

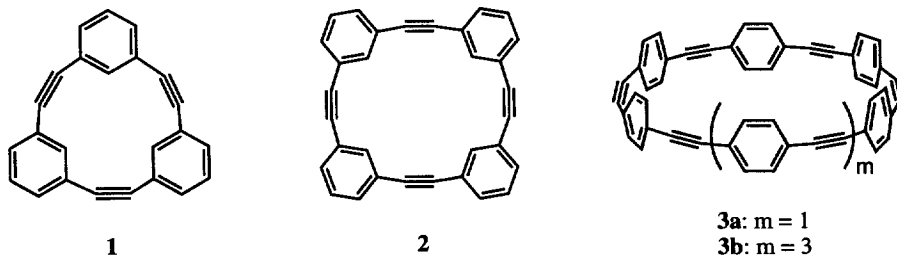
[2.2.2]Metacyclophane-1,9,17-triyne

Takeshi Kawase, Noriko Ueda, and Masaji Oda*

Department of Chemistry, Graduate School of Science, Osaka University
 Toyonaka, Osaka 560, Japan

Abstract: The titled strained cyclophane, the smallest member of this family to be known, was synthesized by bromination-dehydrobromination of the corresponding triene in good yield; its X-ray crystallographic analysis reveals an averaged sp bond angle of 158.6° that is substantially bent from the normal, linear triple bond.
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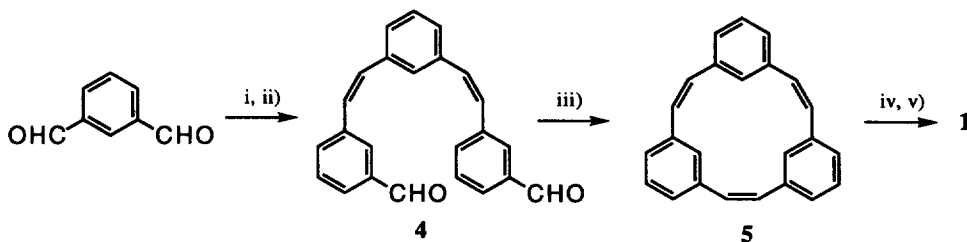
Recently we have reported the synthesis of [2.2.2.2]metacyclophanetetrayne **2** that was the smallest member of [2._n]metacyclophane-*n*-ynes to be known by bromination-dehydrobromination of the corresponding metacyclophanetetraene.¹ The bromination-dehydrobromination approach was also successfully applied to our recent synthesis of cyclic [6]- and [8]paraphenylacetylenes ([2.₆]- and [2.₈]paracyclophanepolyyne), **3a** and **3b**, which have novel belt-shaped conjugation.² Although these compounds are considerably strained with bent triple bonds, the high symmetry in their structures disperses the strain energy over the molecules to allow application of the base-induced dehydrobromination method. Here we report on the synthesis and structure of [2.2.2]metacyclophane-1,9,17-triyne **1**, which is even smaller in ring size than **2**, by application of the bromination-dehydrobromination approach.



A semi-empirical calculation (AM-1)³ predicts that the triple bonds of **1** (159°) is more severely bent by about 10° than those of **2** (observed value: 167.7°-169.9°) but less bent than those of dibenzocyclooctadiyne (observed value: 155.8°).⁴ The strain energy of **1** is calculated to be 48 kcal mol⁻¹ that is about 33 kcal mol⁻¹ larger than the calculated strain energy of **2**.

Possible precursor triene **5** has already been synthesized by Tanner and Wennerström through a three fold Wittig reaction in moderate yield.⁵ On the other hand, we have before employed the McMurry coupling and obtained better yield than the Wittig reaction in the preparation of the precursor tetraene for **2**. We therefore examined the Ti-mediated reductive coupling of (*Z,Z*)-1,3-bis(3-formylstyryl)benzene **4**⁶ and obtained **5** in 68%

yield (Scheme 1). Only trace amounts of cyclic dimers were formed. Bromination of **5** with excess bromine and subsequent dehydrobromination of the crude hexabromide with *t*-BuOK gave the desired triyne **1** in 80-90% yield. Although triyne **1** was sensitive to silica gel and unelutable from the silica gel column, it could be purified by column chromatography on alumina at 0 °C. The isolated triyne **1** is fairly stable, colorless, crystalline substance and thermally decomposes above 180 °C.



