CHEMISTRY LETTERS, pp. 273-276, 1992. © 1992 The Chemical Society of Japan

How Do Ethane-Type Molecules Avoid Eclipsing When Forced as Such? The Case of 7,8,9,10-Tetrachloro-1,1-dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene

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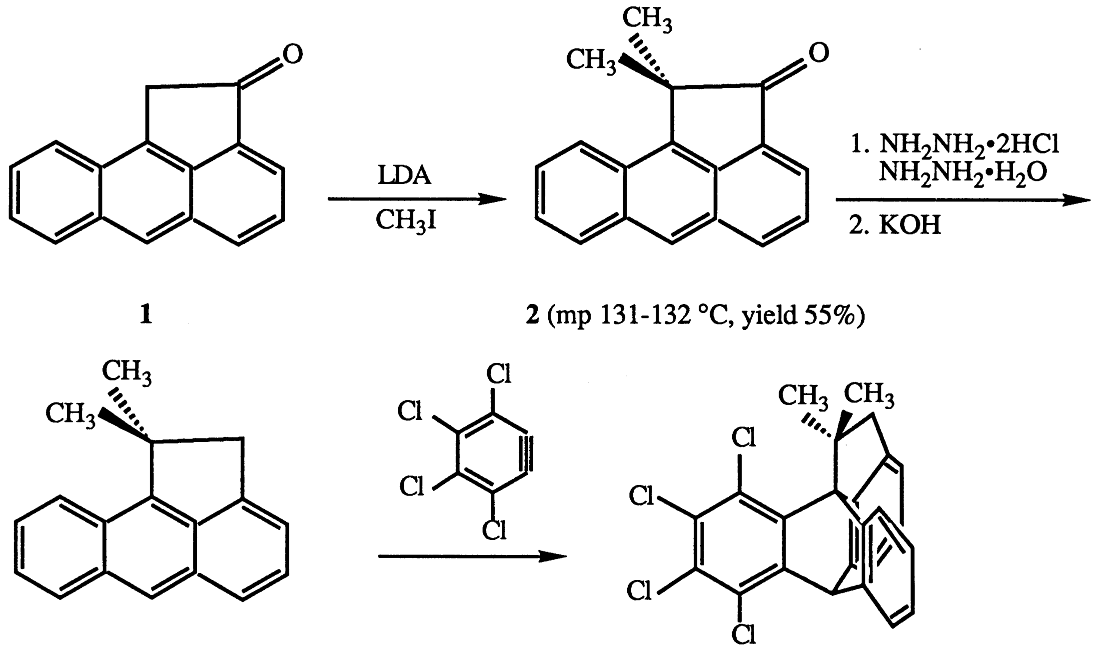
The molecular structure of the title compound was determined by X-ray crystallography. To avoid the eclipsing interactions between the two methyl groups at the 1-position and the triptycene skeleton, the molecule exhibited several unusual bond lengths and bond angles. The benzene rings in the molecule were also deformed from planarity.

Formation of substituted 1,1-dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylenes (*e. g.* **4**) was observed during the course of reactions of rotational isomers.[1-3] The structure of these compounds is interesting, because, if one sees the simple molecular models through the C_1-C_{10b} bond, the two methyl groups at the 1-position have to take eclipsing structure with the two benzeno bridges.

Since the eclipsing interactions are so severe that the molecule must take a structure in which severe interactions are avoided by deformation from the normal structure. In the molecule in question, one of the substituents in the ethane type molecule is fixed by a 5-membered ring. If the 5-membered ring is fixed, there are only two methyl groups which can be dislocated from the normal positions. One of the possibilities of lowering the energy is that a benzeno bridge takes a boat conformation and another is that the molecules undergo extensive bond angle deformations and possibly bond stretching, the strain being distributed to all over the molecule. Although MMP2 (both Nonplanar and Planar) calculations suggested unusual structures for these compounds, X-ray structural analysis was awaited. If the structure of this type of compounds is known, it will help us understand the transition state for internal rotation, which is hardly reproducible by simple calculations. We wish to report the results of X-ray analysis of the title compound (**4**) which was synthesized independently.

