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Letters

Synthesis and properties of tricyclo-[6.4.1.0^{3,6}]trideca-1,3(6),7,9,11-pentaene

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Abstract—A new cyclobutene-fused 1,6-methano[10]annulene was synthesized by pyrolysis of the sulfone and sulfinate adducts of 3,4-bis(methylene)-1,6-methano[10]annulene and its physical and chemical properties were disclosed.

It is well known that benzocyclobutene **3** is a typical strained compound and was first synthesized by Cava a half-century ago.[1a–d] So far, vast amounts of cyclobutene-fused aromatic compounds have been synthesized from the viewpoints of structural interest and synthetic utility.[2] That is, the ring strain of the cyclobutene moiety reduces diatropicity of the fused aromatic rings like benzene and causes a ring-opening reaction to form reactive *o*-quinodimethane **4** having a butadiene moiety as shown in Figure 1. It is of interest to investigate the influence of such ring strain of the cyclobutene fused with a large ring system as 1,6-methan[10]annulene **10** on the diatropicity, chemical properties, and the electrocyclic reaction of the cyclobutene moiety compared to benzocyclobutene. Though the titled tricyclo[6.4.1.0^{3,6}]trideca-1,3(6),7,9,11-pentaene **1** was suggested to have the same degree of diatropicity with **10** by preliminary MO calculation, the precise diatropicity has remained unknown. Herein we report the first synthesis of **1**, discuss its diatropicity, and also elucidate the crystal structure of its 2,9-diacetyl derivative (Scheme 1).

Although **2** can be successfully generated from the dehalogenation of 3,4-bis(bromomethyl)-1,6-methano-[10]annulene **5** by the use of zinc[3] and trapped by a dienophile to give a [4 + 2] adduct, **1** was not obtained in the reaction. Alternatively, successful methods for the synthesis of **1** by the thermolysis of precursors, sulfone **7** and sulfinate **8**, were developed as follows. The reaction of **5** with $Na_2 \cdot H_2O$ in a solution of methanol–acetone at reflux for 3h gave sulfide **6** as pale yellow needles in 89% yield. Treatment of **6** with 2.5equiv of *m*-chloroperbenzoic acid (MCPBA) in $CHCl_3$ for 3h furnished sulfone **7**[10] as pale yellow needles in 69% yield. Flash thermolysis of **7** in a solution of toluene (200mg/50mL) at 400°C under nitrogen atmosphere gave the title compound **1**[10] exclusively as pale yellow needles in 85% yield, which might be formed via the electro-cyclization of a possible intermediate[1c] of 3,4-quinodimethane **2**. Since there were no other products and no detection of formation of **2**, the butadiene moiety of **2** cyclized to **1** immediately after the desulfonation at that temperature. The title compound **1** was also obtained by

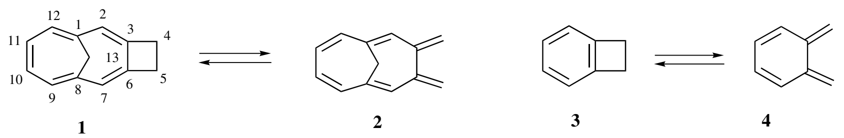

Figure 1.

Keywords: Cyclobutene-fused 1,6-methano[10]annulene; Diatropicity; X-ray analysis.

