A BRIDGED TRIPTYCENE——INTRAMOLECULAR DIELS-ALDER REACTION

OF 16,19-DIMETHOXY-[2](9,10)ANTHRACENO[2]PARACYCLOPHANE

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Abstract: A bridged triptycene was obtained by intramolecular cycloaddition reaction of 16,19-di-methoxy[2](9,10)anthraceno[2]paracyclophane followed by acid-catalyzed elimination of methanol. Internal strain in this molecule was disclosed by X-ray crystallographic analysis.

Although benzene is known to be unreactive under normal conditions for thermal Diels-Alder reaction[1], it reacts as a diene (with dicyano-[2] and bis(trifluoromethyl)acetylene[3] and dehydro-benzenes[4]) and as a dienophile (with hexachlorocyclopentadiene[5]) under extremely drastic conditions. When distorded, however, substituted benzene ring[6] reacts as both 4π and 2π addends in the intra-molecular reactions[7] as exemplified in the reaction of some anthracenophanes[8,9]. We report here a further example of such intramolecular cycloaddition reaction in highly-strained 16,19-dimethoxy[2](9,10)-anthraceno[2]paracyclophane (1). Furthermore, because of the presence of substituents, the cycloadduct underwent elimination reaction to produce for the first time the bridged triptycene 2, which suffers from a severe internal strain as is revealed by X-ray crystallography and molecular mechanics calculations.

Synthesis   The cyclophane 1 was synthesized in 36% yield by photochemical extrusion of sulfur in P(MeO)$_3$ solution from the corresponding dithia[3.3]anthracenophane 3, which in turn was obtained by coupling of 9,10-bis(chloromethyl)anthracene and 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene with NaOH in 58% yield[10]. Heating 1 in refluxing benzene in the presence of p-toluenesulfonic acid (catalytic amount) afforded the enone 4 (61% yield) and the bridged triptycene 2 (31% yield).
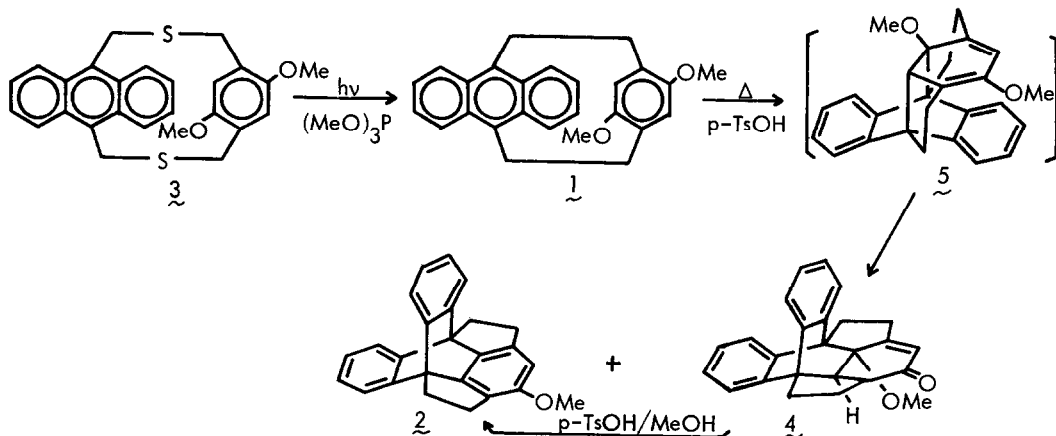
The compound 2̰ can be derived quantitatively from 4̰ by the same acid in refluxing methanol.   Since 1̰ is unchanged on heating under neutral conditions, the initially-formed cycloadduct 5̰ easily reverts to 1̰ unlike in the case of [3](9,10)anthraceno[3]cyclophane[9] unless further reactions (elimination of methanol to 2̰ or demethylation to 4̰) proceed with the acids.

<u>X-ray Analysis</u>   Since 2̰ is the first bridged triptycene and its molecular model suggests severe distortion, an X-ray crystallographic analysis was performed in order to establish the precise molecular dimensions[11].

Bond lengths and bond angles obtained and shown in Fig. 1 revealed sizable deviations from the unstraind standard values[14], especially in the vicinity of the cyclopentene rings and the bridged benzene ring A.

