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LETTERS

Isolation of Two Conformers of *Z*,*Z*-Tribenzo[*c*,*g*,*k*][12]annulene-1,2-dione

Yoshiyuki Kuwatani,[a] Ayako Kusaka,[a] Masahiko Iyoda,[a]* and Gaku Yamamoto[b]*

[a]Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
[b]Department of Chemistry, School of Science, Kitasato University, Sagamihara, Kanagawa 228-8555, Japan

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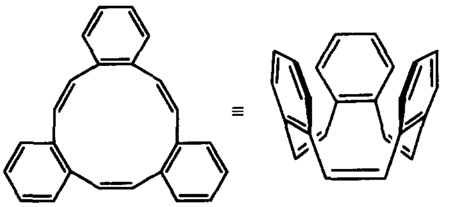
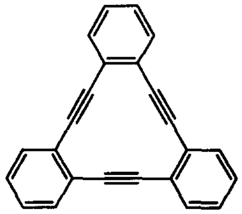
Abstract: Z,Z-Tribenzo[*c*,*g*,*k*]cyclododecapentaene-1,2-dione affords two crystalline forms that differ in conformation, which is revealed by X-ray crystallography. Dynamic conformational behavior in solution was studied by NMR spectroscopy.

Keywords: conformation; diones; NMR; X-ray crystal structures

Tribenzo[*a*,*e*,*i*][12]annulene[1] and its dehydro derivatives[2-5] have received considerable attention because of their symmetric structures with a three-fold axis and their potential as functional molecules.[6,7] Recently, we and the Vollhardt group independently reported the synthesis of Z,Z,Z-tribenzo[12]annulene (**1**) and explored its interesting properties.[8,9] In order to develop a new chemistry based on this new class of compounds, we tried to synthesize the corresponding quinonoid system **3** (Z,Z-tribenzo[*c*,*g*,*k*][12]annulene-1,2-dione), a key intermediate for the synthesis of **1**. We report here the isolation of two conformers (**4** and **5**) as distinct crystalline entities as revealed by X-ray crystallography and the NMR analysis of the dynamic behavior of these isomers in solution.



1



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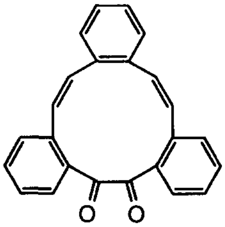

3

Compound **3** was synthesized according to the reaction sequence outlined in Scheme 1. The palladium-catalyzed cross-coupling reaction of 2-hydroxymethylphenylacetylene **6** (2 equiv) with 1,2-diiodobenzene **7** (1 equiv) in refluxing triethylamine in the presence of CuI for 15 min produced **8** in 94% yield.[10] Partial reduction of **8** to **9** using the Lindlar catalyst (Pd-

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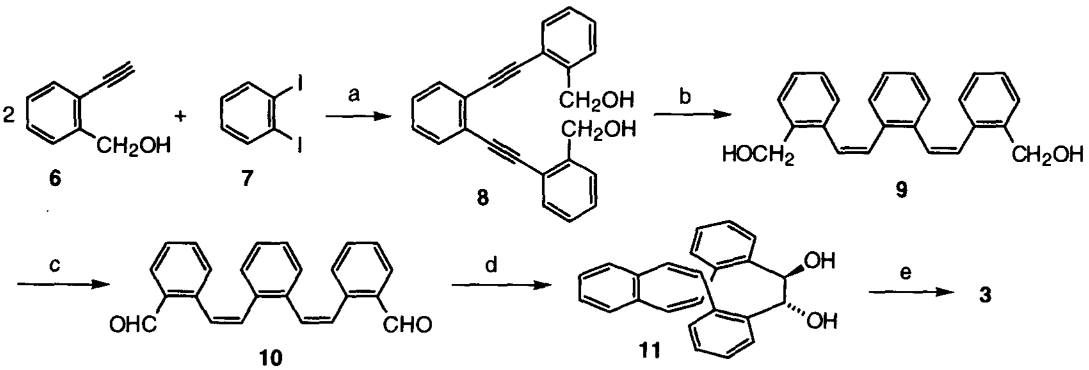
$Pb(OAc)_2$ on $CaCO_3$) in THF at room temperature (70-77%), followed by oxidation of **9** with PCC (82%) afforded the diene-dialdehyde **10**. Pinacol coupling of **10** with a low-valent vanadium complex[11] in THF at room temperature for 5 h yielded the *threo*-diol **11** (82%).[12] Swern oxidation of the diol **11** afforded the annulenedione **3** in 86% yield.



Reagents: a) $Pd(PPh_3)_4$, CuI, Et_3N; b) H_2, 5% Pd-$Pb(OAc)_2$ on $CaCO_3$, THF; c) PCC, CH_2Cl_2; d) $VCl_3(THF)_3$, Zn, THF; e) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2/THF

Scheme 1.