Scheme 1: i) $m\text{-BrC}_6\text{H}_4\text{CH}_2\text{PPh}_3^+ \text{Br}^-$ $t\text{-BuOK/DMSO}$, then chromatographic separation of *Z,Z*-isomer on silica gel; ii) $n\text{-BuLi/THF}$, then DMF, 35% yield from isophthalaldehyde; iii) $\text{TiCl}_4\text{-Zn/DME}$, room temp. overnight then reflux for 6 h, 68%; iv) $\text{Br}_2/\text{CHCl}_3$ (4.5 equiv., room temp); v) $t\text{-BuOK/ether}$ (12 equiv.), reflux, 2h, 80-90%.

The ^1H and ^{13}C NMR spectra of **1** are simple in agreement with the high symmetry of the molecule (Table 1 for data). The inner protons of **1** are observed at δ 8.38 that is even lower magnetic field than those of **2** (δ 8.07) which is in turn down-shifted relative to 1,3-di(phenylethynyl)benzene **6** (δ 7.72), whereas the outer protons remain little changed. The sp carbons of **1** (δ 99.86) resonate at 7.7 ppm lower field than those of **2** (δ 92.20). The Raman frequency of the triple bonds of **1** (ν 2155 cm^{-1}) is also appreciably low-shifted compared to that of **2** (ν 2202 cm^{-1}) and comparable to those of cycloheptynes and cyclooctynes.⁷ These observations point to the bent triple bonds of **1** in greater degree than those of **2**. The electronic spectrum of **1** is similar to that of **2** except for the smaller absorption coefficients. The Stokes shift in the emission spectrum of **1** (28 nm) is only slightly (ca. 5 nm) larger than that of **2** in contrast to the much larger Stokes shift of **3a** (121 nm) and **3b** (91 nm) and their difference (30 nm), which may reflex higher difficulty for deformation of the molecule of **1** in the excited state due to the *meta*-substitutionship.

A prismatic single crystal of **1** suitable for X-ray crystallographic analysis was obtained from dioxane solution. Figure 1 shows the molecular structure of **1**.⁸ The molecule is C_2 symmetric and nearly planar in the crystal: the deformation of the benzene rings from a regular hexagon is within 3.3° and the torsion angles between the benzene rings and three triple bonds are less than 3.5° . Obvious deformation of the molecule due to the strain is found in the large deviation of the triple bonds from linearity; thus, the averaged sp bond angle of **1** (158.6°) is about 10° smaller than those of tetrayne **2** and comparable to those of 1,5-cyclooctadiyne (159.1°),⁹ cyclooctyne (158.5°)¹⁰ and dibenzocyclooctadiyne (155.8°).⁴

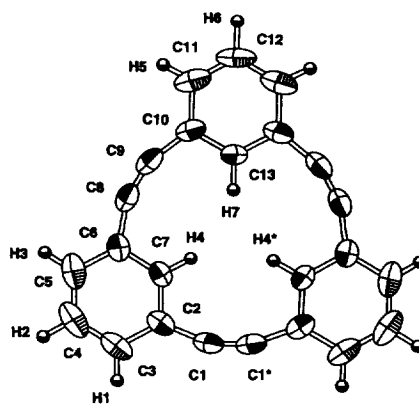


Figure 1. Crystal structure of **1**. (ORTEP; 50% probability)

