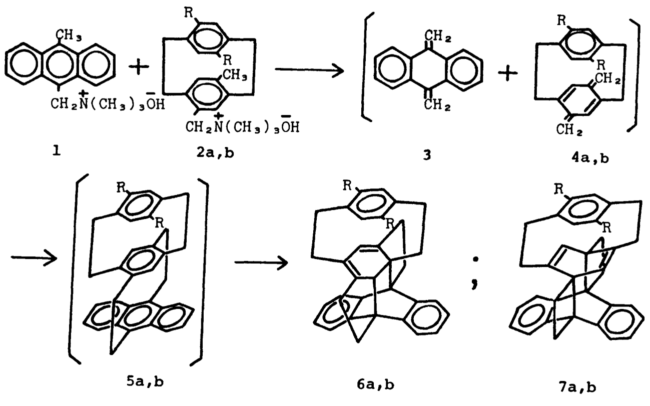
# Layered Compounds. XXXIV.[1] Molecular and Crystal Structure of a Polycyclic Compound from Novel Cycloaddition Reaction of Triple-layered Anthracenophane

Toshihiro Toyoda, Akio Iwama, Tetsuo Otsubo, and Soichi Misumi*
*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565*

(Received May 15, 1976)

An unusual Diels-Alder reaction was observed to give intramolecular cycloadducts during the syntheses of triple-layered cyclophanes containing anthracene nucleus. The structure of the product was determined by spectral and X-ray crystal analyses. The crystal is monoclinic, $P2_1/c$, with $a=15.896$, $b=8.937$, $c=18.575$ Å, $\beta=120.31°$, $Z=4$. The crystal structure was determined by the direct method using the MULTAN program and refined by the block-diagonal least-squares method to an $R$ index of 0.081. The structure of the molecule is fairly strained.

Layered cyclophanes in which benzene rings are closely fixed face-to-face by methylene bridges have been studied as suitable models for examining transannular $\pi$-electron interactions.[2] Reports appeared on the double-layered compounds containing anthracene nuclei as carbophanes of extended aromatic $\pi$-system, and their anomalous physical and chemical behaviors.[3] In order to study further the transannular $\pi$-electron interaction anthracenophanes, we have undertaken the syntheses of triple-layered compounds (**5**) containing anthracene nucleus. In this paper we report on an unusual reaction which takes place to give cycloadducts (**6**) in place of the desired anthracenophanes. The structures of the products were determined by spectroscopic and X-ray crystallographic analyses.



a: R = H, b: R = CH₃

Scheme 1.

*Syntheses and Properties.* A quaternary ammonium hydroxide (**1**) was obtained by treatment of 9-chloromethyl-10-methylanthracene[4] with trimethylamine in ether followed by anion exchange with a resin IRA-400. Pyrolysis of an equimolar mixture of the ammonium hydroxide (**1**) and (7-methyl-4-[2.2]-paracyclophanylmethyl)trimethylammonium hydroxide (**2a**)[5] was carried out in boiling xylene in the presence of a catalytic amount of phenothiazine. After removal of water by azeotropic distillation, and separation of solid material by filtration, the reaction mixture was chromatographed twice on alumina to afford pure colorless product in 7.8% yield along with quadruple-layered cyclophanes[5] derived by self-coupling of an intermediate quinodimethane derivative **4a**. The recrystallized product showed a molecular formula $C_{34}H_{30}$ coinciding with the structure **5a** from elemental analysis, mass spectrum, and osmometric molecular weight determination. However, its electronic spectrum shows only a tailing absorption in a wavelength region longer than 350 nm, indicating the absence of anthracene nucleus (Fig. 1). Its PMR spectrum reveals an olefinic proton at $\delta$ 4.36 and an increase of aliphatic protons at the expense of two aromatic protons as compared with the proton ratio expected from formula **5a** (Table 1). The spectral data indicate that the intermediate **5a** undergoes a certain intramolecular reaction to give a structural isomer.

Two structures (**6a** and **7a**) are possible for the product on the basis of spectral data and examination with molecular models. Structure **6a** is regarded as a $(4\pi+2\pi)$ cycloadduct of the anthracene and the inner benzene moieties of **5a**, and structure **7a** as a $(4\pi+4\pi)$ one. The PMR data (Table 1) is not consistent with **7a** having $C_2$ symmetry. Consequently, the remaining **6a** is presumed as the structure of intramolecular cycloadduct. Similarly, the product $C_{36}H_{34}$ which was obtained by cross-breeding pyrolysis of a mixture of **1** and **2b** shows spectra consistent with **6b** (Fig. 1 and

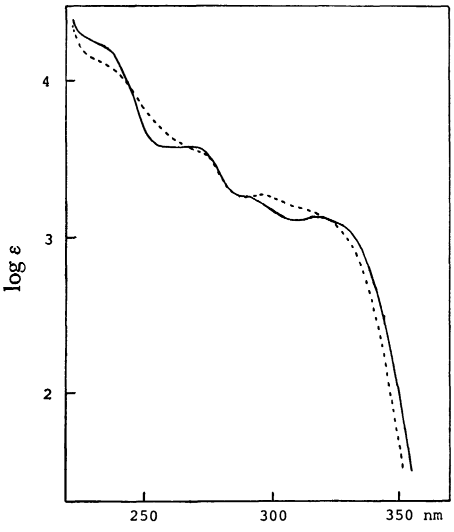


Fig. 1. Electronic spectra of the compounds **6a** (——) and **6b** (----) in tetrahydrofuran.