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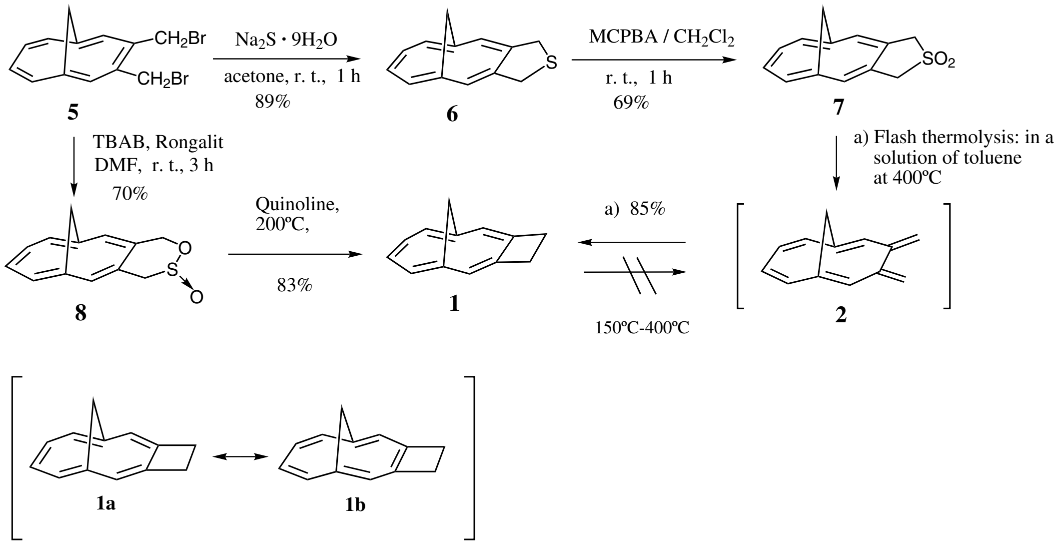
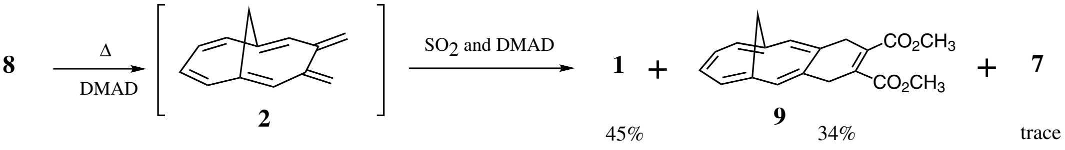


Scheme 1.



Scheme 2. The thermal decomposition of **8** in the presence of DMAD.

thermolysis of the sulfinate **8** under milder conditions, which was prepared by the treatment of **5** with $NaSO_2$-$CH_2OH\cdot 2H_2O$ (Rongalit)[4a,b,c] in dry DMF in the presence of TBAB in 70% yield. Although the thermolysis of **8** in xylene at 100 °C only gave sulfone **7** in 60% yield, **1** was obtained exclusively in quinoline at 200 °C in 83% yield. It should be noted that the thermolysis of **8** in the presence of dimethyl acetylenedicarboxylate (DMAD) at 120 °C gave **1** and cycloadduct **9**[3] in 45% and 34% yield, respectively, along with a small amount of **7** (Scheme 2). It suggests that the formed **2** by Cheletropic reaction[5] of **8** recombined with sulfur dioxide and DMAD to yield **9**[3] and **7**, respectively. The reverse ring-opening reaction of **1** to **2** was not observed, since the mixture of **1** and DMAD on being heated in the range of 150–400 °C under various conditions gave no cyclo-adduct but recovered **1** along with unidentified products. The structure of **1** was determined by the spectral data, especially the ^{1}H and ^{13}C NMR spectra. The assigned proton chemical shifts are shown in Figure 2. The average chemical shift of the ring proton of **1** (δ 7.27 ppm) is slightly lower than that of the parent 1,6-methano[10]annulene **10**, (δ 7.12 ppm)[6], and that of methylene protons of **1** (H13b, H13a: δ −0.86, −0.42: δ av −0.64 ppm) is observed at higher magnetic field than that of **10** (δ −0.51 ppm), indicating greater diatropic ring current of **1** compared to that of **10**. This is contrary to the case of the relationship between benzene and benzocyclobutene **3** as shown in Figure 2.[1d] It may be explained that the ring strain is relieved in the case of **1** by enlargement of the annulene ring as shown in X-ray analysis mentioned below, and the ring current is rather increased by the greater space of the [10]annulene ring having even small bond alternation. Further, this result is also rationally supported by the NEFTY calculation.

