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Conformational Analysis of 9,14-Dihydrotribenzo[*a,c,f*]cyclooctene and Its Derivatives

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Synopsis. 9,14-Dihydrotribenzo[*a,c,f*]cyclooctene, 9,14-dihydrotribenzo[*a,c,f*]cycloocten-9-one, and 9,14-dihydrotribenzo[*a,c,f*]cyclooctene-9,14-dione, which are all new bridged aromatics containing a biphenyl moiety, have been prepared. Saddle conformations have been suggested for all of them on the basis of the spectra data.

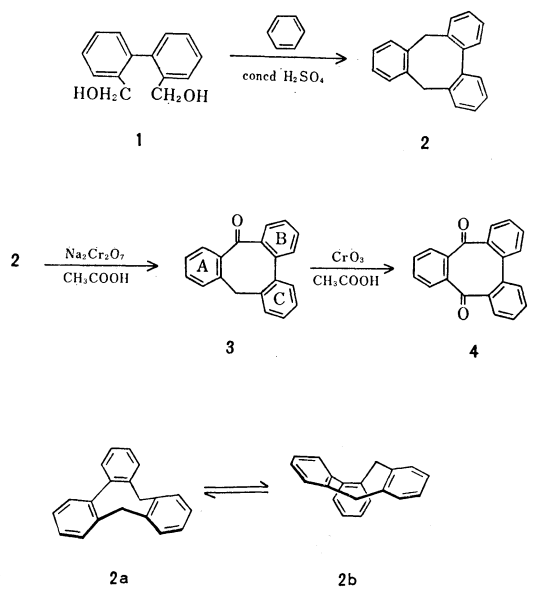
The chemistry of bridged aromatics containing three or more benzene rings has received increasing interest in recent years. There have been a number of reports on the synthesis and conformational analysis of 10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene and its derivatives.[1] Little attention, however, has been paid to the chemistry of 9,14-dihydrotribenzo[*a,c,f*]cyclooctene derivatives, which are new bridged aromatics containing a biphenyl moiety. We wish to report here the preparation and conformational determination of 9,14-dihydrotribenzo[*a,c,f*]cyclooctene (**2**), 9,14-dihydrotribenzo[*a,c,f*] cycloocten-9-one (**3**), and 9,14-dihydrotribenzo[*a,c,f*]-cyclooctene-9,14-dione (**4**).[2]

The hydrocarbon **2** was prepared by the acid-catalyzed cycloalkylation of benzene with 2,2′-bis-(hydroxymethyl)biphenyl (**1**) in almost quantitative yield.[1d,1e,3] Oxidation of **2** with sodium dichromate in acetic acid under reflux gave **3** in 62% yield.[1c,1e] The monoketone **3** resisted further oxidation under the same conditions, but could be oxidized with chromic anhydride in acetic acid under reflux to give **4** in 17% yield.

The PMR spectrum of **2** showed the benzylic protons as a singlet at δ 3.65, indicating that **2** takes a flexible conformation. On lowering the temperature the singlet began to split and at about −40 °C it separated into a distinct AB quartet at δ 3.59 and 3.74 (J=15.0 Hz). The UV absorption spectrum of **2** was the same in shape and band position as that of 2,2′-dimethylbiphenyl.[4] This result suggests that the two benzene rings of the biphenyl moiety in **2** would be twisted by about 70°.[5] A molecular model of **2** shows that the two benzene rings of the biphenyl moiety are nearly coplanar in the crown form, while they are quite twisted in the saddle form. These facts allow assignment of a saddle conformation for **2**. The hydrocarbon **2** undergoes inversion between the two possible saddle forms **2a** and **2b** at normal temperatures, but is frozen in one form at lower temperatures. The free energy of activation ($\Delta F^{\ddagger}$) for the inversion process is calculated to be 15.3 kcal/mol at 25 °C in CD_2Cl_2.[6]

The monoketone **3**, on the other hand, is a rigid molecule at room temperature, since its PMR spectrum showed the benzylic protons as an AB quartet at δ 3.7 and 4.1 (J=14.3 Hz). On raising the temperature the two doublets were observed to broaden and finally at 84 °C to coalesce into a broad singlet, thus permitting calculation of $\Delta F^{\ddagger}$ for the inversion: 17.5 kcal/mol at 84 °C in C_7D_8. The band position of the carbonyl absorption at 1643 cm^{-1} for **3** is approximately the same as that for benzophenone (1647 cm^{-1}), suggesting that the carbonyl group of **3** would conjugate strongly with a benzene ring. A molecular model of **3** reveals that in a crown conformation such a strong conjugation may not be possible because of the non-coplanarity of the carbonyl group with the benzene rings. The alternative assignment of a saddle conformation to **3** would be more compatible with its UV spectrum, which showed a much more intense band at long wavelength (>310 nm) than that of an open chain model compound, *o*-benzylbenzophenone (**5**).[7] This intense band indicates the presence of a longer conjugative system in **3** than in **5**. If the carbonyl group is coplanar with the benzene ring A, the angle of the twist in the biphenyl moiety should be as large as that of 2,2′-disubstituted biphenyl (≈70°). In this case the UV spectrum of **3** should be more similar to that of **5**. On the other hand, if the carbonyl group is coplanar with the benzene ring B, the twist in the biphenyl moiety would be small enough for the benzene rings B and C to be conjugated. Based on the spectral data and the above considerations, we would like to propose that the monoketone **3** may possess the saddle conformation in which the carbonyl group is coplanar with the benzene ring of the biphenyl moiety.