Table 1. PMR spectra of pyrolysis products

| **$1+2a$** $\rightarrow$ $C_{34}H_{30}$ | | | **$1+2b$** $\rightarrow$ $C_{36}H_{34}$ | | |
|---|---|---|---|---|---|
| Chemical shift ppm | Number of protons | | Chemical shift ppm | Number of protons | |
| 1.0—3.0 (m) | 17 | $CH_2$, CH | 0.9—3.3 (m) | 23 | $CH_3$, $CH_2$, CH |
| 4.36 (bs) | 1 | =CH | 4.52 (bs) | 1 | =CH |
| 6.7—7.4 (m) | 12 | ArH | 6.42 ( s ) | 1 | ArH |
| | | | 6.55 ( s ) | 1 | ArH |
| | | | 6.7—7.2 (m) | 8 | ArH |

Table 1). Two singlets at $\delta$ 6.42 and 6.55 on its PMR spectrum are assigned to the aromatic protons of paracyclophane moiety. A considerable high-field shift of the protons as compared to the corresponding ones of **6a** is attributed to the enhanced ortho shift $\sigma_{OE}$.[6]

Attempts to prepare the triple-layered anthracenophane **5** by retro-Diels-Alder reaction of **6** under various thermal and photochemical conditions were unsuccessful.

## Experimental

*Physical Methods.* Melting points are uncorrected. PMR spectra were taken on Hitachi Perkin-Elmer R-20 (60 MHz) and JEOL JNM-TS-100 (100 MHz) spectrometers on dilute solution in deuteriochloroform using tetramethylsilane as an internal standard. UV spectra were measured on Hitachi EPS-3T spectrometer, MS on Hitachi RMU-7 spectrometer, and molecular weights on Knauer vapor pressure osmometer using methylene chloride.

*(9-Methyl-10-anthrylmethyl)trimethylammonium Chloride.* An excess of trimethylamine (4 g) in ether (50 ml) was added with stirring to a solution of 9-chloromethyl-10-methylanthracene (6.5 g, 27 mmol), obtained by chloromethylation of 9-methylanthracene,[4] in benzene (800 ml) at room temp. After prolonged stirring, the resulting yellow ppt was filtered, washed with benzene and dried *in vacuo*. The yield of quaternary ammonium chloride was 7.3 g (90%).

*Cross-breeding Pyrolysis of Ammonium Bases, **1** and **2**. Compound **6a**.* An aq solution (1.5 l) of equimolar mixture of (9-methyl-10-anthrylmethyl)trimethylammonium chloride (4.0 g, 13.3 mmol) and (7-methyl-4-[2.2]paracyclophanylmethyl)trimethylammonium bromide[5] (4.6 g, 13.3 mmol) was passed through a column of anion exchange resin IRA-400 to give aq solution of two ammonium bases, **1** and **2a**. The aq soln was added dropwise for 15 h to a boiling solution of phenothiazine (100 mg) in xylene (200 ml) placed in a three-necked, pear-shaped flask fitted with a mechanical stirrer and a Dean-Stark type water separator. After complete removal of water, insoluble solid was filtered and the filtrate was condensed to *ca.* 5 ml *in vacuo*. Precipitated solid was filtered and the filtrate was chromatographed on neutral alumina (Sumitomo KCG-30). Elution with benzene-hexane (1 : 9) gave 0.51 g (8.7% yield) of **6a**. Compound **6a** was recrystallized from benzene, colorless prisms, mp 238.0—240.5 °C with decomposition near 240 °C.

MS (*m/e*) 438 [M+], 334, 234, 204. Found: C, 92.98; H, 6.81%; mol wt 428 (vapor pressure osmometry). Calcd for $C_{34}H_{30}$: C, 93.12; H, 6.90%; mol wt 438.6.

*Compound **6b**.* Pyrolysis of two ammonium bases, **1** and **2b**, derived from an equimolar solution (1.5 l) of (9-methyl-10-anthrylmethyl)trimethylammonium chloride (3.35 g, 11.2 mmol) and (4,7,12-trimethyl-15-[2.2]paracyclophanylmethyl)trimethylammonium bromide[5] (5.0 g, 12.4 mmol), was carried out in the same manner as that for **6a** to afford a 1.5% yield (78 mg) of **6b**. Compound **6b** was recrystallized from benzene to give colorless prisms, mp 220—235 °C with decomposition over 180 °C.

MS (*m/e*) 466 [M+], 334, 262, 204, 132. Found: C, 92.65; H, 7.23%; mol wt 458 (vapor pressure osmometry). Calcd for $C_{36}H_{34}$: C, 92.66; H, 7.35%; mol wt 466.7.

## X-Ray Structure Determination

The crystal of compound **6a** crystallized in colorless prisms from benzene was used for the measurement of intensities. The space group was determined to be $P2_1/c$ from oscillation and Weissenberg photographs. The cell constant was determined by the least-squares method (Sakurai, 1967)[7] based on the Bragg angles of 30 reflections. The density was measured by floatation in aq zinc bromide at room temperature.

*Crystal Data.* $C_{34}H_{30}$ MW=438.61; monoclinic, space group $P2_1/c$, $a=15.896(3)$, $b=8.937(2)$, $c=18.575(3)$ Å, $\beta=120.31$ °(1), $V=2278.0(6)$ Å[3], Mo $K\alpha$ radiation $\lambda=0.71069$ Å, $D_m=1.275$ g/cm³, $Z=8$, $D_x=1.279$ g/cm³.

Systematic absences $h0l$ when $l$ is odd
$0k0$ when $k$ is odd

Three-dimensional intensity data were collected on a Rigakudenki automatic four-circle diffractometer with Mo $K\alpha$ radiation. The crystal selected for the data collection was 0.33×0.17×0.20 mm in size. The relative intensities were measured with the $\theta$-$2\theta$ scan technique (scan speed 2 °/min($2\theta$)) in a range from $\{2\theta(\alpha_1)-1.0°\}$ to $\{2\theta(\alpha_2)+1.0°\}$. During the course of data collection, the three standard reflections were monitored at every 50 reflections in order to examine the stability of the electronics and the crystal. A total of 5669 independent reflections were measured in the range $0<\sin\theta/\lambda<0.7$, of which 3054 were recorded as observed. The intensities were corrected for Lorentz and polarization factors, but not for absorption. Background intensities were measured for ten seconds at both ends of a scan.

