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Syntheses and Structures of 1,1-Dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylenes: Sterically Congested Triptycenes Carrying Five-Membered Ring[1)]

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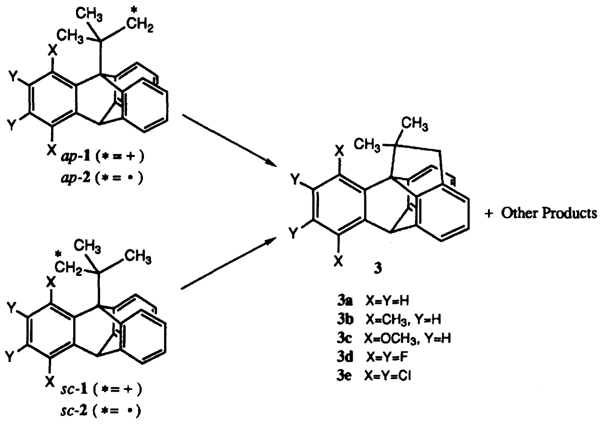
(Received February 26, 1993)

Sterically compressed title compounds which carry a five-membered ring condensed to the triptycene skeleton were synthesized by the Diels-Alder reaction of 1,1-dimethyl-1,2-dihydroaceanthrylene with a benzyne. The structures of three compounds were determined by X-ray crystallography. The molecules have several abnormal bond lengths and angles in addition to significant deformation of the benzene rings as well as the triptycene skeleton to avoid the eclipsed conformation about C(1)–C(10b) and C(1)–C(2) bonds. The effects of the substituents at the 7—10 positions are rather small, but an interesting bond angle deformation is found on comparison of the C(10a)–C(10)–substituent bond angles. Molecular mechanics calculation was performed for the dimethoxy compound to compare the calculated structure with the X-ray structure. Molecular flexibility of the unsubstituted compound was discussed on the basis of MM2 calculation.

Reactivities of rotational isomers have been investigated by generating active chemical species of 2-methyl-2-(substituted 9-triptycyl)propyl cation (**1**)[2,3)] or radical (**2**)[4)] rotamers. During the course of the survey of products, we found a unique product **3** possessing a five-membered ring condensed to the triptycene skeleton, this sturcture being assigned from the spectroscopic data. For instance, the cyclized product **3b** was obtained by diazotization of both *ap*- and *sc*-rotamers of 2-(1,4-dimethyl-9-triptycyl)-2-methylpropylamine in about 10% yield (Scheme 1).[2)] The primary cation produced by the diazotization attacks the peri carbon before rearrangement to a tertiary cation and the subsequent deprotonation gives the product. A product of the same type was also obtained by diazotization of a 1,2,3,4-tetrachloro compound.[3)] The corresponding radical species of *ap*-isomer (*ap*-**2**) produces the same compound in a fair yield as well, whereas the *sc*-isomer does not due to facile hydrogen transfer from the 1-methyl group.[4)]

It was very difficult to separate the compound from the reaction mixture because its polarity was close to those of other hydrocarbons, triptycene derivatives that carry a C_4-olefinic substituent at the 9-position,[2,3,5)] and chlorinated hydrocarbons, e.g. *ap*-9-(2-chloro-1,1-dimethylethyl)-1,4-dimethyltriptycene.[4)] The small scale of the reactions also prevented the isolation of large enough quantity of the compound for characterization as well as further investigations of the products. In order to overcome these problems, we decided to synthesize the compounds by an independent route in a practical scale.



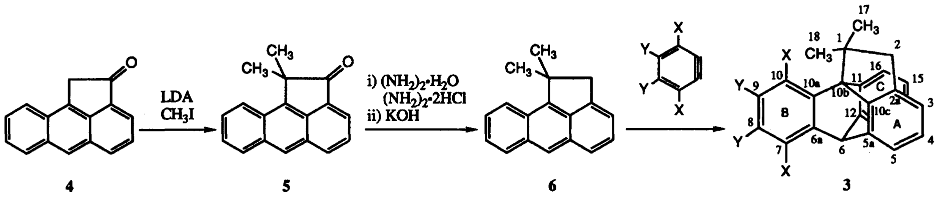
Scheme 1.

The molecular structure of the compounds is interesting. This molecule is expected to subject to severe steric congestion by carrying a five-membered ring condensed to the rigid triptycene skeleton. When one tries to construct a simple molecular model of the compound, one will encounter difficulties in connecting some bonds. Even though one can manage to construct the model, one will find that the model is compelled to take an eclipsed conformation about the C(1)–C(10b) and the C(1)–C(2) bonds and then the five-membered ring results in a planer structure. This structure, however, must be very unfavorable from a steric point of view. A real molecule should release its steric strain by a means or others, which can not be reproduced by a simple molecular model, such as deformation of benzene rings from planarity and other abnormal bond lengths or bond angles. It is worthwhile investigating the structures of these strained compounds by X-ray crystallography as well as MM2 calculation to see how molecules avoid severe congestion.

Results and Disscussion

Syntheses and NMR Spectra of Compounds 3a—3e.

These compounds were synthesized by the Diels-Alder reaction of 1,1-dimethyl-1,2-dihydroaceanthrylene (**6**) with the corresponding benzyne as shown in Scheme 2. The aceanthrylene **6** could be prepared from 1,2-dihydroaceanthrylen-2-one (**4**)[6)] by the fol-



Scheme 2.

lowing two steps. Two methyl groups at the 1-position were introduced at the same time by a treatment of **4** with an excess of iodomethane in the presence of lithium diisopropylamide (LDA). The obtained ketone (**5**) was reduced under conditions of the Wolff-Kishner reaction employed for the reduction of sterically hindered ketones, where hydrazine hydrochloride was used together with hydrazine hydrate,[7)] to form the hydrazone followed by heating in the presence of potassium hydroxide. The treatment of the hydrocarbon (**6**) with a substituted benzyne afforded a desired compound. A benzyne was generated from an anthranilic acid and isopentyl nitrite for compounds **3a**—**3c**, and from a pentahalochlorobenzene and butyllithium[8)] for compounds **3d** and **3e**.

The yields of **3** in the reaction were at most 30%, these values being lower than those for similar reactions,[9)] and moreover a moderate amount of the starting hydrocarbon was recovered, although the less aceanthrylene **6** was recovered in the case of the non-substituted compound (**3a**). The poor conversion is ascribed to the steric hindrance of the aceanthrylene, in which the two methyl groups at the 1-position hinder an approach of a benzyne to the diene moiety. The methyl groups can hardly avoid the steric interaction with the reactant because their positions are nearly fixed by the cyclic structure in contrast to the case of 9-*t*-alkylanthracenes, in which the alkyl group rotates. For the tetrahalo-substituted compounds, the separation of the product from the starting hydrocarbon was more difficult than the other compounds, this being another reason for the low yield.

