MS *m/z* 448 (M^+ 100).
9. (a) Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567. (b) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 741. and references cited therein.
10. X-Ray diffraction data for **4**, $C_{34}H_{40}$: triclinic, space group $P\bar{1}$(#2), a= 9.482(2) Å, b= 10.432(2) Å, c= 6.263(1) Å, α= 98.12(1)°, β= 102.15(1)° , γ= 77.79(1)°, V= 588.9(2) Å^3, Z= 1, D_{calcd} = 1.265 g cm^{-3}. The intensity data were collected on a Rigaku AFC7R diffractometer by using graphite monochromated Cu-Kα radiation at 293 K. A total of 1892 reflections were measured, of which 1772 were unique. The structure was solved by direct methods (SHELXS86). The refinements converged to R = 0.044, R_w = 0.068. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.
11. Sim, G. A. *Acta Crystallogr., Sect. B* **1982**, *38*, 623.
12. (a) Barbour, R. H.; Freer, A. A.; MacNicol, D. D. *J. Chem. Soc., Chem. Commun.* **1983**, 362. (b) MacNicol, D. D.; Mallinson, P. R.; Robertson, C. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1649.
13. For example, see ref 11 and (a) Herbstein, F. H. *Acta Crystallogr., Sect. B* **1979**, *35*, 1661. (b) Brady, J. H.; Redhouse, A. D.; Wakefield, B. J. *J. Chem. Res.* **1982**, 1541.
14. Oku, A.; Ohnishi, Y.; Mashio, F. *J. Org. Chem.* **1972**, *37*, 4264.
15. Mosby, W. L. *J. Am. Chem. Soc.* **1953**, *75*, 3348.