Recrystallization of **3** from CH_2Cl_2-hexane gave two types of crystals, yellow plates and colorless plates. X-ray crystallography revealed that the molecular structures of the two crystalline forms differ in conformation, as shown in Figures 1 and 2 for the yellow and colorless crystals, respectively.[13] The conformation **4** in the yellow form has a C_1 symmetry (Fig. 1), and the two carbonyl groups are almost anti-periplanar with the dihedral angle of 171 °. Thus, the bibenzil chromophore can give rise to a yellow color. The dihedral angle between the carbonyl and the adjacent benzene ring is ca. 50 °. In contrast, the conformation **5** in the colorless form has an approximate C_2 symmetry with a two-fold axis passing through the midpoints of the C(1)-C(2) and C(7)-C(8) bonds (Fig. 2). The two carbonyl groups are almost perpendicular, and this may be responsible for the colorless nature of **5**, while the carbonyl and the adjacent benzene ring are almost coplanar.

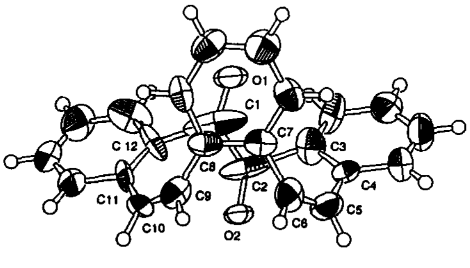


Figure 1. Structure of **4** in the yellow crystals.

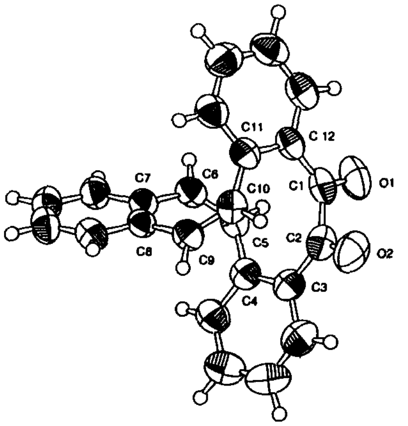


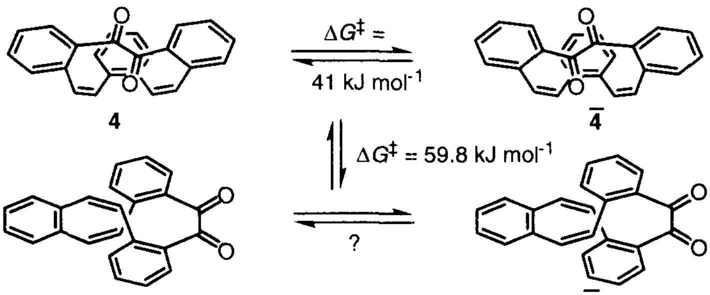
Figure 2. Structure of **5** in the colorless crystals.

Upon the conventional melting point measurements, it was noted the yellow crystals melt at 195–197 °C, while the white crystals turn yellow without melting around 120 °C and melt at 199 °C. Differential scanning calorimetry (DSC) shows only a sharp endothermic peak corresponding to melting at 195.8 and 197.0 °C for the yellow and white crystals, respectively, without any indication of an exo- or endothermic peak around 120°C for the latter. It is tentatively inferred that the white crystals might make phase transition around 120° C without emission or absorption of heat and the molecules in both crystals adopt the same conformation at melting. Details of the dynamic behavior of **3** in the crystalline state await further study.

Dissolution of either crystalline form in CD_2Cl_2 gives a yellow solution that shows the same ^1H NMR spectrum with extremely broadened signals at 24 °C, indicating that the conformational interconversion is taking place. At –30 °C, two kinds of conformers afford distinct signals in a ratio of ca. 7:3. The minor conformer gives an AB-type quartet signal at δ 5.76 and 6.40 with J=12.5 Hz ascribed to the olefinic protons, while those due to the major conformer are at δ 6.75 and 6.92 with J=11.9 Hz. We tentatively assume that these two conformers have similar structures as observed in the crystalline state, *i.e.*, **4** and **5**. The appearance of the olefinic protons of the minor conformer at a significantly high field suggests that the structure **5** should be assigned to this conformer, because the olefinic hydrogens of **5** are located in the shielding region of the opposing benzene ring. Thus, the major conformer would have a structure similar to that of **4**. Further lowering of the temperature causes broadening and resharpening of the signals due to the major conformer, while those due to the minor conformer show no further change. However, the complex overlap of the aromatic/olefinic signals hinders detailed analysis.

In the ^{13}C NMR spectrum of **3** in CD_2Cl_2, twenty-four peaks are observed at –30 °C, twelve peaks for each of **4** and **5**, while a total of 36 peaks, 12 for **5** and 24 for **4**, is observed at –100 °C. Particularly, the carbonyl carbon signals appear at δ 196.3 for **5** and at δ 185.3 and 186.0 with equal intensities for **4** at –100 °C.