In contrast to the inactivity of tetrayne **2** towards cyclopentadiene (CP) and furan, triyne **1** reacts with CP at room temperature to give a stereoisomeric mixture of 1 : 2 adducts **7** (*syn* : *anti* = *ca* 1 : 1) in 76% yield as air sensitive solid. Neither mono- nor triadducts were obtained. The considerably low chemical shifts of the sp carbons of **7** (97.4 ppm) is comparable to the corresponding value of [2.2.2]metacyclophanedienyne **8** (97.86 ppm) which was prepared through bromination-dehydrobromination from **5** similar to the synthesis of **3** using one equivalent of pyridinium hydrobromideperbromide for the bromination. According to AM-1 calculation, the triple bond(s) of triyne **1**, diene-monoynne **8**, and monoene-diyne **9** are more bent in the order of **9** > **1** > **8** (see Figure 2) in agreement with no detection of monoadduct which should be more reactive than **1**.

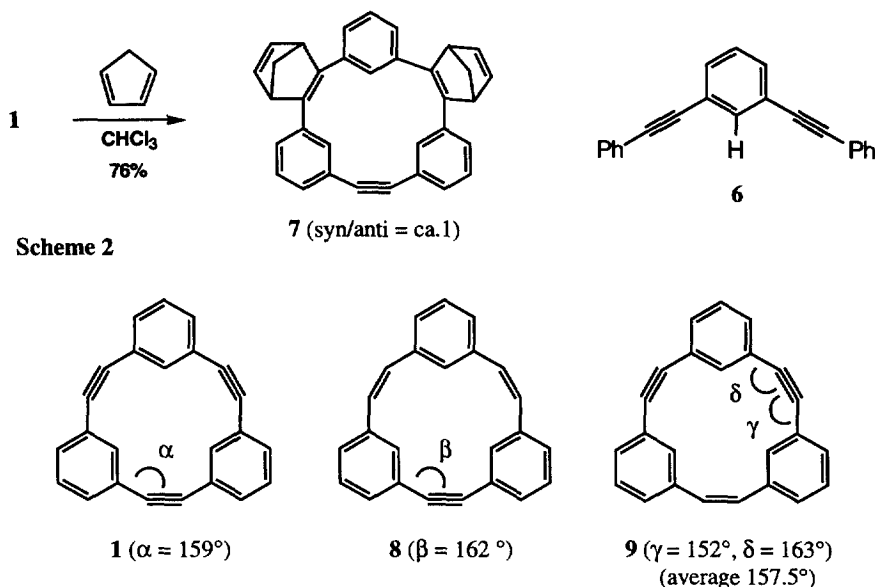


Figure 2. Calculated bond angles of triple bonds of **1**, **8**, and **9**

Table 1. Selected physical and spectral data of **1**, **7**, and **8**.

1: colorless crystals, decomp. > 180 °C; MS(FAB): m/z 300 (M^+); ^1H NMR (270 MHz, CDCl_3): δ = 7.23 (A_2BX , 6H), 7.35 (A_2BX , 3H), 8.38 (t, A_2BX , J = 1.7 Hz, 3H); ^{13}C NMR (67.8 MHz, CDCl_3): δ = 99.86, 124.94, 125.82, 129.58, 145.18; UV (cyclohexane): λ_{max} (ϵ) = 272 (32,800), 288 (51,400), 304 (28,800), 318 (12,500 sh), 329 (10,500); fluorescence (cyclohexane): λ_{max} = 333, 348, 358; Raman: ν = 2155 cm^{-1} ($\text{C}\equiv\text{C}$).

7: colorless solid (*syn* : *anti* = *ca.* 1 : 1), decomp. > 200 °C; MS(FAB): m/z 432 (M^+); ^1H NMR (600 MHz, CDCl_3): δ = 2.15-2.20 (m, 2H), 2.40-2.46 (m, 2H), 3.82-3.84 (m, 2H), 3.96-4.10 (m, 2H), 6.48 (br. d, J = 7.7 Hz, 0.5H), 6.51 (dd, J = 7.7, 1.7 Hz, 1H), 6.77 (br. t, J = 1.7 Hz, 0.5H), 6.88-7.40 (m, 13.5H), 7.53 (br. t, J = 1.7 Hz, 0.5H).