The synthesis was carried out in the following way. 1,2-Dihydroaceanthrylen-2-one (**1**)[4] was methylated with LDA and methyl iodide and the product (**2**) was



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2 (mp 131-132 °C, yield 55%)

3 (mp 94-94 °C, yield 92%)

4 (mp 235.5-237.5 °C, yield 15%)

reduced under forcing Wolf-Kishner reduction conditions.[5] 1,1-Dimethyl-1,2-dihydroaceanthrylene (**3**) thus obtained was submitted to a reaction with tetrachlorobenzyne[6] to afford the desired compound (**4**).[7]

Some selected bond lengths, bond angles, and torsion angles, that are obtained by X-ray crystallography,[8] are listed in Tables 1, 2, and 3, respectively. An ORTEP diagram is shown in Fig. 1 with numbering of carbons and designation of benzene rings. The features of the molecular structure can be summarized in the following ways, dividing them into bond lengths, bond angles, and torsion and dihedral angles.

Table 1. Selected Bond Lengths

Carbon atoms A and B	Distance/Å
1 - 2	1.563(3)
1 - 10b	1.599(2)
1 - 17	1.533(3)
1 - 18	1.547(2)
10a - 10b	1.559(2)
10b - 10c	1.527(2)
10b - 11	1.555(2)

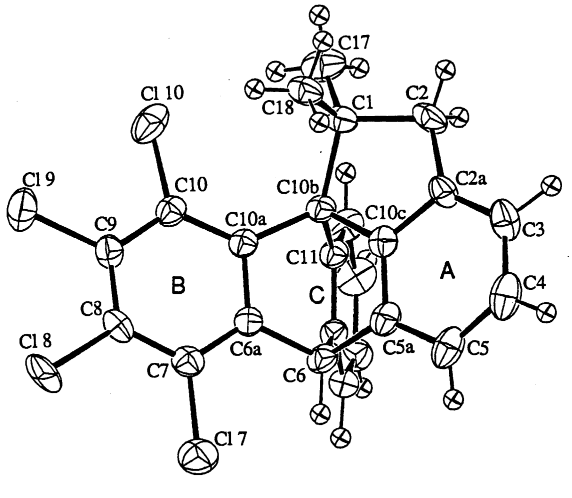

Fig. 1. An ORTEP diagram of compound **4**.

Table 2. Selected Bond Angles

Carbon atoms A-B-C	Angle/°
2 - 1 - 10b	103.4(1)
2 - 1 - 17	109.8(2)
2 - 1 - 18	104.2(1)
10b - 1 - 17	118.8(1)
10b - 1 - 18	108.3(1)
1 - 2 - 2a	104.3(1)
1 - 10b - 10a	121.6(1)
1 - 10b - 10c	99.4(1)
1 - 10b - 11	123.3(1)
10a - 10b - 10c	107.2(1)
10a - 10b - 11	101.6(1)
10c - 10b - 11	100.8(1)

Table 3. Selected Torsion Angles

Carbon atoms A-B-C-D	Angle/°
2 - 1 - 10b - 10a	145.1
2 - 1 - 10b - 10c	28.1
17 - 1 - 10b - 10a	–93.0
17 - 1 - 10b - 10c	150.0
17 - 1 - 10b - 11	40.3
18 - 1 - 10b - 10a	34.9
18 - 1 - 10b - 10c	–82.1
18 - 1 - 10b - 11	168.3
1 - 2 - 2a - 10c	21.9
2a - 2 - 1 - 10b	–31.3
2 - 2a - 10c - 10b	–2.9
1 - 10b - 10c - 2a	–16.5

Although the atomic distance between C(10a) and C(10b) and that between C(10b) and C(11) are long as sp^3-sp^2 bonds, this feature is always observed for 1-substituted triptycenes that carry a tertiary substituent at the 9-position to avoid steric hindrance.[9) The most important deviation from the normal value is seen in elongation of the atomic distance between C(1) and C(10b). The bond between C(1) and C(17) and that between C(1) and C(18) are normal.