The non-substituted compound (**3a**) gave only one signal (δ=1.86) for the two methyl groups and one set of aromatic signals for the non-annelated two benzo groups in its ^{1}H and ^{13}C NMR spectra. These signals exhibited no line shape changes although the temperature was lowered down to −90 °C in dichloromethane-d_2. This finding will be discussed later in connection with the molecular structure.

Other substituted compounds have some common features in ^{1}H NMR spectra as follows. They gave two signals for the two methyl groups at the 1-position at ca. 1.5 and 2.2 ppm and an AB signal for the methylene protons at the 2-position at 3.1 ppm. A small long range coupling between one of the methyl signals at the higher magnetic field and one of the methylene signals at the lower field was observed in every compound. A signal due to one aromatic proton appeared at a relatively low field compared to other aromatic protons, being assigned to the peri proton at the 16-position. Such a low field shift caused by the steric compression effect is usual for peri protons in triptycene compounds.

An NOE experiment provides further information on the assignment of the signals and the structure. When the methyl signal at $\delta=2.27$ in **3b** was irradiated, a large enhancement (22%) was observed at the signal due to the peri proton (16-H). This result indicates that the methyl signal at the lower field is due to the *syn* methyl group to the nonsubstituted benzeno group, C(17), and another methyl at the higher field is *anti*, C(18). The difference in chemical shifts of the two methyls can be explained from their location; C(18) lies at a shielding region of the two benzeno groups, whereas C(17) at a deshielding region as mentioned in the next section. The same assignment of the methyl groups can be applied to the other substituted compounds **3c**—**3e**.

X-Ray Structure of Compounds with Substituents. Molecular structures of compounds **3c**, **3d**, and **3e** were determined by the X-ray crystallography. The final atomic coordinates are listed in Table 1 and ORTEP drawings are shown in Fig. 1. Selected structural parameters—interatomic distances, bond angles, and torsion and dihedral angles—are listed in Tables 2, 3, and 4, respectively. The molecular structures of the three compounds are, as a whole, similar with each other and they have several structural features, which are mostly attributed to the steric strain. The numbering of the atoms and the designation of the benzene rings are shown in the ORTEP drawings or in the structural formula in Scheme 2.

First of all we wish to discuss the structure of the five-membered ring. Torsion angles in the five-membered ring indicate that the ring takes an envelope conformation, in which C(1) deviates from the plane made by four other atoms toward the opposite direction to the substituent-free benzeno group (Benzene C). The puckering angle of the envelope is about 32° in every compound, this value being much larger than that in MM2 optimized structure of 2,2-dimethylindane (12°) as a reference compound. The conformations about C(1)–C(2) and C(1)–C(10b) bonds are far from eclipsed as revealed by the dihedral angles in Table 4. Because the motion of C(2) and C(10b) are restricted by the rigid benzeno bridge, this structure will be most effective in view of the avoidance of the steric repulsion.

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in Compounds **3c**, **3d**, and **3e**[a)]