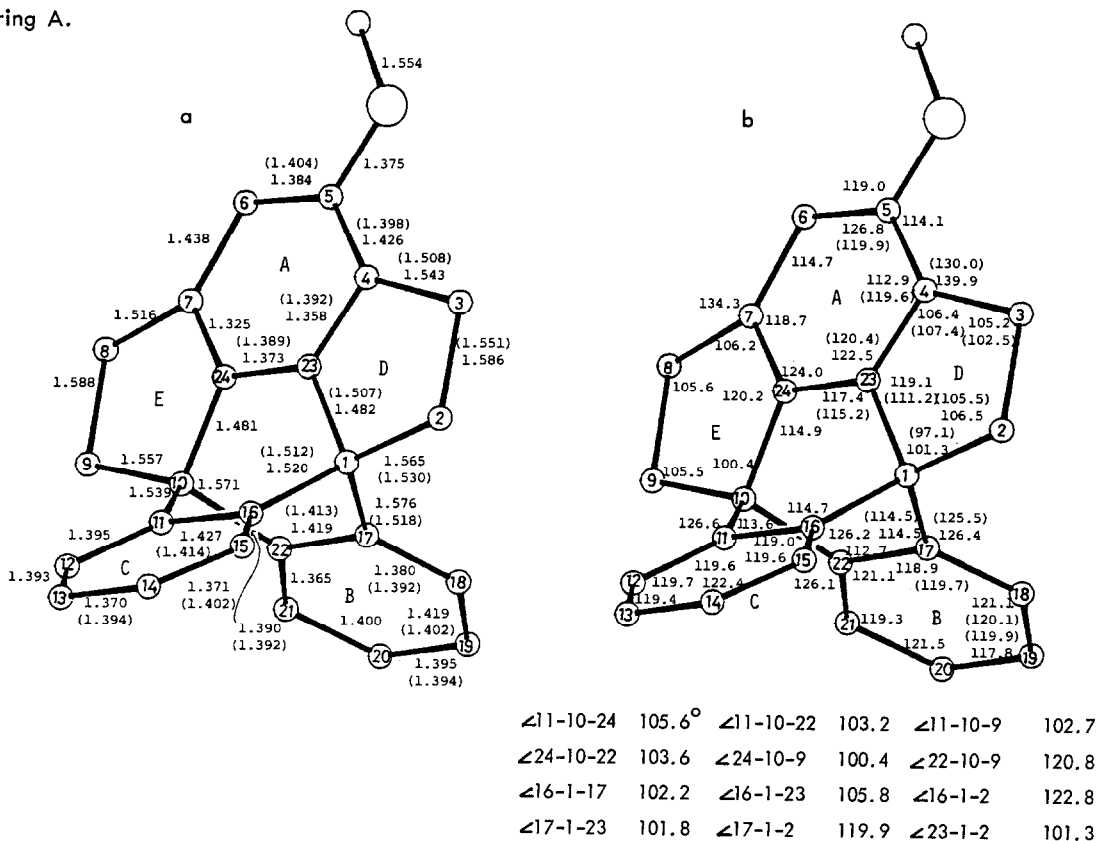| ∠11-10-24	105.6°	∠11-10-22	103.2	∠11-10-9	102.7
∠24-10-22	103.6	∠24-10-9	100.4	∠22-10-9	120.8
∠16-1-17	102.2	∠16-1-23	105.8	∠16-1-2	122.8
∠17-1-23	101.8	∠17-1-2	119.9	∠23-1-2	101.3

Fig. 1   Bond lengths (a) and bond angles (b) of 2̰ determined by X-ray analysis.
Values in parentheses are those obtained by MMI/MMPI calculations for
the parent hydrocarbon.

In the fused ring system D-A-E, two carbons, C_1 and C_{10}, shift as if pulled toward each other. Thus, C_1-C_2, C_2-C_3, C_3-C_4 and C_4-C_5 are elongated and C_4-C_{23}, C_1-C_{23} and C_{23}-C_{24} shortened. Bond angles change accordingly; in ring D, the interior angles of C_1 and C_4 are much smaller than those of C_3 and C_{23}, and in ring A the interior angle of C_4 is much smaller than those of C_{23} and C_5.   The situation is the same for ring E and its vicinity.   Furthermore, the bonds connecting the

central carbons, C_1 and C_{10}, to ring B are much longer than the corresponding bonds to ring C, (and fused bonds in ring B and C is somewhat longer than the rest of the benzene bond, contrary to the corresponding bond in ring A).

Unsymmetrical geometry of the molecule is clearly shown by the side biew (Fig. 2). The central bicyclo[2.2.2]octatriene part is deviated from D_3h symmetry; in addition to the difference in bond lengths, three dihedral angles α, β and γ are all different. Ring A is tilted (δ) further from the C_1-C_{23}-C_{24}-C_{10} plane. The ethano bridges, which are again further tilted (ϵ) out of the plane of ring A, have skewed conformation with tortion angles $12.4°$ (C_1-C_2-C_3-C_4) and $9.8°$ (C_7-C_8-C_9-C_{10}). Thus, all of these data disclosed the way the molecule minimize the internal strain inherent in the symmetrical C_s structure and indicated the presence of the sizable strain remaining in the molecule.