Although it seems abnormally small for angles involving C(10b) as an apex of a trigonal pyramid, of which base is comprised by C(10a), C(10c), and C(11), this is again normal for the substituted triptycenes. There are two bond angles which are especially of interest. They are C(10b)-C(1)-C(17) and C(1)-C(10b)-C(10c). The former is unusually large 118.8° and the latter unusually small 99.4°. These deformations from the normal values are all caused by the steric interactions between the methyl groups and the 10-chloro substituent. Since the deformation of the geometry of the chloro substituent requires large energy, the deformation mainly occurs at the C(1). That is, the methyl groups are kept as far away as possible from the 10-chloro substituent.

The steric interactions also cause abnormal dihedral angles and torsion angles. The 5-membered ring condensed to the triptycene skeleton is strongly puckered, with carbons C(2), C(2a), C(10c), and C(10b) almost in a plane and C(1) out of the plane. The extent of the puckering can be understood by the torsion angles C(10c)-C(10b)-C(1)-C(2) and C(2a)-C(2)-C(1)-C(10b) of 28.1 and –31.3°, respectively. This is again for avoidance of the steric interactions.

The benzene rings, except the one having no substituent (ring C), are distorted to make a room for C(18). Carbon atoms except C(10c), C(4), C(10a), and C(8) are pushed away from C(18) to make a boat form,10) though the dislocation of tips, C(8) and C(4), which are far from C(18), from the average plane made by other four carbons in the same ring is not so severe as C(10a) and C(10c), respectively. The torsion angles, C(5)-C(5a)-C(10c)-C(2a) and C(9)-C(10)-C(10a)-(6a), are 7.6 and 10.8°, respectively.

The positions of the two methyl groups are interesting. While the distance between the C(17), which is bent away from the triptycene skeleton as is seen from the bond angle cited above, and the 10-chloro substituent is 3.299 Å, that between another C(18) and the 10-chloro is 3.224 Å. The dihedral angles made by two benzeno bridges, as revealed by the average planes made by 4 carbon atoms excluding the two which are in peri-positions of the triptycene skeleton, are 133.5° for A and B which flank the methyl (C_{18}), 115.1° for B and C which flank the bent-away methyl (C_{17}), and 108.9° for A and C which do not have a methyl group inbetween. The methyl (C_{18}) group which extends from C(1) with normal bond angles is almost perpendicular to the average plane of carbons 2, 2a, 10c, and 10b.

In summary, when a molecule is forced to take an eclipsed form in its ethane type portion, the molecule seems to take every possible deformation to avoid the steric interference. The molecule is flexible and two rigid spinning tops for ethane type molecules are only coarse models for intramolecular rotation.

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7) ^{1}H NMR ($CDCl_3$, δ): 1.59 (3H, s), 2.34 (3H, s), 3.06 and 3.12 (ABq, J = 15 Hz), 5.84 (1H, s)

8) X-Ray crystallography was carried out on a Mac Science MXC18 diffractometer which was installed at Analytical Center of Okayama University of Science. The diffraction data were collected with the use of Mo $K\alpha$ radiation and 4307 independent reflections were used for solving the structure by the Crystan program. Crystal data: $C_{24}H_{16}Cl_4$, FW = 446.20, monoclinic, space group $P2_1/n$, a = 18.10(1) Å, b = 10.974(5) Å, c = 9.804(2) Å, β = 97.79(3)°, V = 1929(1) Å^3, Z = 4, D_{calc} = 1.54 g/cm^3, R = 0.037, R_w = 0.051.

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(Received October 23, 1991)