*Structure Refinement.* The structure was determined by the direct method using the MULTAN program[8] with 494 reflections having E's>1.5. The sets of phases selected by the program were:

| $h$ | $k$ | $l$ | Phase | |
|---|---|---|---|---|
| 4 | 1 | $\bar{1}$ | 0 | origin fixing |
| 4 | 1 | $\bar{2}$ | 0 | |
| 5 | 4 | $\overline{23}$ | 0 | |

TABLE 2. ATOMIC FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) OF THE CARBON ATOMS

Anisotropic thermal parameters are expressed in the form of $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.
The estimated standard deviation, given in parentheses, refers to the last significant figure.

| Atom | x/a | y/b | z/c | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 3002(3) | 7648(5) | 3835(2) | 58(2) | 127(6) | 29(1) | −33(6) | 39(3) | 15(5) |
| C(2) | 4135(3) | 7673(5) | 4388(3) | 56(2) | 122(6) | 44(2) | −41(6) | 67(4) | −16(6) |
| C(3) | 4485(3) | 7996(4) | 5296(2) | 41(2) | 106(6) | 44(2) | −37(5) | 54(3) | −5(5) |
| C(4) | 4176(3) | 9253(5) | 5525(3) | 49(2) | 108(6) | 43(2) | −33(6) | 38(3) | −12(5) |
| C(5) | 4159(3) | 9277(5) | 6267(3) | 49(2) | 122(6) | 42(2) | −35(6) | 39(3) | −52(6) |
| C(6) | 4471(3) | 8054(5) | 6793(2) | 47(2) | 147(7) | 29(1) | −62(6) | 29(3) | −35(5) |
| C(7) | 5002(3) | 6966(5) | 6660(2) | 36(2) | 152(7) | 34(2) | −28(6) | 13(3) | 6(6) |
| C(8) | 5003(2) | 6932(5) | 5913(3) | 29(2) | 134(6) | 47(2) | −6(5) | 36(3) | −6(6) |
| C(9) | 3991(3) | 7687(6) | 7298(3) | 61(3) | 225(9) | 33(2) | −88(8) | 46(4) | −52(7) |
| C(10) | 3126(3) | 6555(6) | 6787(2) | 64(3) | 249(10) | 32(2) | −120(8) | 57(4) | −61(7) |
| C(11) | 2795(2) | 6489(5) | 5864(2) | 36(2) | 169(7) | 26(1) | −66(6) | 34(3) | −32(5) |
| C(12) | 2184(3) | 7713(5) | 5307(2) | 39(2) | 133(6) | 42(2) | −18(6) | 43(3) | −53(6) |
| C(13) | 1971(2) | 7857(4) | 4519(2) | 38(2) | 95(5) | 39(2) | 20(5) | 28(3) | −6(5) |
| C(14) | 2380(2) | 6793(4) | 4145(2) | 32(2) | 92(5) | 24(1) | 1(5) | 21(2) | 8(4) |
| C(15) | 2877(2) | 5436(4) | 4671(2) | 30(2) | 77(4) | 26(1) | 6(4) | 28(2) | 11(4) |
| C(16) | 3034(2) | 5366(4) | 5528(2) | 32(2) | 133(6) | 24(1) | −41(5) | 19(2) | 5(5) |
| C(17) | 3369(3) | 3767(5) | 5809(2) | 64(3) | 150(7) | 31(2) | −7(7) | 21(3) | 41(6) |
| C(18) | 3004(3) | 2860(5) | 4974(3) | 56(2) | 98(6) | 46(2) | 14(6) | 42(4) | 33(6) |
| C(19) | 2325(2) | 3931(4) | 4284(2) | 34(2) | 86(5) | 36(2) | −15(5) | 39(3) | −9(5) |
| C(20) | 2155(2) | 3882(4) | 3400(2) | 37(2) | 112(6) | 36(2) | −25(5) | 44(3) | −27(5) |
| C(21) | 2492(3) | 2777(5) | 3078(3) | 56(2) | 144(7) | 60(3) | −44(7) | 79(4) | −61(7) |
| C(22) | 2295(3) | 2900(6) | 2262(3) | 78(3) | 214(9) | 64(3) | −96(9) | 106(5) | −114(8) |
| C(23) | 1773(4) | 4092(6) | 1778(3) | 95(4) | 252(10) | 43(2) | −123(10) | 96(5) | −82(8) |
| C(24) | 1439(3) | 5214(6) | 2091(3) | 69(3) | 182(8) | 31(2) | −70(8) | 44(4) | −21(6) |
| C(25) | 1632(3) | 5118(4) | 2909(2) | 44(2) | 107(5) | 28(1) | −19(5) | 36(3) | −20(5) |
| C(26) | 1369(2) | 6258(4) | 3366(2) | 37(2) | 115(6) | 26(1) | 15(5) | 18(3) | 2(5) |
| C(27) | 830(2) | 5367(5) | 3709(2) | 35(2) | 133(6) | 32(2) | −19(5) | 30(3) | −53(5) |
| C(28) | −102(3) | 5679(6) | 3563(3) | 36(2) | 199(8) | 54(2) | −1(7) | 32(4) | −91(7) |
| C(29) | −524(3) | 4750(7) | 3888(3) | 48(2) | 296(11) | 68(3) | −100(9) | 78(4) | −167(9) |
| C(30) | −36(3) | 3531(6) | 4352(3) | 75(3) | 277(11) | 53(2) | −177(9) | 96(5) | −136(8) |
| C(31) | 908(3) | 3192(6) | 4514(3) | 71(3) | 190(8) | 43(2) | −103(8) | 73(4) | −52(7) |
| C(32) | 1325(2) | 4122(4) | 4183(2) | 38(2) | 121(6) | 28(1) | −41(5) | 36(3) | −34(5) |
| C(33) | 897(3) | 7780(5) | 2999(3) | 57(3) | 127(7) | 39(2) | 42(7) | 5(3) | 21(6) |
| C(34) | 1162(3) | 8753(5) | 3790(3) | 54(2) | 120(6) | 48(2) | 59(6) | 12(4) | −7(6) |

TABLE 3. ATOMIC FRACTIONAL COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS (in Å$^2$) OF THE HYDROGEN ATOMS