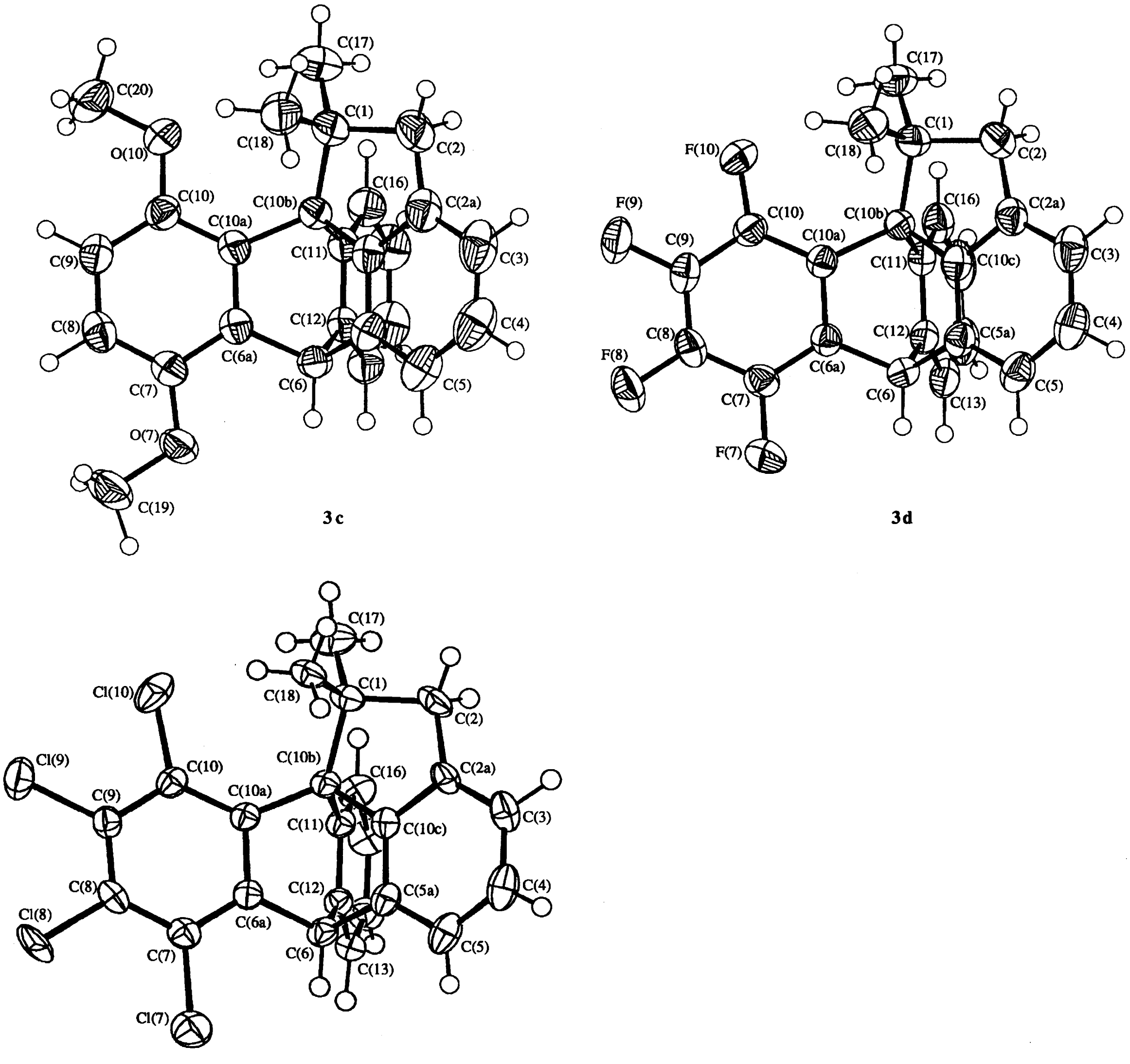
Atom	x	y	z	B_{eq}[b)]
Compound **3c**				
O(7)	1.00190(7)	0.8795(1)	0.35856(8)	4.13(4)
O(10)	0.70308(8)	1.0432(2)	0.05640(8)	4.88(4)
C(1)	0.6080(1)	1.1060(2)	0.1868(1)	4.15(6)
C(2)	0.5654(1)	1.1246(3)	0.2606(2)	5.34(8)
C(2a)	0.6319(1)	1.0459(2)	0.3451(1)	4.42(6)
C(3)	0.6297(2)	0.9951(3)	0.4295(2)	5.95(8)
C(4)	0.7083(2)	0.9492(3)	0.4995(2)	5.93(8)
C(5)	0.7900(2)	0.9616(2)	0.4905(1)	4.61(7)
C(5a)	0.7918(1)	1.0150(2)	0.4072(1)	3.40(5)
C(6)	0.8676(1)	1.0731(2)	0.3816(1)	3.08(5)
C(6a)	0.8588(1)	0.9913(2)	0.2915(1)	3.02(5)
C(7)	0.9273(1)	0.9054(2)	0.2801(1)	3.29(5)
C(8)	0.9178(1)	0.8542(2)	0.1931(1)	3.88(6)
C(9)	0.8422(1)	0.8975(2)	0.1176(1)	3.93(6)
C(10)	0.7747(1)	0.9852(2)	0.1291(1)	3.34(5)
C(10a)	0.7792(1)	1.0229(2)	0.2176(1)	2.98(5)
C(10b)	0.7116(1)	1.1169(2)	0.2465(1)	3.06(5)
C(10c)	0.7126(1)	1.0451(2)	0.3362(1)	3.34(5)
C(11)	0.7622(1)	1.2775(2)	0.2882(1)	3.08(5)
C(12)	0.8452(1)	1.2506(2)	0.3547(1)	3.04(5)
C(13)	0.9003(1)	1.3787(2)	0.3954(1)	3.77(6)
C(14)	0.8740(1)	1.5348(2)	0.3647(2)	4.68(7)
C(15)	0.7936(1)	1.5613(2)	0.2941(2)	4.91(7)
C(16)	0.7372(1)	1.4334(2)	0.2527(1)	3.94(6)
C(17)	0.5677(2)	1.2254(3)	0.1083(2)	5.57(8)
C(18)	0.5864(1)	0.9308(3)	0.1504(2)	5.11(7)
C(19)	1.0715(2)	0.7864(3)	0.3476(2)	5.60(8)
C(20)	0.7013(2)	1.0258(4)	−0.0343(2)	5.76(8)
Compound **3d**				
F(7)	−0.7536(1)	−0.3040(1)	−0.7500(1)	5.02(3)
F(8)	−0.4655(1)	−0.48687(9)	−0.6339(1)	5.02(3)
F(9)	−0.2844(1)	−0.3660(1)	−0.5752(1)	4.81(3)
F(10)	−0.3757(1)	−0.0693(1)	−0.64272(9)	4.86(3)
C(1)	−0.5702(2)	0.2494(2)	−0.8394(2)	3.73(5)
C(2)	−0.6652(2)	0.3965(2)	−0.9501(2)	4.50(5)
C(2a)	−0.7507(2)	0.3442(2)	−1.0132(2)	3.61(4)
C(3)	−0.8340(2)	0.4114(2)	−1.1275(2)	4.41(5)
C(4)	−0.9235(2)	0.3407(2)	−1.1482(2)	4.59(6)
C(5)	−0.9410(2)	0.2096(2)	−1.0557(2)	4.19(5)
C(5a)	−0.8585(2)	0.1439(2)	−0.9423(2)	3.20(4)
C(6)	−0.8790(2)	0.0254(2)	−0.8149(1)	3.28(4)
C(6a)	−0.7082(2)	−0.0864(1)	−0.7691(1)	2.95(4)
C(7)	−0.6583(2)	−0.2409(2)	−0.7315(1)	3.42(4)
C(8)	−0.5132(2)	−0.3361(2)	−0.6699(1)	3.50(4)
C(9)	−0.4214(2)	−0.2750(2)	−0.6418(1)	3.50(4)
C(10)	−0.4692(2)	−0.1188(2)	−0.6809(1)	3.34(4)
C(10a)	−0.6078(2)	−0.0215(1)	−0.7505(1)	2.86(4)
C(10b)	−0.6848(2)	0.1535(1)	−0.7991(1)	2.90(4)
C(10c)	−0.7597(2)	0.2085(2)	−0.9281(1)	2.98(4)
C(11)	−0.8418(2)	0.1796(1)	−0.7091(1)	2.82(4)
C(12)	−0.9439(2)	0.1117(2)	−0.7205(1)	2.95(4)
C(13)	−1.0919(2)	0.1243(2)	−0.6512(2)	3.59(5)
C(14)	−1.1405(2)	0.2051(2)	−0.5688(2)	4.12(5)
C(15)	−1.0411(2)	0.2690(2)	−0.5543(2)	4.29(5)
C(16)	−0.8901(2)	0.2560(2)	−0.6235(1)	3.68(4)
C(17)	−0.5307(2)	0.2866(2)	−0.7344(2)	5.42(7)
C(18)	−0.4092(2)	0.1678(2)	−0.9038(2)	3.73(6)
Compound **3e**				
Cl(7)	−0.02349(3)	−0.29345(5)	0.68958(5)	4.10(1)
Cl(8)	0.08581(3)	0.16080(4)	0.67210(5)	4.33(1)
Cl(9)	−0.01757(3)	−0.02247(5)	0.79192(6)	4.79(2)
Cl(10)	0.18787(3)	0.08083(4)	0.46541(5)	4.08(1)
C(1)	0.28406(9)	−0.1764(2)	0.4243(2)	2.82(4)
C(2)	0.3296(1)	−0.2969(2)	0.4195(2)	3.44(5)
C(2a)	0.28928(9)	−0.3870(2)	0.4974(2)	2.95(4)
C(3)	0.3071(1)	−0.5022(2)	0.5511(2)	3.64(5)
C(4)	0.2520(1)	−0.5732(2)	0.5962(2)	3.94(5)
C(5)	0.1774(1)	−0.5348(2)	0.5829(2)	3.50(5)
C(5a)	0.1608(1)	−0.4189(2)	0.5314(2)	2.78(4)
C(6)	0.0870(1)	−0.3578(2)	0.4833(2)	2.73(4)
C(6a)	0.09056(9)	−0.2324(2)	0.5506(2)	2.53(4)
C(7)	0.04073(9)	−0.1931(2)	0.6362(2)	2.84(4)
C(8)	0.04131(9)	−0.0717(2)	0.6799(2)	3.01(4)
C(9)	0.0890(1)	0.0094(2)	0.6276(2)	2.87(4)
C(10)	0.13968(9)	−0.0309(2)	0.5406(2)	2.69(4)
C(10a)	0.14575(9)	−0.1544(2)	0.5111(2)	2.42(4)
C(10b)	0.20059(9)	−0.2236(2)	0.4281(2)	2.41(4)
C(10c)	0.21748(9)	−0.3465(2)	0.4978(2)	2.53(4)
C(11)	0.14766(9)	−0.2626(2)	0.2970(2)	2.43(4)
C(12)	0.08720(9)	−0.3331(1)	0.3294(2)	2.54(4)
C(13)	0.0338(1)	−0.3756(2)	0.2262(2)	3.05(4)
C(14)	0.0402(1)	−0.3505(2)	0.0901(2)	3.45(4)
C(15)	0.0994(1)	−0.2830(2)	0.0575(2)	3.66(5)
C(16)	0.1535(1)	−0.2388(2)	0.1613(2)	3.09(4)
C(17)	0.2998(1)	−0.0915(2)	0.3082(2)	3.98(6)
C(18)	0.3132(1)	−0.1207(2)	0.5669(2)	3.24(5)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/\text{Å}^2=(8\pi^2/3)\sum_i\sum_j U_{ij}\,a_i^*\,a_j^*\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