The electrophilic substitution reactions of 1

The reaction of **1** with $Cu(NO_3)_2$ in acetic anhydride at rt for 20 min gave monosubstituted products **12** and **13**, and disubstituted product **14**[10] in proper total yield as shown in Scheme 3. Also, the reaction of **1** with acetyl chloride in the presence of $SnCl_4$ in CH_2Cl_2 at rt for 20 min gave two products, **15** and **17**,[10] without **16**,

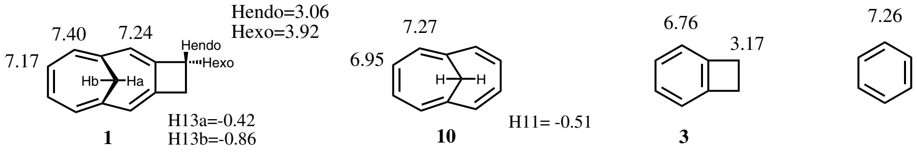
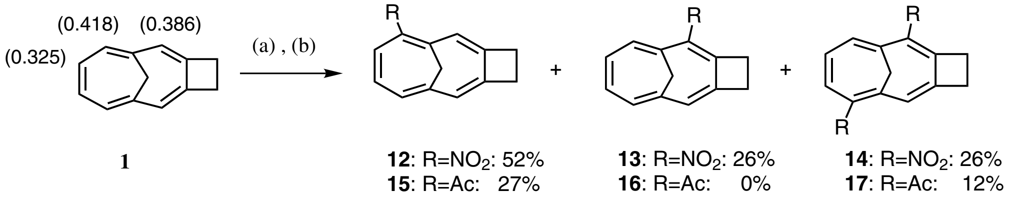


Figure 2. ^{1}H NMR chemical shifts of **1**, **10**, **3**, and benzene (δ ppm).



Scheme 3. (a) $Cu(NO_3)_2/Ac_2O$, rt, 20 min; (b) Ac_2O, $SnCl_4$, rt, 20 min, along with 37% of recovered **1**. And the figures in parentheses of **1** are the orbital coefficients of next HOMO calculated by PM3, because those of the HOMO are greater on the quarternary carbons and the difference of the energy between HOMO and next HOMO is small.

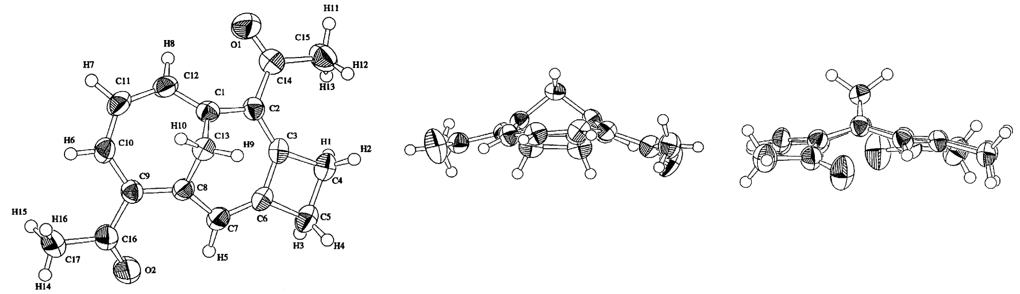


Figure 3. The ORTEP drawings of **17**.

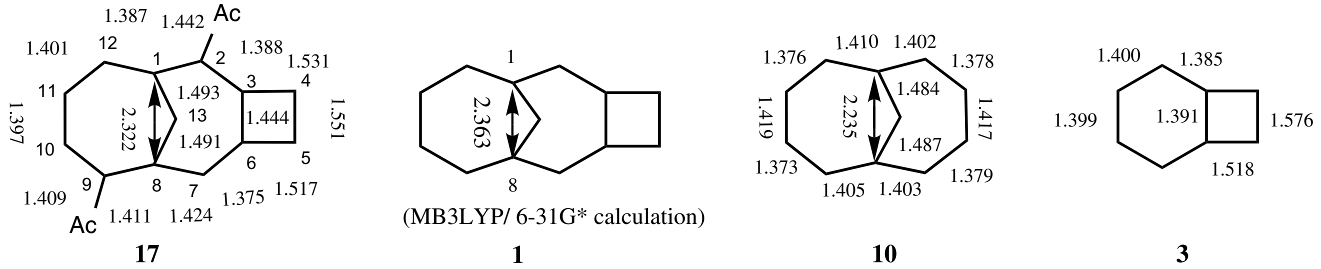


Figure 4. The bond lengths (Å) of **3**, **10**, and **17** by X-ray crystallographical analysis and **1** optimized by the MB3LYP/6-31G* calculation.