The numbering follows that of the carbon atoms to which the hydrogens are attached.

| Atom | x/a | y/b | z/c | *B* | Atom | x/a | y/b | z/c | *B* |
|---|---|---|---|---|---|---|---|---|---|
| H(1A) | 284(3) | 724(5) | 330(3) | 4(1) | H(1B) | 276(3) | 874(5) | 371(3) | 4(1) |
| H(2A) | 437(3) | 664(5) | 432(3) | 4(1) | H(2B) | 433(3) | 862(5) | 414(3) | 4(1) |
| H(4) | 378(3) | 999(5) | 506(3) | 4(1) | H(5) | 378(3) | 1009(5) | 634(3) | 4(1) |
| H(7) | 528(3) | 602(5) | 705(3) | 4(1) | H(8) | 528(3) | 603(5) | 578(3) | 4(1) |
| H(9A) | 443(3) | 721(6) | 781(3) | 5(1) | H(9B) | 367(3) | 867(6) | 737(3) | 5(1) |
| H(10A) | 335(3) | 553(5) | 704(3) | 4(1) | H(10B) | 259(3) | 681(5) | 687(3) | 4(1) |
| H(12) | 189(3) | 837(5) | 552(3) | 4(1) | H(15) | 352(3) | 531(5) | 471(2) | 3(1) |
| H(17A) | 409(3) | 370(5) | 621(3) | 4(1) | H(17B) | 305(3) | 343(5) | 611(3) | 4(1) |
| H(18A) | 358(3) | 261(5) | 490(3) | 4(1) | H(18B) | 272(3) | 184(5) | 498(3) | 4(1) |
| H(21) | 284(3) | 188(5) | 343(3) | 4(1) | H(22) | 251(3) | 199(6) | 199(3) | 5(1) |
| H(23) | 163(3) | 422(6) | 119(3) | 5(1) | H(24) | 105(3) | 605(5) | 177(3) | 5(1) |
| H(28) | −45(3) | 649(5) | 325(3) | 5(1) | H(29) | −121(3) | 498(6) | 377(3) | 5(1) |
| H(30) | −26(3) | 281(5) | 461(3) | 5(1) | H(31) | 119(3) | 229(5) | 479(3) | 5(1) |
| H(33A) | 120(3) | 830(6) | 265(3) | 5(1) | H(33B) | 16(3) | 765(6) | 264(3) | 5(1) |
| H(34A) | 146(3) | 981(6) | 378(3) | 5(1) | H(34B) | 63(3) | 887(6) | 393(3) | 5(1) |

| | | | | |
|---|---|---|---|---|
| 8 | 2 | $\bar{2}$ | 0 | by $\sum_1$ formula |
| 2 | 2 | $\bar{8}$ | 0 | |
| 12 | 1 | $\overline{15}$ | 0, $\pi$ | |
| 12 | 4 | $\bar{2}$ | 0, $\pi$ | |
| 1 | 5 | $\overline{12}$ | 0, $\pi$ | |
| 1 | 8 | $\bar{1}$ | 0, $\pi$ | |

Of the 16 possible solutions, one set of phases (12,1,$\overline{15}$ and 1,5,$\overline{12}=0$;12,4,$\bar{2}$ and 18$\bar{1}=\pi$) giving the figure of merit of 1.23 seemed to be correct. An E map generated from this set of phases gave starting positions for all carbon atoms which gave an initial $R$=0.27. After refinement with the block-diagonal least-squares method ($R$=0.17), a difference synthesis revealed the positions of all the hydrogen atoms. The refinement with isotropic thermal parameters for all the atoms, followed by further cycles of refinement using the block-diagonal least-squares method[9] with carbon atoms anisotropic and hydrogen atoms isotropic temperature factors, yielded the final residual $R$ of 0.081. The final atomic coordinates, thermal parameters, and the corresponding standard deviations are listed in Tables 2 and 3.* Computation was done on a NEAC 2200-700 computer at Osaka University. Atomic scattering factors were taken from those of Suzuki.[10]

## Results and Discussion

The molecular geometry is shown in Fig. 2. The structure obtained is in complete agreement with that of **6a** determined by spectroscopy. For the dimethyl derivative $C_{36}H_{34}$, structure **6b** can be assigned on the basis of the fact that it shows electronic and PMR spectra similar to those of **6a** and that the cell constant and the reflection pattern of the crystal of **6b** (space group $P2_1/c$) closely resemble those of **6a**.

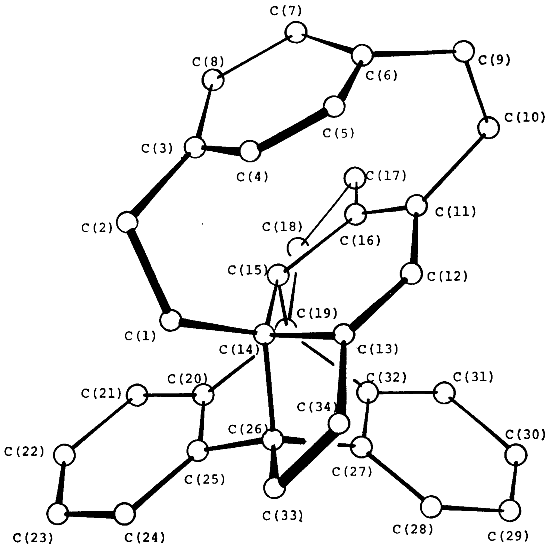


Fig. 2. Projection of the molecular structure along the b-axis.

The bond distances and angles for the molecule of **6a** are given in Tables 4 and 5 with their estimated standard deviations. The C–C bond lengths of the benzene ring, C(3)—C(8), are normal. On the other hand, the two aromatic C–C bonds, C(22)–C(23) and C(29)–C(30), are slightly shorter, which is probably attributable to intermolecular repulsions and/or the inaccuracy of the present crystal analysis.