The bond lengths of C(1)–C(10b) and C(1)–C(2) are large with respect to the normal value of sp^3–sp^3 bonds and, especially, the former bond (1.60 Å) is lengthened. In contrast, the C(10b)–C(10c) bond seems to be short as a bridging bond from an sp^2-benzeno carbon to an sp^3-apex carbon in triptycenes which carry a tertiary alkyl substituent at the 9-position.[11,12)]

The five-membered ring has unusual bond angles—small angles inside and large angles outside the ring. For example the bond angles of C(1)–C(10b)–C(10c), 99°, are smaller by ca. 10° than a normal bond angle for an sp^3 carbon. In order to compensate this bending, C(1)–C(10b)–C(11) takes a large value of 124°. A similar relation is held for the C(2)–C(2a)–C(10c) and C(2)–C(2a)–C(3) angles. The severe strain caused by the construction of the five-membered ring leads to such a characteristic structure.

The location of the two methyl groups at the 1-position deserves mention. The 18-methyl extends in an almost perpendicular direction and the 17-methyl does in an almost parallel direction to the average plane made by C(2), C(2a), C(10b), and C(10c) atoms. The bond distances from the methyls to C(1) are normal and the distance of C(1)–C(18) bond tends to be slightly longer than that of C(1)–C(17). The C(10b)–C(1)–C-



3c **3d** **3e**

Fig. 1. ORTEP drawings of compounds **3c**, **3d**, and **3e** with thermal ellipsoids with 50% probabilities.

(18) bond angle is normal, whereas C(10b)–C(1)–C(17) is very large compared to 109.5°. This bending deformation can be attributed to the steric repulsion of the 17-methyl with the peri hydrogen, 16-H. The nonbonding distance between C(17) and C(16) is only 3.3 Å in all compounds, this geometry being consistent with the large NOE value between the 17-methyl protons and 16-H. The envelope conformation of the five-membered ring makes the 18-methyl group direct toward the notch between the two benzeno groups A and B. As a result, this methyl is located in the shielding region of the benzene rings as can be seen from the short nonbonding distances from C(18) to C(10) or the substituent at C-(10), X(10). This structure well interprets the high field shift of the 18-methyl protons in ^{1}H NMR.

Torsion angles in the aromatic carbons indicate that the benzene rings, except Benzene C, are significantly distorted from a planar structure. These benzene rings take a distorted shallow boat structure where C(10c)/C-(4) and C(10a)/C(8) are bows in Benzenes A and B, respectively, and other carbons are dislocated away from the 18-methyl. The dislocations of the C(10c) and C(10a) bows are more significant than those of the opposite bows. In compound **3e**, the torsion angles around bonds including C(10a) atom even exceed 10°. These deformations result from the steric interactions between the 18-methyl and the benzene moieties. When the steric interactions are severe, benzene rings are no longer rigid to avoid the interactions, as were observed in several sterically hindered aromatic compounds, regardless of loss of aromatic resonance energy, and a boat conformation is preferred.[13)]

The triptycene skeleton itself considerably deforms from a standard structure, in which each dihedral angle between the three benzeno wings is 120°. The dihedral angles between the average benzene planes, calculated from a best fitting of four benzene carbons excluding two peri carbons, are listed in Table 4. The angles

Table 2. Selected Bond Distances and Nonbonding Distances (Å) in Compounds **3c**, **3d**, and **3e**[a]

Compound	3c	3c[b]	3d	3e
Bond distance				
C(1)–C(2)	1.563(3)	1.568	1.564(2)	1.560(3)
C(1)–C(10b)	1.591(2)	1.575	1.595(2)	1.602(2)
C(1)–C(17)	1.524(3)	1.539	1.527(4)	1.528(3)
C(1)–C(18)	1.558(3)	1.556	1.545(2)	1.551(2)
C(2)–C(2a)	1.507(3)	1.492	1.503(3)	1.498(3)
C(10b)–C(10a)	1.548(2)	1.533	1.545(2)	1.564(2)
C(10b)–C(10c)	1.522(2)	1.515	1.522(2)	1.522(2)
C(10b)–C(11)	1.558(2)	1.524	1.557(2)	1.554(2)
C(6)–C(5a)	1.511(3)	1.497	1.515(2)	1.510(2)
C(6)–C(6a)	1.525(2)	1.517	1.523(2)	1.522(2)
C(6)–C(12)	1.541(2)	1.526	1.536(2)	1.535(2)
C(7)–X(7)[c]	1.380(2)	1.368	1.357(2)	1.732(2)
C(10)–X(10)[d]	1.373(2)	1.366	1.351(2)	1.727(2)
Nonbonding distance				
C(1), X(10)	3.036(2)	3.070	3.134(1)	3.366(2)
C(17), X(10)	3.023(3)	3.073	3.143(2)	3.302(2)
C(18), X(10)	2.957(3)	2.992	2.972(2)	3.224(2)
C(10), C(18)	3.231(3)	3.245	3.209(2)	3.267(2)
C(16), C(17)	3.317(3)	3.343	3.311(3)	3.263(3)

a) Estimated standard deviations in parentheses. b) Values for an optimized structure by MMP2 calculation. c) Attached heteroatom at the 7-position. d) Attached heteroatom at the 10-position.