colorless crystals, mp 151.5-152.5 °C; MS(FAB): m/z 304 (M^+); ^1H NMR (600 MHz, CDCl_3): δ = 6.64 (d, J = 11.7 Hz, 2H), 6.89 (br. d, J = 7.7 Hz, 2H), 6.93 (d, J = 11.7 Hz, 2H), 7.00 (dt, J = 7.7, 1.4 Hz, 2H), 7.01 (br. t, 7.7 Hz, 1H), 7.16 (m, 2H), 7.17 (br. d, J = 7.7 Hz, 2H), 7.24 (dt, J = 7.7, 0.6 Hz, 2H), 7.30 (m, 1H); ^{13}C NMR (67.8 MHz, CDCl_3): δ = 97.86, 122.99, 124.60, 126.24, 127.98, 128.54, 128.77, 129.51, 130.30, 132.28, 136.39, 139.03, 140.00; Raman: ν = 2178 cm^{-1} ($\text{C}\equiv\text{C}$).

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References and Notes

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6. (Z,Z)-4: ¹H NMR (270 MHz, CDCl₃): δ = 6.59 (s, 4H), 7.03-7.07 (m, 3H), 7.10 (m, 1H), 7.35 (br. t, J = 7.6 Hz, 2H), 7.44 (dt, J = 7.6, 1.7 Hz, 2H), 7.68 (dt, J = 7.6, 1.7 Hz, 2H), 7.70 (d, J = 1.7 Hz, 2H), 9.90 (s, 2H).
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8. Crystal data for **2**: C₂₄H₁₂, crystallized from dioxane; *M*r = 300.4, monoclinic, space group C2/c (#15), *a* = 18.187(5), *b* = 11.754(4), *c* = 7.483(4) Å, β = 104.66(3)°, *V* = 1547.6(9) Å³, *Z* = 4, ρ_{calcd} = 1.289 g cm⁻³, μ = 0.73 cm⁻¹, 752 independently observed reflections with [F > 3σ(F), 3° ≤ 2θ ≤ 60°], refined to *R* (*R*_w) = 0.040 (0.041). Rigaku AFC5R diffractometer with graphite monochromated MoKα radiation at 295 K. The structure was solved by direct methods (SIR88) and refined with the TEXSAN crystallographic software package of Molecular Structure Corporation. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper was deposited with the Cambridge Crystallographic Data Center.
Selected bond lengths [Å], angles [°] and non-bonded contacts [Å] (standard deviation in parentheses): C1-C1* 1.193(5), C8-C9 1.190(3), C1*-C1-C2 158.6(1), C1-C2-C3 129.0(3), C1-C2-C7 113.3(2), C3-C2-C7 117.6(3), C2-C3-C4 119.4(3), C3-C4-C5 122.4(3), C4-C5-C6 119.2(3), C2-C7-C6 123.3(3), C5-C6-C7 117.9(3), C7-C6-C8 -C2-C3 129.0(3), C1-C2-C7 113.3(2), C3-C2-C7 117.6(3), C2-C3-C4 119.4(3), C3-C4-C5 122.4(3) 17.6(3), C2-C3-C4 119.-C3-C4 119.4(3), C3-C4-C5 122.4(3), C4-C5-C6 119.2(3), C2-C7-C6 123.3(3), C5-C6-C7 117.9(3), C7-C6-C8 112.9(2), C6-C8-C9 158.7(3), C8-C9-C10 158.4(3), 58.7(3), C8-C9-C10 158.4(3), C9-C10-C11 129.2(3), C9-C10-C13 113.2(2), C10-C11-C12 119.8(4) 3), C9-C10-C13 113.2(2), C10-C11-C12 119.8(4), C10-C13-C10* 123.3(4), C11-C12-C11* 121.9(4), C11-C10-C13 117.6(3), H4-H7 2.28(4), H4-H4* 2.31(5).
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