In the cyclohexadiene moiety C(11)—C(16), the bond lengths of the double bonds, C(11)–C(16) and C(12)–C(13), and the single bond C(11)–C(12) are normal as compared to the common butadiene system (C=C 1.31—1.34 Å and C–C 1.37—1.53 Å), whereas the single bonds, C(14)–C(15) and C(15)–C(16), are appreciably shorter than the normal values (C–C 1.54 Å and C–C= 1.51 Å). As shown in Fig. 3 and Table 6, the marked steric compressions of C(15) and H(15) by benzene C(3)—C(8) and the bridged methylene, C(2) and C(18), are responsible for the shortening of these two single bonds. Other two single bonds,

Table 4. Bond lengths and their estimated standard deviations

| | | | |
|---|---|---|---|
| C(1)---C(2) | 1.562(6) | C(1)---C(14) | 1.571(6) |
| C(2)---C(3) | 1.513(6) | C(3)---C(4) | 1.375(7) |
| C(3)---C(8) | 1.393(6) | C(4)---C(5) | 1.392(7) |
| C(5)---C(6) | 1.381(6) | C(6)---C(7) | 1.389(6) |
| C(6)---C(9) | 1.515(7) | C(7)---C(8) | 1.388(6) |
| C(9)---C(10) | 1.581(7) | C(10)---C(11) | 1.519(7) |
| C(11)---C(12) | 1.482(6) | C(11)---C(16) | 1.335(6) |
| C(12)---C(13) | 1.332(6) | C(13)---C(14) | 1.504(6) |
| C(13)---C(34) | 1.539(7) | C(14)---C(15) | 1.506(5) |
| C(14)---C(26) | 1.600(5) | C(15)---C(16) | 1.484(5) |
| C(15)---C(19) | 1.567(5) | C(16)---C(17) | 1.523(6) |
| C(17)---C(18) | 1.579(7) | C(18)---C(19) | 1.527(6) |
| C(19)---C(20) | 1.523(6) | C(19)---C(32) | 1.513(6) |
| C(20)---C(21) | 1.394(7) | C(20)---C(25) | 1.406(6) |
| C(21)---C(22) | 1.389(8) | C(22)---C(23) | 1.369(8) |
| C(23)---C(24) | 1.393(8) | C(24)---C(25) | 1.394(6) |
| C(25)---C(26) | 1.512(6) | C(26)---C(27) | 1.526(6) |
| C(26)---C(33) | 1.538(6) | C(27)---C(28) | 1.393(7) |
| C(27)---C(32) | 1.390(6) | C(28)---C(29) | 1.381(8) |
| C(29)---C(30) | 1.362(8) | C(30)---C(31) | 1.409(7) |
| C(31)---C(32) | 1.387(6) | C(33)---C(34) | 1.527(6) |
| C(1)---H(1A) | 0.97(5) | C(1)---H(1B) | 1.03(5) |
| C(2)---H(2A) | 1.03(5) | C(2)---H(2B) | 1.00(5) |
| C(4)---H(4) | 1.01(5) | C(5)---H(5) | 0.99(5) |
| C(7)---H(7) | 1.06(5) | C(8)---H(8) | 1.01(5) |
| C(9)---H(9A) | 0.95(5) | C(9)---H(9B) | 1.05(5) |
| C(10)---H(10A) | 1.01(5) | C(10)---H(10B) | 0.97(5) |
| C(12)---H(12) | 0.96(5) | C(15)---H(15) | 0.99(4) |
| C(17)---H(17A) | 1.00(5) | C(17)---H(17B) | 0.97(5) |
| C(18)---H(18A) | 1.01(5) | C(18)---H(18B) | 1.02(5) |
| C(21)---H(21) | 1.00(5) | C(22)---H(22) | 1.10(5) |
| C(23)---H(23) | 1.00(5) | C(24)---H(24) | 0.96(5) |
| C(28)---H(28) | 0.92(5) | C(29)---H(29) | 1.02(5) |
| C(30)---H(30) | 0.97(5) | C(31)---H(31) | 0.94(5) |
| C(33)---H(33A) | 1.08(5) | C(33)---H(33B) | 1.03(5) |
| C(34)---H(34A) | 1.06(5) | C(34)---H(34B) | 1.01(5) |

---

* A list of structure factors has been deposited with the Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo 101 (Document No. 7630).