Table 3. Selected Bond Angles (°) in Compounds **3c**, **3d**, and **3e**[a]

Compound	3c	3c[b]	3d	3e
C(2)–C(1)–C(10b)	103.0(1)	107.5	103.0(1)	103.3(1)
C(2)–C(1)–C(17)	111.0(2)	108.7	115.2(2)	109.8(2)
C(2)–C(1)–C(18)	105.2(2)	104.2	105.6(1)	104.2(1)
C(10b)–C(1)–C(17)	118.3(2)	116.8	117.4(1)	119.1(1)
C(10b)–C(1)–C(18)	108.2(1)	110.4	108.8(2)	108.2(1)
C(17)–C(1)–C(18)	110.2(2)	108.5	109.8(2)	111.0(2)
C(1)–C(2)–C(2a)	103.6(2)	101.1	104.2(1)	104.3(1)
C(2)–C(2a)–C(10c)	108.0(2)	108.6	108.4(1)	108.4(2)
C(2)–C(2a)–C(3)	134.0(2)	130.7	133.6(2)	133.6(2)
C(6a)–C(7)–X(7)[c]	116.3(2)	119.4	120.7(1)	120.4(1)
C(10a)–C(10)–X(10)[d]	117.1(2)	120.0	122.6(1)	122.8(1)
C(1)–C(10b)–C(10c)	99.2(1)	95.7	99.6(1)	99.4(1)
C(1)–C(10b)–C(10a)	120.5(1)	123.1	120.1(1)	121.5(1)
C(1)–C(10b)–C(11)	123.9(1)	127.1	124.8(1)	123.1(1)
C(10a)–C(10b)–C(10c)	108.1(1)	106.6	108.0(1)	107.3(1)
C(10a)–C(10b)–C(11)	101.7(1)	101.1	100.9(1)	101.6(1)
C(10c)–C(10b)–C(11)	100.7(1)	98.0	100.9(1)	101.0(1)
C(2a)–C(10c)–C(10b)	114.5(1)	116.5	114.0(2)	114.6(1)

a) Estimated standard daviations in parentheses. b) Values for an optimized structure by MMP2 calculation. c) Attached heteroatom at the 7-position. d) Attached heteroatom at the 10-position.

Table 4. Selected Tortion and Dihedral Angles (°) in Compounds **3c**, **3d**, and **3e**

Compound	3c	3c[a]	3d	3e
Torsion angles[b]				
C(1)–C(2)–C(2a)–C(10c)	22.0	18.4	19.9	21.7
C(2)–C(2a)–C(10c)–C(10b)	−1.4	1.5	0.5	−2.7
C(2a)–C(10c)–C(10b)–C(1)	−19.2	−20.2	−20.0	−16.6
C(10c)–C(10b)–C(1)–C(2)	30.6	30.5	30.1	28.0
C(10b)–C(1)–C(2)–C(2a)	−32.9	−31.5	−31.3	−31.0
C(17)–C(1)–C(2)–C(2a)	−160.6	−158.8	−158.2	−159.1
C(18)–C(1)–C(2)–C(2a)	80.3	85.7	82.6	81.9
C(2)–C(1)–C(10b)–C(10a)	148.2	144.5	147.5	145.2
C(17)–C(1)–C(10b)–C(10a)	−89.0	−93.1	−89.5	−92.7
C(18)–C(1)–C(10b)–C(10a)	37.2	31.5	35.8	35.2
C(17)–C(1)–C(10b)–C(10c)	153.5	152.9	153.1	150.2
C(18)–C(1)–C(10b)–C(10c)	−80.4	−82.6	−81.6	−82.0
C(5)–C(5a)–C(10c)–C(2a)	8.7	6.4	7.4	7.7
C(5a)–C(10c)–C(2a)–C(3)	−7.4	−7.9	−7.1	−8.7
C(9)–C(10)–C(10a)–C(6a)	9.6	5.9	6.5	11.2
C(10)–C(10a)–C(6a)–C(7)	−8.7	−7.9	−7.4	−11.4
C(6a)–C(7)–O(7)–C(19)	178.0	−163.4		
C(10a)–C(10)–O(10)–C(20)	172.0	166.0		
Dihedral angles[c]				
Benzene A–Benzene B	140.3	142.3	143.7	135.5
Benzene B–Benzene C	111.8	110.7	110.7	115.1
Benzene C–Benzene A	107.9	106.9	105.5	108.9
Plane D–Plane E	33.6	33.5	32.4	31.2

a) Values for an optimized structure by MMP2 calculation. b) Angles are calculated for 10b*R* molecules. c) Angles between average planes made by the following carbons; Benzene A: C(3), C(4), C(5a), C(10b); Benzene B: C(6a), C(8), C(9), C(10a); Benzene C: C(11), C(12), C(13), C(15); Plane D: C(1), C(2), C(10b); Plane E: C(2), C(2a), C(10b), C(10c).

are 140°, 112°, and 108° for the A–B, B–C, and C–A notches, respectively, in compound **3c** and other two compounds give similar values. As expected from the intervention of the 18-methyl to the A–B notch, this space is expanded to a certain extent and the others become small. Although this kind of deformation is also observed in triptycenes carrying a substituent at the 9-position, the degree is not so much as the case in these cyclized compounds. A triptycene skeleton is also flexible rather than rigid when a molecule is subjected to a severe steric congestion.

In order to get further insight into the influence of the substituents at the 7—10 positions, we wish to compare the three structures in detail. The steric size of the substituent increases in the order of F(1.47 Å), OCH$_3$(1.52 Å), and Cl(1.73 Å) according to the van der Waals radius shown in parentheses.[14]

One of the apparent trends in the structural parameters is that the larger the substituent at the 10-position, the more bent the benzene ring B is at C(10a), whereas the extent of nonplanarity of Benzene A is scarcely affected by the size of the substituent. It is also noted that the deformation of the triptycene skeleton becomes small, i.e. dihedral angles tend to change toward 120°, when the size of the substituent increases. It is likely that the deformation of the skeleton requires additional energy when it has heavy atoms as substituents. The deformation of the benzene ring may compensate this disadvantage in releasing the steric repulsion though it is difficult to dissect the observed deformation into the two factors.