Molecular Mechanics Calculations   In order to estimate strain energy in 2, the molecular mechanics calculations were performed on the parent bridged triptycene using Allinger's MMI and MMPI program[15]. Starting from the geometry defined by the X-ray analysis, a structure of the minimum steric energy was obtained. Total steric energy inherent in the structure is 50.0 kcal/mol, 23.4 kcal/mol excess of that of triptycene itself. In the calculated structure, abnormal bond lengths and angles disclosed by X-ray analysis were reproduced, but to the lesser extent (Fig. 1). On the other hand, the tilting angle of ring A is by far greater than the observed value, although the angles α, β and γ are similar (Fig. 2). The tilting of the benzene ring

Fig. 2   Side view of 2 obtained by X-ray analysis

[( ): Obtained by MMI/MMPI]

would be resulted mainly by two competing factors, the presence of ethano bridges which force C_1 (C_{10}) and C_4 (C_7) closer and resistance of benzene ring against tortional deformation. The present result of calculations therefore underestimate the tortional force constants around an aromatic ring compared to those of the bond stretching and angle bending on sp^3 carbons. Since the tortional force constants of conjugated polyene system in this program is given by the VESCF type of molecular orbital calculations, the present result suggests the need of more sophisticated molecular orbital calculations in order to reproduce the geometry obtained by X-ray of such a strained aromatic system.

Electronic Spectrum   The effect of deformation seems to be very small, since electronic spectrum of 2, is extremely similar with that of triptycene[16].
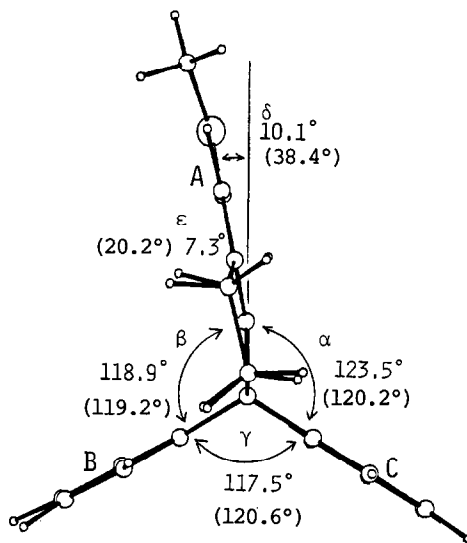
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10) All new compounds show the following properties. IR and NMR spectra were measured in KBr and and $CDCl_3$, respectively.

1: Yellow needles, m.p. 199-205°C; m/e 368 (M^+), 204, 164 (b.p.); ^1H δ 2.34-4.32 (8H, m), 2.94 (6H, s), 4.77 (2H, s), 7.05-7.39 (4H, m), 7.85-8.20 (4H, m).

2: Colorless prisms, m.p. 248-251°C; m/e 336 (M^+, b.p.), 321, 308, 305, 293, 258, 205; ν 1626, 1490, 1440, 1103, 1050, 820, 758 cm^{-1}; ^1H δ 3.30 (8H, br.s), 3.70 (3H, s), 6.27 (1H, s), 6.80-6.97 (4H, m), 7.20-7.37 (4H, m); $\lambda_{max}^{cyclohexane}$ (log ε) 262 (sh, 3.40), 275 (3.51), 282 (3.60). (cf. triptycene[18] λmax 263 (sh, 3.25), 271 (3.66), 278 (3.56)).

3: Yellow prisms, m.p. 236-241°C; m/e 432 (M^+), 222 (b.p.), 180; ^1H δ 2.97 (6H, s), 3.24 (2H, d, J=15), 4.20 (2H, d, 15), 4.52 (2H, d, 15), 5.18 (2H, d, 15), 5.95 (2H, s), 7.28-7.53 (4H, m), 8.19-8.44 (4H, m).

4: Pale yellow prisms, m.p. 248-251°C; m/e 354 (M^+); ν 1700, 1482, 1232, 1119, 788, 772, 768 cm^{-1}; λ_{max}^{MeOH} (log ε) 243 nm (3.90), 249 (3.80), 254 (3.80), 260 (370); ^1H δ 2.28-2.87 (8H, m), 3.11 (3H, s), 3.28 (2H, br.d), 5.51 (1H, s), 6.94-7.35 (8H, m); ^{13}C δ 21.8, 25.7, 28.2, 29.0, 43.1, 52.4, 52.6, 55.4, 58.9, 84.4, 120.0, 121.8, 123.4, 125.4, 125.7, 126.0, 128.2, 139.3, 141.2, 144.7, 145.6, 163.3, 199.1.

11) 2 crystallizes in the tetragonal prisms of space group $P4_1$ with 4 molecule in a unit cell of dimensions, a=12.173(2), c=11.958(2) Å. The structure was solved by MULTAN78[12] and refined by block-diagonal least squares calculation. The final R is 7.8%. All computation except MULTAN78 were carried out using UNICSIII[13] program system. Final crystallographic coordinates have been deposited in the Cambridge Crystallographic Data Center. The authors are grateful to Professor Yoichi Iitaka, The University of Tokyo, for his permission to use Philip's automatic 4-circle diffractometer.

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