Table 5. Bond angles and their estimated standard deviations

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(14) | 119.7(4) | C(1)-C(2)-C(3) | 112.9(4) |
| C(2)-C(3)-C(4) | 120.9(4) | C(2)-C(3)-C(8) | 121.1(4) |
| C(4)-C(3)-C(8) | 117.3(4) | C(3)-C(4)-C(5) | 120.5(4) |
| C(4)-C(5)-C(6) | 120.6(4) | C(5)-C(6)-C(7) | 117.5(4) |
| C(5)-C(6)-C(9) | 119.7(4) | C(7)-C(6)-C(9) | 120.1(4) |
| C(6)-C(7)-C(8) | 120.0(4) | C(3)-C(8)-C(7) | 120.6(4) |
| C(6)-C(9)-C(10) | 108.9(4) | C(9)-C(10)-C(11) | 113.8(4) |
| C(10)-C(11)-C(12) | 119.5(4) | C(10)-C(11)-C(16) | 122.6(4) |
| C(12)-C(11)-C(16) | 117.9(4) | C(11)-C(12)-C(13) | 123.6(4) |
| C(12)-C(13)-C(14) | 121.1(4) | C(12)-C(13)-C(34) | 130.7(4) |
| C(14)-C(13)-C(34) | 106.7(4) | C(1)-C(14)-C(13) | 111.1(3) |
| C(1)-C(14)-C(15) | 114.1(3) | C(1)-C(14)-C(26) | 110.1(3) |
| C(13)-C(14)-C(15) | 114.7(3) | C(13)-C(14)-C(26) | 97.9(3) |
| C(15)-C(14)-C(26) | 107.7(3) | C(14)-C(15)-C(16) | 118.5(3) |
| C(14)-C(15)-C(19) | 113.9(3) | C(16)-C(15)-C(19) | 102.0(3) |
| C(11)-C(16)-C(15) | 122.6(4) | C(11)-C(16)-C(17) | 132.7(4) |
| C(15)-C(16)-C(17) | 104.3(3) | C(16)-C(17)-C(18) | 104.7(4) |
| C(17)-C(18)-C(19) | 104.8(4) | C(15)-C(19)-C(18) | 99.1(3) |
| C(15)-C(19)-C(20) | 105.8(3) | C(15)-C(19)-C(32) | 105.7(3) |
| C(18)-C(19)-C(20) | 123.6(4) | C(18)-C(19)-C(32) | 115.4(4) |
| C(20)-C(19)-C(32) | 105.4(3) | C(19)-C(20)-C(21) | 125.8(4) |
| C(19)-C(20)-C(25) | 113.6(4) | C(21)-C(20)-C(25) | 120.5(4) |
| C(20)-C(21)-C(22) | 119.2(5) | C(21)-C(22)-C(23) | 120.5(5) |
| C(22)-C(23)-C(24) | 121.2(5) | C(23)-C(24)-C(25) | 119.4(5) |
| C(20)-C(25)-C(24) | 119.2(4) | C(20)-C(25)-C(26) | 114.0(3) |
| C(24)-C(25)-C(26) | 126.7(4) | C(14)-C(26)-C(25) | 105.9(3) |
| C(14)-C(26)-C(27) | 107.3(3) | C(14)-C(26)-C(33) | 100.3(3) |
| C(25)-C(26)-C(27) | 104.8(3) | C(25)-C(26)-C(33) | 124.0(4) |
| C(27)-C(26)-C(33) | 113.3(3) | C(26)-C(27)-C(28) | 125.6(4) |
| C(26)-C(27)-C(32) | 115.1(4) | C(28)-C(27)-C(32) | 119.4(4) |
| C(27)-C(28)-C(29) | 119.9(5) | C(28)-C(29)-C(30) | 120.7(5) |
| C(29)-C(30)-C(31) | 120.8(5) | C(30)-C(31)-C(32) | 118.2(5) |
| C(19)-C(32)-C(27) | 113.2(3) | C(19)-C(32)-C(31) | 125.8(4) |
| C(27)-C(32)-C(31) | 121.1(4) | C(26)-C(33)-C(34) | 103.5(4) |
| C(13)-C(34)-C(33) | 104.2(4) | | |
| C(14)-C(1)-H(1A) | 107.8(28) | C(14)-C(1)-H(1B) | 108.1(27) |
| C(2)-C(1)-H(1A) | 107.0(28) | C(2)-C(1)-H(1B) | 107.9(27) |
| C(1)-C(2)-H(2A) | 106.4(27) | C(1)-C(2)-H(2B) | 102.2(28) |
| C(3)-C(2)-H(2A) | 110.8(27) | C(3)-C(2)-H(2B) | 110.0(28) |
| C(6)-C(9)-H(9A) | 111.4(32) | C(6)-C(9)-H(9B) | 109.2(30) |
| C(10)-C(9)-H(9A) | 106.5(32) | C(10)-C(9)-H(9B) | 106.4(30) |
| C(9)-C(10)-H(10A) | 108.0(29) | C(9)-C(10)-H(10B) | 108.0(30) |
| C(11)-C(10)-H(10A) | 108.6(29) | C(11)-C(10)-H(10B) | 110.6(30) |
| C(16)-C(17)-H(17A) | 112.5(29) | C(16)-C(17)-H(17B) | 106.5(30) |
| C(18)-C(17)-H(17A) | 114.0(29) | C(18)-C(17)-H(17B) | 111.5(30) |
| C(17)-C(18)-H(18A) | 109.7(28) | C(17)-C(18)-H(18B) | 113.2(28) |
| C(19)-C(18)-H(18A) | 108.8(28) | C(19)-C(18)-H(18B) | 116.0(28) |
| C(26)-C(33)-H(33A) | 112.1(28) | C(26)-C(33)-H(33B) | 109.4(30) |
| C(34)-C(33)-H(33A) | 109.2(28) | C(34)-C(33)-H(33B) | 109.9(30) |
| C(33)-C(34)-H(34A) | 112.9(29) | C(33)-C(34)-H(34B) | 115.6(31) |
| C(13)-C(34)-H(34A) | 106.9(29) | C(13)-C(34)-H(34B) | 104.7(31) |
| C(16)-C(15)-H(15) | 107.8(25) | C(19)-C(15)-H(15) | 104.5(25) |
| C(14)-C(15)-H(15) | 109.1(25) | C(3)-C(4)-H(4) | 115.7(27) |
| C(5)-C(4)-H(4) | 121.3(27) | C(4)-C(5)-H(5) | 117.2(28) |
| C(6)-C(5)-H(5) | 120.7(28) | C(6)-C(7)-H(7) | 121.6(26) |
| C(8)-C(7)-H(7) | 117.1(26) | C(7)-C(8)-H(8) | 119.1(27) |
| C(3)-C(8)-H(8) | 119.4(27) | C(11)-C(12)-H(12) | 116.4(29) |
| C(13)-C(12)-H(12) | 119.8(29) | C(20)-C(21)-H(21) | 119.0(29) |

Table 5. (Continued)

| | | | |
|---|---|---|---|
| C(22)-C(21)-H(21) | 121.7(29) | C(21)-C(22)-H(22) | 118.9(28) |
| C(23)-C(22)-H(22) | 120.5(28) | C(22)-C(23)-H(23) | 122.6(31) |
| C(24)-C(23)-H(23) | 116.2(31) | C(23)-C(24)-H(24) | 124.1(32) |
| C(25)-C(24)-H(24) | 116.4(31) | C(27)-C(28)-H(28) | 120.8(33) |
| C(29)-C(28)-H(28) | 119.3(33) | C(28)-C(29)-H(29) | 119.3(30) |
| C(30)-C(29)-H(29) | 120.0(30) | C(29)-C(30)-H(30) | 128.3(30) |
| C(31)-C(30)-H(30) | 110.9(30) | C(30)-C(31)-H(31) | 117.9(31) |
| C(32)-C(31)-H(31) | 123.5(31) | | |
| H(1A)-C(1)-H(1B) | 105.5(39) | H(2A)-C(2)-H(2B) | 114.3(39) |
| H(9A)-C(9)-H(9B) | 114.2(44) | H(10A)-C(10)-H(10B) | 107.8(42) |
| H(17A)-C(17)-H(17B) | 107.4(42) | H(18A)-C(18)-H(18B) | 104.3(39) |
| H(33A)-C(33)-H(33B) | 112.3(41) | H(34A)-C(34)-H(34B) | 111.5(42) |