There are some substituent effects on the bond lengths and bond angles as well. The length of the C(10a)–C(10b) bond slightly increases with the size of the substituent and the tetrachloro compound (**3e**) has the largest bond length of 1.564 Å of the three, which is longer by 0.05 Å than a standard sp^3–sp^2 single bond. The bulkier the substituent, the smaller the bond angle of C(2)–C(1)–C(17) and the larger the C(10b)–C(1)–C(17) angle. These tendencies are also caused by the steric repulsion between the 10-substituent and the two methyls.

We notice one more unique feature of the direction of peri substituents in the 7,10-dimethoxy compound (**3c**). The bond angles of C(10a)–C(10)–X(10) are larger than a usual value in **3d** and **3e**, this bending being caused by the steric interaction of the substituent with the tertiary alkyl group at the bridgehead position. However, the corresponding angle in compound **3c** becomes smaller than the normal, that is, the oxygen atom is tilted toward, rather than away, to the methyl groups. This structure is observed in spite of the absence of the buttressing effect. Although the 7-methoxyl group shows a small C–C–O angle as well, it is striking to note that the 10-methoxyl group takes this bond angle at a strongly congested position. The similar phenomenon is also observed in a series of triptycene compounds.15) There should be a certain attractive interaction. A hydrogen bond, which is discussed as the cause of abnormal geometry of certain methoxyl groups as reported in a previous paper,11) may well be a part of the reasons for this structure. The C(10a)–C(10)–O(10)–C(20) torsion angle of 172.0° indicates that the methyl group in the 10-methoxyl group is a little out of the benzene ring, to which it is attached. This conformation implies the presence of the $CH_3 \cdots O$ hydrogen bond. The X-ray structure shows that the distances between the 10-oxygen and the nearest hydrogens in the 17,18-methyls are only 2.2—2.3 Å.

Comparison of MM2 Structure of Compound 3c with That Obtained by X-ray Analysis. It will be interesting to compare the structure of compounds **3** obtained by calculation with that produced by X-ray analysis because of the congestion. The comparison will afford the extent of reliability of calculation because these compounds possess extreme structures.

We performed MMP2 calculations of compound **3c** because this is the only compound of the three which can be calculated with original MM2 parameters. In the calculation, the nonplanar parameters were used for the conjugated π-system, because these are known to give satisfactory results in the calculation of structures of triptycene derivatives.10,16) The X-ray structure was used for the initial coordinates and relaxed to optimize the energy of the structure with MM2(85) program. Only one structure, except its enantiomer, was obtained after optimization. Its structural parameters are shown in Tables 2, 3, and 4 together with the X-ray data.

Grossly speaking, the results obtained by the MMP2 calculation were in good agreement with those obtained by X-ray analysis. The typical example is the conformation of the five-membered ring. The dihedral angles involved in the envelope conformations are satisfactorily reproduced. Deformation of the benzene rings is also in good agreement with the results of the X-ray diffraction.

Careful comparison, however, reveals some discrepancies which cannot be ignored. The most significant difference is found in the bond distance of C(10b)–C(11): The calculated value is shorter by 0.034 Å than that in the X-ray structure. The deviations in bond lengths exceed 0.015 Å in several bonds, especially those at bonds in the condensed ring. The calculated bond distances tend to be shorter than the observed ones except the C(1)–C(17) bond among the selected bonds listed in Table 2.

The bond angles seem to be in better agreement than the bond distances; the deviations are 3.5° at the most. As for torsion angles, the calculated value of C(6a)–C(7)–O(7)–C(19) angle, −163.4°, is fairly distant from the observed one, 178.0°. These angles mean that the methyl group in the 7-methoxyl group is distorted to the opposite direction from the coplanarity with the benzene ring, to which it is attached, with each other.

Although the deviations discussed above may become negligibly small, if we can perform MM3 calculations,17) the results are satisfactory for discussion of the gross structure of such congested molecules as are treated in this paper. The results obtained by MM2 calculations may be used for discussion of structures, if certain reservations are made.

Structure of Compound 3a. Compound **3a** afforded single crystals that were used for data collection of X-ray diffraction. However, we were not able to analyze the data due to several difficulties including a very large cell and dislocations. Therefore, we wish to discuss the structure of this compound with use of MM2 calculation results, that are proved to be reliable to an extent which suffices for identifying the existing structure(s).

Differing from other substituted compounds, compound **3a** has structures that can be interconverted with ease. This is evidenced by the fact that the two methyl groups at the five-membered ring and the two unsubstituted benzeno bridges are equivalent in ^{1}H NMR spectra even at −90 °C at 400 MHz together with the similar results in the ^{13}C NMR for the two methyl carbons and the two benzeno bridges. As was observed for other compounds, it is unlikely that these signals possess fortuitously identical chemical shifts under the conditions. Nor is it likely that the molecule takes a C_s

structure which should be disfavored because of eclipsing interactions.

MM2 calculations show that the molecule can exist in two enantiomeric forms which are shown in Scheme 3. The methyl groups are diastereotopic but their magnetic sites are exchanged by enantiomerization. Therefore, if the barrier to the enantiomerization is low, the observation of equivalent methyls and two equivalent benzeno groups can be accommodated.

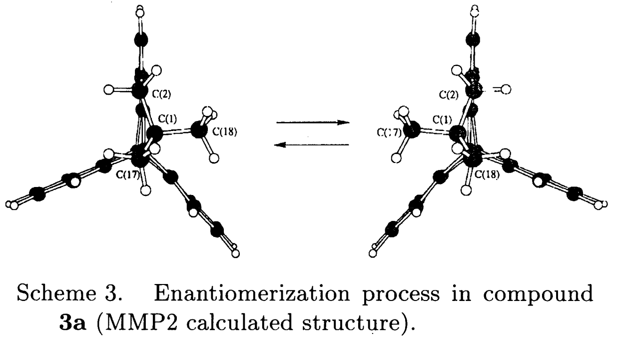
We believe that this is really the case because compound **3a** lacks substituents at the 10-position, which should enhance the barrier to enantiomerization (diastereomerization) processes, in addition to the fact that the MM2 calculation does not imply the presence of any particular destabilization of the ground state. Thus our conclusion is that this compound is a flexible molecule which enantiomerizes easily even at −90 °C on the NMR time scale.