and 37% of recovered **1**. The above result indicates that the direction of electrophilic substitution in the order of the 2- and 9-positions is consistent with the order of the orbital coefficients of the next HOMO calculated by the PM3 method shown in parentheses of **1** in Scheme 3.[7] The structures of these compounds were determined by the spectral data and more precise information of the structure **17** was obtained by the X-ray crystallographical analysis as follows.[7] The X-ray crystallography of **17** as shown in Figures 3 and 4 showed that the bond lengths between C2–C3 and C6–C7 are a little shorter than that of the other bonds of **17**, and the bond length of C3–C6 fused with cyclobutene is longer than that of the other bond of **5** and also the corresponding bond C3–C4 of **10**.[8] Then the differences in bond lengths mainly depend upon the fused cyclobutene ring rather than the effect of acetyl groups, because the difference in bond length between C8–C9 and C1–C12 is small. The C2–C3–C4–C5–C6 moiety of **17** is nearly planar and the planarity of the whole molecule is almost the same as that of **10**. The bond angles between C2–C3–C6 (130.3°) and C3–C6–C7 (132.3°) of **17** are larger than those of C9–C10–C11 (127.9°) and C10–C11–C12 (128.1°) and correspond to those of **10** (127.3° and 126.8°) due to the angle strain of cyclobutene to make the greater space of the annulene moiety as shown in Figures 3 and 4. The carbon–carbon distance between C1–C8 of **17** bridged with the methylene group is longer than that of **10**. The MB3LYP/6-31G* calculations predict the distance between C1–C8 of **1** is 2.363 Å, which is longer than that of **17**.

Furthermore, the canonical resonance form of **1** is favored to form **1a** rather than **1b**, as can be seen in the X-ray analysis as shown in Figure 4. It also supports the result that the ring-opening reaction of **1** to form **2** is not favored, since the C3–C6 bond is longer than the C2–C3 and C6–C7 bonds and has a single bond character to make no cyclobutene moiety in **1** contrary to the case of benzocyclobutene **3**.[9]