Table 6. Some intramolecular nonbonding distances around C(15) and H(15) with e.s.d.'s

| | | | |
|---|---|---|---|
| C(15)...C(2) | 3.055(6) | H(15)...C(2) | 2.53(4) |
| C(15)...C(3) | 3.182(6) | H(15)...C(3) | 2.77(4) |
| C(15)...C(8) | 3.266(6) | H(15)...C(8) | 2.71(4) |
| C(15)...H(18A) | 2.70(5) | H(15)...H(18A) | 2.42(7) |

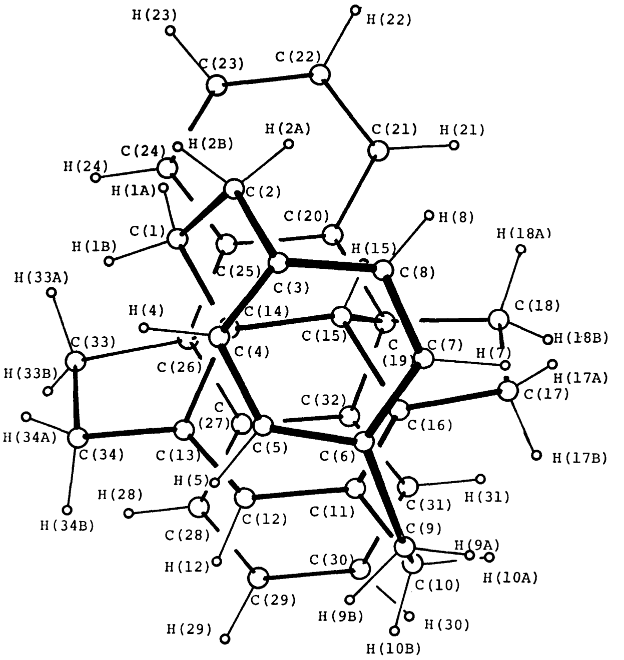


Fig. 3. A view of the molecule along the normal to the plane defined by four carbon atoms, C(20), C(25), C(27), and C(32).

Table 7. Some intramolecular nonbonding distances around C(1) and between cyclohexadiene C(11)—C(16) and two benzene rings, C(20)—C(25) and C(27)—C(32), with e.s.d.'s

| | | | |
|---|---|---|---|
| C(1)...C(3) | 2.563(6) | C(12)...C(27) | 3.375(6) |
| C(1)...C(13) | 2.536(6) | C(13)...C(27) | 2.785(6) |
| C(1)...C(15) | 2.582(6) | C(14)...C(20) | 2.883(6) |
| C(1)...C(25) | 3.005(6) | C(14)...C(25) | 2.484(5) |
| C(1)...C(26) | 2.598(6) | C(14)...C(27) | 2.517(5) |
| C(1)...C(33) | 2.894(6) | C(14)...C(32) | 2.938(5) |
| C(1)...C(34) | 3.047(7) | C(15)...C(20) | 2.465(6) |
| | | C(15)...C(25) | 2.856(5) |
| | | C(15)...C(27) | 2.813(5) |
| | | C(15)...C(32) | 2.455(5) |
| | | C(16)...C(32) | 2.829(6) |

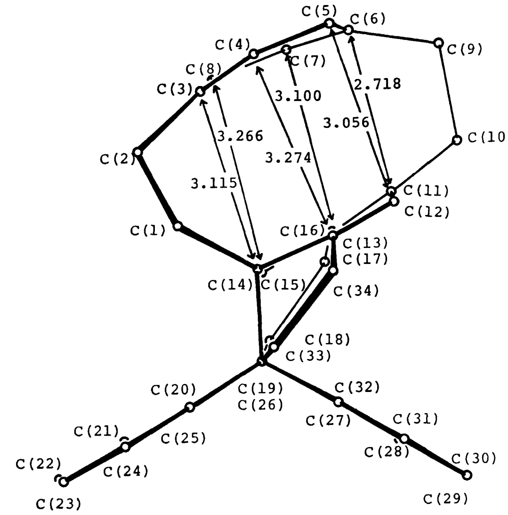


Fig. 4. A view of the molecule along the bond C(19)-C(26).

C(14)-C(26) and C(15)-C(19), formed by the intramolecular Diels-Alder reaction are considerably elongated to 1.600 and 1.567 Å, respectively, from the normal value. This may be caused by the steric repulsions acting on methylene C(1) and the cyclohexadiene moiety C(11)—C(16) from the dihydroanthracene moiety C(19)—C(32) (Table 7). As shown in Fig. 4, the cyclohexadiene moiety has a nearly planar structure in spite of a severe overlapping of the $\pi$-electron cloud with that of the benzene ring C(3)—C(8). Intramolecular nonbonding distances are given in Table 8. Such unexpected planarity of the cyclohexadiene moiety can be explained by a compensation of the repulsions acting on both upper and lower sides of the diene moiety. An unsymmetrical boat-shape deformation of the para-substituted benzene ring C(3)—C(8) is observed (Fig. 5), which may result from the $\pi$-electron repulsion between the benzene ring and the diene moiety (Table 8). The repulsion would also affect the bond lengths of the

Table 8. Intramolecular nonbonding distances between benzene ring C(3)—C(8) and cyclohexadiene ring C(11)—C(16) with e.s.d.'s

| | | | |
|---|---|---|---|
| C(3)...C(14) | 3.115(6) | C(6)...C(11) | 2.718(6) |
| C(3)...C(15) | 3.182(6) | C(6)...C(12) | 3.287(6) |
| C(4)...C(12) | 3.285(6) | C(6)...C(16) | 3.331(6) |
| C(4)...C(13) | 3.274(6) | C(7)...C(11) | 3.072(6) |
| C(5)...C(11) | 3.135(6) | C(7)...C(16) | 3.100(6) |
| C(5)...C(12) | 3.056(6) | C(8)...C(15) | 3.266(6) |
| | | C(8)...C(16) | 3.165(6) |

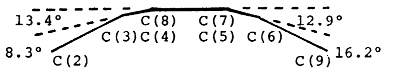


Fig. 5. The distortion angles of benzene.