The ^{13}C NMR spectrum of **4** showed a carbonyl carbon resonance at 200.7 ppm and its IR spectrum showed a carbonyl band at 1670 cm^{-1}, indicating that the two carbonyl groups would take the same conformation. The carbonyl stretching frequency for **4** is 12 cm^{-1} higher than that for the open chain compound, *o*-dibenzoylbenzene (**6**) (1658 cm^{-1}). The carbonyl bond force constant for **4**, calculated by using the equation proposed by Halford,[8] is greater by 0.12 than that for **6**.[9] This result suggests that the two carbonyl groups of **4** would not lie in the plane of any benzene ring, but would make a certain angle with the benzene rings. The angle, however, would not be so large as to impede completely the conjugation of the carbonyl group with the benzene ring, since the UV spectrum of **4** showed a much more intense band at 330 nm (ε 641) than that for **6** (ε 269). This intense band, compared with that of **6**, may be explained in terms of the conjugation of the two carbonyl groups with the benzene ring. Thus the UV data are inconsistent with the assignment of a crown conformation for **4**, because the crown conformation would lead to inhibition of the conjugation due to the orthogonality of the carbonyl groups with the benzene rings. Consequently, we feel that it is reasonable to assign a saddle conformation for **4**, although the



present spectral data are not sufficient to confirm the definitive structure of **4**.

Experimental

All melting points are uncorrected. The IR spectra were obtained on a JASCO IR-G spectrophotometer or a Hitachi Perkin-Elmer 225 grating infrared spectrophotometer in a potassium bromide pellet. The PMR spectra were recorded on a JEOL JNM-PS-100 spectrometer using tetramethylsilane as an internal standard. The ^{13}C NMR spectra were recorded on a JEOL PS 100-EC 100 spectrometer. The mass spectra were taken on a Hitachi RMU-6E mass spectrometer and the UV spectra on a Hitachi two-wavelength double beam spectrophotometer 356. 2,2′-Bis(hydroxymethyl)biphenyl (**1**) (mp 110—111 °C, lit,[10] 112 °C) was prepared from dimethyl diphenate according to the procedure of Kakis *et al.*[10]

9,14-Dihydrotribenzo[a,c,f]*cyclooctene (2).* The hydrocarbon **2** was prepared according to the procedure of Dagan and Rabinovitz.[1e,3] The crude product was recrystallized from petroleum ether–benzene to give pure **2** as colorless plates, mp 137—139 °C. IR: 3060, 3030, 2920, 1475, 1430, 775, 745 cm^{-1}; MS: *m/e* 256 (M^+, base peak); PMR (CD_2Cl_2): δ 3.65 (s, 4H), 7.16 (bs, 4H), 7.32 (bs, 8H); UV: $\lambda_{max}^{95\%EtOH}$ 233 (ε 7970), 263 (1130), 272 nm (733). Found: C, 93.54; H, 6.22%. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29%.

9,14-Dihydrotribenzo[a,c,f]*cyclooctene-9-one (3).* The hydrocarbon **2** (423 mg, 1.65 mmol) and sodium dichromate (2.8 g, 9.4 mmol) in acetic acid (140 ml) and water (25 ml) were refluxed for 53 h. The reaction mixture was poured into ice–water and the product was collected by filtration, washed successively with aqueous sodium hydrogencarbonate and water, and then chromatographed on a silica gel column. Elution with petroleum ether recovered the unreacted **2** (113 mg). Elution with benzene–petroleum ether (2: 3) afforded the monoketone **3** (213 mg, 62%) which was recrystallized from methanol to give colorless prisms, mp 131—133 °C. IR: 1643 cm^{-1}; MS: *m/e* 270 (M^+, base peak); PMR ($CDCl_3$): δ 3.7 (d, 1H, J=14.3 Hz), 4.1 (d, 1H, J=14.3 Hz), 7.1—7.5 (m, 11H), 7.9 (bd, 1H), ^{13}C NMR ($CDCl_3$): δ 40.0 (>CH_2), 200.0 ppm (>C=O); UV: $\lambda_{max}^{95\%EtOH}$ 235 (ε 16750), 255 sh (8710), 295 sh (1380), 335 sh nm (367). Found: C, 88.76; H, 5.07%. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22%.

9,14-Dihydrotribenzo[a,c,f]*cyclooctene-9,14-dione (4).* An acetic acid solution (20 ml) of **3** (350 mg, 1.3 mmol) and chromic anhydride (1.2 g. 12 mmol) was refluxed for 44 h. The same workup as that described above and purification by column chromatography on silica gel gave the unreacted monoketone **3** (110 mg) and the desired diketone **4** (36 mg, 17%). Recrystallization from methanol gave pure **4** as colorless needles, mp 201—203 °C. IR: 1670 cm^{-1}; MS: *m/e* 284 (M^+), 255 (base peak); PMR ($CDCl_3$): δ 6.94—7.74 (m); ^{13}C NMR (C_6D_6): δ 200.7 ppm (>C=O); UV: $\lambda_{max}^{95\%EtOH}$ 230 (ε 29400), 285 sh (2840), 330 sh nm (641). Found: C, 84.57; H, 4.30%. Calcd for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25%.

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