References and notes

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7. X-Ray data for **17**: $M = 252.31$, $C_{17}H_{16}O_2$ prismatic, space group *P*-1 (#2), $a = 8.990(6)$ Å, $b = 10.256(3)$ Å, $c = 7.389(2)$ Å, $V = 639.0(5)$ Å^3 $Z = 2$, $D_{calc} = 1.311$ g/cm^3, $R = 0.087$, $R_w = 0.066$. Crystallographic data (excluding structure) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 243488 for **17**. Copies of the data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ. UK DIRECT LINE: +44 1223 762910, fax: +44 (0) 1223-336033 or e-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk. Estimated standard deviations for the bond lengths and angles are 0.004 Å and 0.2–0.3°, respectively, for the nonhydrogen atoms.
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10. Physical properties of the new compounds:
Compound **1**: pale yellow needles, mp < 30 °C, IR (KBr) ν_{max} = 3019w, 2952m, 2935m, 1631s, 1474s, 1377s, 1265m, 1193m, 1100m, 998m, 935m, 879m, 825m, 798m, 756w, 711w, 692w cm^{-1}; ^{1}H NMR(CDCl$_3$–TMS) δ ppm 7.42 (m, 2H, H-7, -9), 7.27 (s, 2H, H-2, -7), 7.17 (m, 2H, H-9, -10), 3.29 (d-like, $J = 10.4$ Hz, 2H, H-4, -5; *endo*), 3.06 (d-like, $J = 10.4$ Hz, 2H, H-4, -5, *exo*), −0.42 (d, $J = 9.5$ Hz, 1H, H-13a), −0.86 (d, $J = 9.5$ Hz, 1H, H-13b).; ^{13}C NMR(CDCl$_3$–TMS) δ ppm 149.1, 128.8, 127.4, 125.5, 117.6, 36.2, 29.8; UV–vis (MeOH) λ_{max} (log ε) 261 (4.77), 299 (3.47), 375 (1.21), 382 nm (1.21); MS *m*/*z* 168 (M$^+$, 90%), 167 (100%), 152 (76%), 141 (29%), 115 (52%); HRMS calcd: 168.0939, Found: 168.0949.
Compound **7**: pale yellow needles, mp 243–248 °C, IR (film) ν_{max} = 3075w, 2927m, 2852m, 1735w, 1630w, 1543w, 1500w, 1455m, 1439m, 1385m, 1305vs, 1256m, 1231s, 1136vs, 1091s, 985m, 925m, 886m, 853m, 814m, 791m, 734m, 707m, 665m, 616m cm^{-1}; ^{1}H NMR(CDCl$_3$–TMS) δ ppm 7.47 (m, 2H), 7.32 (s, 2H), 7.11 (m, 2H), 4.62 (d, $J = 15.5$ Hz, 2H, H-4, -5, *exo*), 4.28 (d, $J = 15.5$ Hz, 2H, H-4, -5, *endo*), −0.21 (d, $J = 9.2$ Hz, 1H, H-13b), −0.40 (d, $J = 9.2$ Hz, 1H, H-13a); UV–vis (CH$_2$Cl$_2$) λ_{max} (log ε) 263 (4.77), 304 (3.75), 365 (2.36), 405 nm (2.11); MS *m*/*z* 232 (M$^+$, 12%), 167 (100%), 153 (31%), 128 (22%), 115 (30%),83 (19%).
Compound **14**: pale yellow oil, IR (film) ν_{max} = 3075w, 2973s, 2854m, 1735w, 1549s, 1496vs, 1451m, 1313vs, 1282m, 1259m, 1187m, 1123m, 1072m, 1028w, 831m, 809m, 794m, 738m, 705m, 626w cm^{-1}; ^{1}H NMR(CDCl$_3$–TMS) δ ppm 8.64 (d, $J = 8.84$ Hz, 1H, H-10), 8.51 (s, 1H, H-7), 8.43 (d, $J = 10.8$ Hz, 1H, H-12), 7.71 (dd, $J = 8.8$, 10.8 Hz, 1H, H-11), 3.77 (m, 1H, H-4, *exo*), 3.56 (m, 2H, H-4, -5, *endo* and *exo*), 3.24 (m, 1H, H-5, *endo*), −0.15 (dd, $J = 11.2$, 0.8 Hz, 1H, H-13a), −0.68 (d, $J = 11.2$ Hz, 1H, H-13b); UV–vis (MeOH) λ_{max} (log ε) 227 (4.22), 287 (4.23), 378 (3.87), 444 nm (3.28); MS *m*/*z* 258 (M$^+$, 91%), 241 (48%), 211 (35%), 165 (100%), 152 (67%), 139 (60%), 115 (12%).
Compound **17**: pale yellow prisms, mp 160–163 °C; IR (KBr) ν_{max} = 3035m, 2923s, 2852m, 1664vs, 1600s, 1495m, 1354s, 11354m, 1162s, 1250m, 1228m, 1019m, 973w, 930m, 865w, 782m, 602m cm^{-1}; ^{1}H NMR (CDCl$_3$–TMS) δ ppm 8.32 (d, $J = 8.4$ Hz, 1H, H-10), 8.27 (s, 1H, H-2), 7.91 (d, $J = 10.0$ Hz, 1H, H-12), 7.37 (dd, $J = 8.4$, 10.0 Hz, 1H, H-11), 3.57 (m, 1H, H-4, *exo*), 3.38 (m, 2H, H-4, -5, *endo* and *exo*), 3.13 (m, 1H, H-5, *endo*), 2.70 (s, 3H, 9-COMe), 2.65 (s, 3H, 2-COMe), −0.17 (d, $J = 10.0$ Hz, 1H, H-13a), −0.71 (d, $J = 10.0$ Hz, 1H, H-13b); ^{13}C NMR(CDCl$_3$–TMS) δ ppm 149.1, 128.8, 127.4, 125.5, 117.6, 36.2, 29.8; UV–vis (MeOH) λ_{max} (log ε) 278 (4.05), 356 nm (2.10); MS *m*/*z* 252 (M$^+$, 100%), 237 (55%), 209 (86%), 165 (69%), 152 (18%); HRMS calcd for $C_{17}H_{16}O_2$: 252.0863, Found: 252.0886.