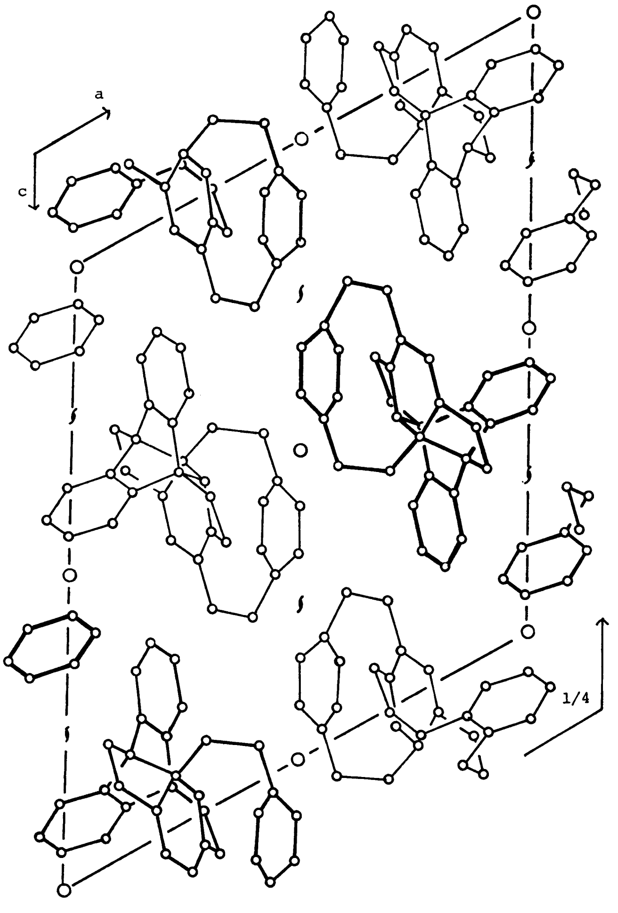


Fig. 6. Molecular arrangement in the crystal.

two bridged single bonds, C(1)–C(2) and C(9)–C(10), both of them, especially the latter, being longer than the normal C–C bond length.

The molecular arrangement in the crystal is shown in Fig. 6. Some intermolecular nonbonding distances are so short that will cause the strain of the molecule.

In conclusion, it is shown from spectral and X-ray crystal analyses that the unexpected cycloadducts **6** were formed in place of the desired triple-layered anthracenophane **5** by cross-breeding pyrolysis of the ammonium bases **1** and **2**. The formation of **6** is explainable by the intramolecular Diels-Alder addition of the inner benzene ring as a dienophile to the 9,10-positions of the anthracene moiety in the intermediate **5**. Recently, Korte and his co-workers[11] reported the first example of benzene and its derivatives being allowed to react as dienophile with hexachlorobutadiene under the high pressure of 10 kbar to afford 1:2 adducts. The unusual cycloaddition reaction of the intermediate **5** under ordinary conditions can be explained by the close fixing of the anthracene against the inner benzene moieties with short methylene bridges, and by the severe molecular strain of the intermediate as seen in the structures of triple-[12] and quadruple-layered cyclophanes.[13] In other words, strain releasing forces would act as a driving force for the unusual reaction.

The authors are greatly indebted to Professors M. Kakudo and N. Kasai of Osaka University for the X-ray crystallographic analysis. The research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

## References

1) Part XXXIII, M. Yoshida, H. Tatemitsu, Y. Sakata, S. Misumi, H. Masuhara, and N. Mataga, *J. Chem. Soc., Chem. Commun.*, **1976**, 587.

2) For reviews: D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971); F. Vögtle, *Chem.-Ztg.*, **95**, 668 (1971); S. Misumi, *Mem. Inst. Sci. & Ind. Res., Osaka Univ.*, **33**, 53 (1976).

3) J. H. Golden, *J. Chem. Soc.*, **1961**, 3741; T. Toyoda, I. Otsubo, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, **1972**, 1731; A. Iwama, T. Toyoda, T. Otsubo, and S. Misumi, *Chem. Lett.*, **1973**, 587; *Tetrahedron Lett.*, **1973**, 1725.

4) M. W. Miller, R. W. Amiden, and P. O. Tawney, *J. Am. Chem. Soc.*, **77**, 2845 (1955).

5) T. Otsubo, S. Mizogami, I. Otsubo, Z. Tozuka, A. Sakagami, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3519 (1973).

6) H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3534 (1969); T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3831 (1973).

7) "The Universal Crystallographic Computation Program System (I)," ed. by T. Sakurai, The Crystallographic Society of Japan, Tokyo (1967), p. 45.

8) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **A27**, 368 (1971).

9) T. Ashida, "The Universal Crystallographic Computing System-Osaka," the Computation Center, Osaka University (1973), p. 20.

10) T. Suzuki, *Nippon Butsuri Gakkai Shi*, **13**, 793 (1958).

11) W. Jarre, D. Bieniek, and F. Korte, *Angew. Chem.*, **87**, 201 (1975).

12) Y. Koizumi, T. Toyoda, H. Horita, and S. Misumi, The 32nd National Meeting of The Chemical Society of Japan, Abstr. Vol. I, p. 184, Tokyo, April 1975.

13) H. Mizuno, K. Nishiguchi, T. Toyoda, T. Otsubo, S. Misumi, and N. Morimoto, *Tetrahedron Lett.*, **1972**, 4981.