Experimental

^{1}H and ^{13}C NMR spectra were measured on a JEOL GSX-400 spectrometer operating at 399.8 and 100.2 MHz, respectively. Elemental analyses were performed by a Perkin Elmer 240C analyzer. Melting points are uncorrected. Chloropentafluorobenzene, hexachlorobenzene, and anthranilic acid were purchased from Tokyo Kasei Co. or Nacalai Tesque Inc.

1,1-Dimethyl-1,2-dihydroaceanthrylen-2-one (5). To a solution of lithium diisopropylamide, prepared from 0.93 g (9.2 mmol) of diisopropylamine and 17.7 mL (9.2 mmol) of 15% hexane solution of butyllithium, in 50 mL of dry THF was added a solution of 1.0 g (4.6 mmol) of 1,2-dihydroaceanthrylen-2-one (**4**)[6] in 20 mL of THF and then 2.0 g (14 mmol) of iodomethane at −78 °C under a nitrogen atmosphere. The solution was stirred for 2 h at room temperature and treated with water. The mixture was extracted with dichloromethane and the organic layer was dried and evaporated. The residue was chromatographed on alumina with 10:1 hexane–dichloromethane eluent. Recrystallization from hexane–dichloromethane gave the desired compound in 59% yield as yellow crystals. Mp 130.5—132.0 °C; ^{1}H NMR (CDCl$_3$) δ=1.76 (6H, s), 7.49—7.62 (2H, m), 7.75 (1H, dd, J=8.4 and 6.7 Hz), 8.01 (1H, d, J=6.7 Hz), 8.14 (1H, app. d, J=7.6 Hz), 8.26 (1H, dd, J=8.5 and 0.9 Hz), 8.28 (1H, d, J=8.5 Hz), and 8.46 (1H, s); IR 1714 cm^{-1} (C=O). Found: C, 87.78; H, 5.76%. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73%.

1,1-Dimethyl-1,2-dihydroaceanthrylene (6). 1,1-Dimethyl-1,2-dihydroaceanthrylen-2-one (1.0 g or 4.1 mmol), 14 g (280 mmol) of hydrazine hydrate, and 3.4 g (32 mmol) of hydrazine dihydrochloride were dissolved in 80 mL of triethylene glycol. This solution was heated at 130° C under a nitrogen atmosphere for 2.5 h. After the mixture was cooled to room temperature, 5.1 g (91 mmol) of potassium hydroxide was added and the flask was connected to a distillation apparatus. The reaction mixture was gradually heated with removing volatile materials until the temperature reached 210 °C. After being kept at the temperature for 2.5 h, the mixture was treated with water and extracted with dichloromethane. The extract was dried and evaporated under reduced pressure. The residue was purified by chromatography on alumina (eluent: hexane). Subsequent recrystallization from hexane-dichloromethane gave colorless crystals in 92% yield. Mp 93.0—94.0 °C; ^{1}H NMR (CDCl$_3$) δ=1.79 (6H, s), 3.43 (2H, s), 7.20 (1H, dd, J=6.6 and 0.7 Hz), 7.40—7.49 (3H, m), 7.75 (1H, d, J=8.5 Hz), 8.07 (1H, m), 8.22 (1H, s), and 8.33 (1H, m). Found: C, 92.99; H, 6.83%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%.



Scheme 3. Enantiomerization process in compound **3a** (MMP2 calculated structure).

1,1-Dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (3a). To a refluxing solution of 0.50 g (2.2 mmol) of 1,1-dimethyl-1,2-dihydroaceanthrylene and 290 μL (2.2 mmol) of isopentyl nitrite in 10 mL of dichloromethane were added a solution of 1.2 g (8.6 mmol) of anthranilic acid in 10 mL of acetone and a solution of 0.86 mL (6.4 mmol) of isopentyl nitrite in 10 mL of dichloromethane from respective dropping funnels during the course of 30 min. The reaction mixture was refluxed for 1 h and then the volatile materials were removed under reduced pressure. The residue was chromatographed on alumina (eluent: hexane) to give 0.40 g (61%) of the desired compound with recovery of 28% of the starting aceanthrylene. Mp 158.5—160.0 °C; ^{1}H NMR (CDCl$_3$) δ=1.86 (6H, s), 3.05 (2H, s), 5.25 (1H, s), 6.85—6.93 (5H, m), 6.95 (1H, t, J=7.4 Hz), 7.19 (1H, dd, J=7.2 and 0.7 Hz), 7.29 (2H, dd, J=6.9 and 1.4 Hz), and 7.68 (2H, dd, J=7.2 and 0.7 Hz); ^{13}C NMR (CDCl$_3$) δ=28.5, 44.9, 51.1, 54.6, 63.7, 120.0, 121.2, 123.7, 123.8, 124.1, 126.2, 138.0, 142.4, 146.7, 148.8, and 152.0. Found: C, 93.36; H, 6.54%. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54%.

1,1,7,10-Tetramethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (3b). This compound was similarly obtained from the aceanthrylene and 3,6-dimethylanthranilic acid.[18] Yield was 30% with 45% recovery of the starting material. Mp 190.0—191.0 °C; ^{1}H NMR (CDCl$_3$) δ=1.50 (3H, s), 2.27 (3H, s), 2.52 (3H, s), 2.56 (3H, s), 3.04 and 3.10 (2H, ABq, J=15.1 Hz), 5.45 (1H, s), 6.70—6.78 (3H, m), 6.82—6.88 (2H, m), 6.97 (1H, dt, J=1.3 and 7.2 Hz), 7.14 (1H, d, J=7.2 Hz), 7.20 (1H, d, J=7.5 Hz), and 7.73 (1H, d, J=7.2 Hz). Found: C, 92.84; H, 7.21%. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%. An NOE experiment was performed with a degassed chloroform-*d* solution. Irradiation time was 5 s and 45° pulse was used. When the methyl signal at δ=2.27 was irradiated with power of IRA=350, the peri proton (16-H) at δ=7.73 was enhanced by 22% and small enhancements (3—4%) were also observed for the 10-CH$_3$ (δ=2.56) and the 2-methylene proton signals.