These temperature-dependent spectral features are interpreted as follows (see Scheme 2). At –100 °C, the major isomer **4** is frozen into a C_1-chiral conformation similar to the one observed in the crystal. Thus, the two halves of the molecule are mutually nonequivalent, affording 24 carbon peaks. Upon raising the temperature, interconversion between this chiral conformation **4** and its enantiomer $\bar{\mathbf{4}}$ is accelerated, averaging out the carbon signals to 12 peaks. The rate constant for this process is roughly estimated to be ca. 400 s^{-1} at –60 °C, corresponding to $\Delta G^{\ddagger}$ = 41 kJ mol^{-1}. On the other hand, the minor isomer **5** is inferred to



Scheme 2.

adopt a C_2-chiral conformation at −100 °C as in the crystal, affording 12 carbon peaks. No information is available on whether the enantiomer interconversion (**5** ↔ **5**) takes place, because no spectral change is expected irrespective of the enantiomerization rate for the C_2 structure. Above −30 °C, interconversion between **4** and **5** becomes fast on the NMR timescale. Saturation transfer experiments give the rate constant for the **5** → **4** process as 2.4 s^{-1} at −20 °C which corresponds to $\Delta G^{\ddagger} = 59.8$ kJ mol^{-1}. The synthesis of **1** from **3** is now in progress.

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10. All new compounds reported in this paper were fully characterized spectroscopically and satisfactory elemental analyses were obtained; **4**: yellow plates; MS (*m/z*) 336 (M^+); IR (KBr) 1694, 1673 (C=O) cm^{-1}. **5**: colorless plates; MS (*m/z*) 336 (M^+); IR (KBr) 1652 (C=O) cm^{-1}. **8**: colorless crystals, mp 124.0-125.5°C; MS (*m/z*) 338 (M^+); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.57 (4H, m), 7.45 (2H, d, *J* = 7.5 Hz), 7.38-7.35 (4H, m), 7.29 (2H, td, *J* = 7.5, 1.5), 4.84 (4H, d, *J* = 6.0), 2.64 (2H, t, *J* = 6.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 132.4, 132.2, 129.1, 128.4, 127.8, 127.6, 125.2, 121.2, 92.6, 90.9, 63.8. **9**: colorless crystals, mp 111.5-113.5°C; MS (*m/z*) 342 (M^+); ^{1}H NMR (500 MHz, acetone-d_6) δ 7.47 (2H, d, *J* = 7.0), 7.18 (2H, t, *J* = 8.5), 7.01-6.78 (12H, m), 4.68 (4H, d, *J* = 5.5), 4.15 (2H, t, *J* = 5.5); ^{13}C NMR (125 MHz, acetone-d_6) δ 141.0, 137.2, 136.2, 130.4, 130.2, 130.1, 130.0, 127.91, 127.87, 127.3, 127.2, 62.7. **10**: colorless crystals, mp 99.0-101.0°C; MS (*m/z*) 338 (M^+); IR (KBr) 1693 cm^{-1} (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21 (2H, s), 7.81 (2H, dd, *J* = 7.0, 2.0), 7.37-7.32 (4H, m), 7.10 (2H, d, *J* = 12.0), 6.96 (2H, dd, *J* = 7.0, 2.0), 6.92 (2H, d, *J* = 12.0), 6.91-6.87 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 140.1, 135.4, 133.5, 131.6, 130.8, 130.2, 129.9, 128.4, 127.6, 127.1. **11**: colorless plates, mp 216.5-217.5°C; MS (*m/z*) 340 (M^+); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (2H, d, *J* = 7.5), 7.26-7.21 (4H, m), 7.05-7.03 (2H, m), 6.93 (2H, t, *J* = 7.5), 6.63 (2H, d, *J* = 7.5), 5.89 (2H, d, *J* = 12.0), 5.70 (2H, d, *J* = 12.0), 4.91 (2H, s), 3.37 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 137.2, 133.6, 132.0, 129.2, 127.6, 127.45, 127.37, 127.3, 126.8, 124.5, 73.4.
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12. Details of the stereochemistry of **11** will be reported elsewhere.
13. X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with Mo-Kα (λ = 0.71069 Å) radiation up to $2\theta = 55.1°$. The intensities were corrected for Lorentz and polarization effects. The analytical absorption corrections were carried out. The structures were solved by direct methods and refined using full-matrix least-squares analyses using reflections with $I > 3.00\sigma(I)$. Anisotropic thermal parameters were used for non-hydrogen atoms. **4**: $C_{24}H_{16}O_2$, FW = 336.39, monoclinic, space group C2/c (#15), $a = 12.240(5)$, $b = 10.892(7)$, $c = 26.896(6)$ Å, $\beta = 101.46(3)°$, $V = 3514(2)$ Å^3, $Z = 8$, $D_{calc} = 1.272$ g cm^{-3}, $F(000) = 1408.00$, $R = 0.036$, $R_w = 0.034$, GOF = 1.38 for 1260 observed reflection out of 300 unique reflections. **5**: $C_{24}H_{16}O_2$, FW = 336.39, monoclinic, space group $P2_1/n$ (#14), $a = 10.637(7)$, $b = 14.997(5)$, $c = 11.193(5)$ Å, $\beta = 100.59(4)°$, $V = 1755(1)$ Å^3, $Z = 4$, $D_{calc} = 1.273$ g cm^{-3}, $F(000) = 704.00$, $R = 0.051$, $R_w = 0.050$, GOF = 1.72 for 613 observed reflection out of 236 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.