7,10-Dimethoxy-1,1-dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (3c). This compound was also similarly obtained from the 1,1-dimethylaceanthrylene and 3,6-dimethoxylanthranilic acid.[19] The yield

Table 5. Crystal and Structure Analysis Data of Compounds **3c**, **3d**, and **3e**

Compound	**3c**	**3d**	**3e**
Formula	$C_{26}H_{24}O_2$	$C_{24}H_{16}F_4$	$C_{24}H_{16}Cl_4$
F.W.	368.48	380.39	446.20
Crystal size/mm^3	0.45×0.45×0.25	0.50×0.40×0.25	0.30×0.25×0.25
Radiation	Mo$K\alpha$	Mo$K\alpha$	Cu$K\alpha$
Scan rate/° min^{-1}	4	5	12
Scan range (A°+B°tanθ)			
A	1.00	1.04	1.47
B	0.35	0.35	0.30
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	16.243(5)	8.957(6)	18.097(4)
b/Å	8.322(3)	10.353(3)	10.959(3)
c/Å	15.673(4)	11.319(2)	9.812(2)
α/°	90	66.60(2)	90
β/°	112.14(2)	78.56(3)	97.87(2)
γ/°	90	65.55(3)	90
V/Å^3	1962(1)	876.2(6)	1927.7(8)
Z	4	2	4
D_c/g cm^{-3}	1.25	1.44	1.54
μ/cm^{-1}	0.41	0.70	54.59
2θ range/°	2—55	2—57	2—130
No. of data	4510	4433	3200
No. of data used	3551	3726	3081
R	0.053	0.045	0.035
R_w	0.041	0.056	0.050
g	1.8×10^{-5}	2.4×10^{-4}	4.0×10^{-4}

was 19% and 80% of the aceanthrylene was recovered. Mp 223.5—224.0 °C; ^{1}H NMR ($CDCl_3$) δ=1.47 (3H, d, J=0.7 Hz), 2.16 (3H, s), 2.96 and 3.06 (2H, ABq, J=14.7 Hz), 3.77 (3H, s), 3.84 (3H, s), 5.75 (1H, s), 6.54 and 6.61 (2H, ABq, J=8.9 Hz), 6.72 (1H, dt, J=1.0 and 7.5 Hz), 6.81 (1H, dt, J=1.4 and 7.5 Hz), 6.85 (1H, d, J=7.5 Hz), 6.95 (1H, t, J=7.5 Hz), 7.15 (1H, dd, J=1.0 and 7.2 Hz), 7.12 (1H, d, J=7.2 Hz), and 7.74 (1H, d, J=7.5 Hz). Found: C, 84.72; H, 6.61%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57%.

7,8,9,10-Tetrafluoro-1,1-dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (3d). To a solution of 1.1 mL (8.5 mmol) of chloropentafluorobenzene in 20 mL of dry ether was added 6.5 mL (10.2 mmol) of 15% hexane solution of butyllithium at −78 °C under a nitrogen atmosphere. The mixutre was stirred for 3 h at the temperature. To the solution was added a solution of 0.40 g (1.7 mmol) of the 1,1-dimethylaceanthrylene in 5 mL of dry ether. The reaction mixture was stirred for 2 h at the temperature, for 1 h at 0 °C, and for 2 days at room temperature. The solution was refluxed for 1 h and treated with dilute hydrochloric acid. The organic layer was separated, dried, and evaporated. The residue was chromatographed on silica gel. Since the separation is insufficient at this stage, further purification was performed by HPLC and chromatography on silica gel-$AgNO_3$. Subsequent recrystallization from hexane–dichloromethane afforded the pure desired compound as colorless crystals in 20% yield with 20% recovery of the starting material. Mp 160.5—161.0 °C; ^{1}H NMR ($CDCl_3$) δ=1.50 (3H, d, J=1.7 Hz), 2.09 (3H, d, J=2.1 Hz), 3.04 and 3.10 (2H, ABq, J=14.7 Hz), 5.64 (1H, d, J=1.7 Hz), 6.83 (1H, dt, J=1.4 and 7.4 Hz), 6.90 (1H, dt, J=1.4 and 7.5 Hz), 6.94 (1H, d, J=7.5 Hz), 7.03 (1H, t, J=7.4 Hz), 7.21 (1H, dd, J=7.2 and 1.0 Hz), 7.23 (1H, d, J=7.2 Hz), and 7.75 (1H, d, J=7.5 Hz). Found: C, 75.52; H, 4.24%. Calcd for $C_{24}H_{16}F_4$: C, 75.78; H, 4.24%.

7,8,9,10-Tetrachloro-1,1-dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (3e). This compound was similarly prepared from the 1,1-dimethylaceanthrylene and hexachlorobenzene. Yield 15%. Mp 235.5—237.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.59 (3H, s), 2.34 (3H, s), 3.06 and 3.12 (2H, ABq, J=15.2 Hz), 5.84 (1H, s), 6.84 (1H, dt, J=1.2 and 7.4 Hz), 6.92 (1H, dd, J=7.5 and 0.8 Hz), 6.95 (1H, dt, J=1.4 and 7.5 Hz), 7.06 (1H, t, J=7.5 Hz), 7.22 (1H, dd, J=7.2 and 1.2 Hz), 7.27 (1H, d, J=7.5 Hz), and 7.83 (1H, d, J=7.5 Hz). Found: C, 64.40; H, 3.63%. Calcd for $C_{24}H_{16}Cl_4$: C, 64.60; H, 3.61%.

MMP2 Calculation. The molecular mechanics calculations of the non-substituted compound (**3a**), the methoxy compound (**3c**), and 2,2-dimethylindane were performed by MM2(85) program with an NEC 98-series computer. Nonplanar parameters were used for conjugated π-systems. Other parameters were used without modification.

X-Ray Crystallography.[20] All crystals used for the X-ray measurements were grown from hexane–dichloromethane solutions. X-Ray data were collected on an MAC Science MXC18 four circle diffractometer with Cu $K\alpha$ (λ=1.54178 Å) or Mo $K\alpha$ (λ=0.71073 Å) radiation. The scan mode was the ω–2θ method in all range for Cu radiation and both the 2θ method ($2\theta<30°$) and the ω–2θ method ($2\theta>30°$) for Mo radiation. The structure was solved by the direct method and refined by the full-matrix least-squares method by using CRYSTAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. An analytical absorption correction was applied for compound **3e** and no absorption correction for compounds **3c** and **3d**. Reflection data within $|F_o| > 3\sigma(F_o)$ were used for the structure determination and refinement for compounds **3c** and **3d**. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)^2]$, where $w = [(\sigma_c|F_o|)^2 + g|F_o|^2]^{-1}$. Further experimental data are compiled in Table 5.

This work was supported by a Grant-in-Aid for Scientific Research No. 03453034 from the Ministry of Education, Science and Culture. The X-ray analysis and the measurement of the 400 MHz NMR were performed at the Analytical Center, Okayama University of Science. The authors are also indebted to MAC Science Co. for the X-ray analysis of compound **3e**.

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20) Tables of coordinates for the hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, and complete $F_o - F_c$ data are deposited as Document No. 66029 at the Office of the Editor of Bull. Chem. Soc. Jpn.