The Crystal and Molecular Structure of *syn*-[2.2](1,4)-Anthracenophane and Its Photoisomer

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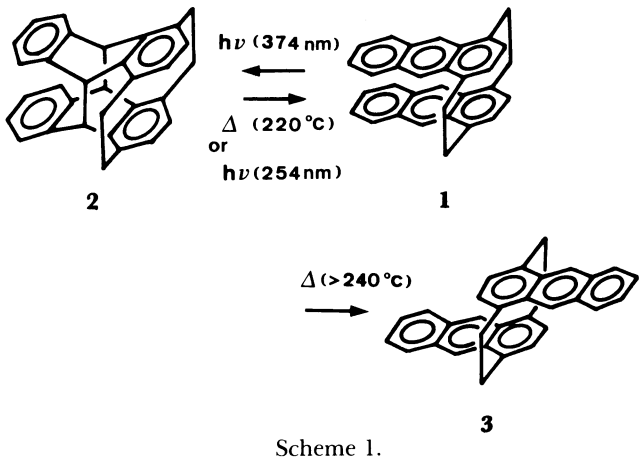
(Received March 18, 1985)

Molecular structure of *syn*-[2.2](1,4)anthracenophane (**1**) and its photoisomer (**2**) have been determined by means of X-ray diffraction; **1**, monoclinic, space group A2, a=25.539(2), b=8.152(1), c=20.561(3) Å, β=106.03(1)° (−149 °C), Z=8; **2**, monoclinic, space group $P2_1/c$, a=8.065(6), b=12.963(9), c=19.580(5) Å, β=91.46(5)°, Z=4. The structure of **1** was solved by the vector search method and **2** by the direct method. Both structures were refined including all hydrogen atoms by the block-diagonal least-squares procedure: R=0.053 and 0.043 for 4413 and 2003 observed reflections for **1** and **2**, respectively. Two anthracene nuclei, connected by ethylene bridges at the 1 and 4 positions, in each of the two independent molecules (A and B) of **1** are approximately parallel. However, their overlappings differ slightly. In the photoisomer **2** the two anthracene nuclei are bound by newly formed bonds at the 9 and 10 positions: bond distances are 1.628(5) and 1.637(5) Å whereas the corresponding nonbonded distance in **1** are 3.312(6) and 3.301(6) Å (A molecule) and 3.357(6) and 3.366(6) Å (B molecule).

Previously, the preparation of *syn*-[2.2](1,4)anthracenophane (**1**), its photoisomer (**2**), and *anti*-[2.2](1,4)-anthracenophane (**3**) by pyrolysis of ammonium base and interesting photochemical interconversion of **1** and **2** have been reported.[1]



Scheme 1.

Each of the anthracenophane isomers contains anthracene nuclei with ethylene bridges at their 1- and 4-carbon atoms. They are of special interest for studying transannular electronic interaction and steric effect. Spectral properties of these isomers have been studied. The *syn*-[2.2](1,4)anthracenophane, **1**, shows an excimer fluorescence spectrum, with shorter life time, in longer wavelength region than the other anthracenophane, *anti*-[2.2](1,4)anthracenophane, **3** and [2.2](1,4)-(9,10)anthracenophane, and anthracene excimer.[2] On the other hand, [2.2](9,10)anthracenophane gives no fluorescence spectrum. The comparison of these fluorescence spectra indicates distinctly that the nonbonded distance between the active sites, 9- and 10-positions, of two anthracene nuclei is the most important factor to solve a relationship between the excimer structure and fluorescence spectrum.

As the structure difference of the molecules before and after the photoisomerization is also of much interest, this paper deals with the X-ray crystal structure analysis of *syn*-[2.2](1,4)anthracenophane†† and its photoisomer.††† A brief account of the *syn*-anthracenophane structure[3] and a profile of both structures[4] have been reported.

Experimental

Crystal Data. (**1**) *syn*-Anthracenophane, $C_{32}H_{24}$, M=408.5, monoclinic, space group A2, a=25.344(5), b=8.1340(2), c=20.743(4) Å, β=104.80(15)°, V=4238.9(15) Å^3, D_m=1.29 g cm^{-3}, D_c=1.280 g cm^{-3} for Z=8 (room temperature); a=25.539(2), b=8.152(1), c=20.561(3) Å, β=106.03(1)°, V=4114.3(9) Å^3, D_c=1.319 g cm^{-3} for Z=8 (−149 °C). (**2**) Photoisomer, $C_{32}H_{24}$, M=408.5, monoclinic, space group $P2_1/c$, a=8.065(5), b=12.963(9), c=19.580(5) Å, β=91.46(5)°, V=2046.3(12) Å^3, D_m=1.32 g cm^{-3}, D_c=1.323 g cm^{-3} for Z=4 (room temperature).

Oscillation and Weissenberg photographs determined the possible space group for *syn*-anthracenophane as A2 (No. 5), Am (No. 8), or A2/m (No. 12) (absent reflections; hkl: $k+l=2n+1$) and that for photoisomer as $P2_1/c$ (No. 14) (absent reflections; $h0l$: $l=2n+1$, $0k0$: $k=2n+1$). Unit-cell dimensions and reflection intensities were measured on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation (λ=0.71069 Å).

The θ—2θ scan technique was employed for the intensity data collection at a 2θ rate of 2° min^{-1}. The scan width was from $\{2\theta(\alpha_1)-0.7\}$ to $\{2\theta(\alpha_2)+0.7\}$°. Backgrounds were measured for 10 s at both ends of a scan. Three standard reflections measured after every 50 reflections to monitor the stability and orientation of the crystal showed no significant decay throughout the data collection.

syn-*Anthracenophane*: The intensity measurement was first carried out at room temperature, but later at −149 °C, in a dark room in order to avoid the photochemical cycloaddition of the present compound. The low temperature data were used for the structure analysis. In total 4477 independent

††Called as *syn*-anthracenophane hereafter.

†††Called as photoisomer hereafter.

reflection data were collected ($2\theta \leqq 100°$), of which 4413 could be observed ($|F_o| \leqq 3\sigma(F_o)$). Low temperature was attained by the gas flow method of liquid nitrogen.

Photoisomer: A total of 3740 independent reflections was measured at room temperature($2\theta \leqq 100°$), of which 2003 were non-zero reflections.

Intensity data of both crystals were corrected for usual Lorents and polarization effects but not for absorption [μ(Mo $K\alpha$)=0.767 and 0.785 cm^{-1} for *syn*-anthracenophane and photoisomer, respectively.]

Structure Solution and Refinement

The structures of *syn*-anthracenophane and photoisomer were solved by the Patterson function and direct method, respectively. Both structures were refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).[5]

syn-*Anthracenophane*: The unit-cell has a short b axis and contains eight molecules. Of the three possible space groups, Am and A2/m could be excluded by considering the packing of molecules with expected dimensions. The structure was then solved by assuming the space group as A2, which was later proved correct by the structure determined. Trials to establish the structure by the *MULTAN* program[6] were not successful. The deduction of the structure was then carried out by translational and rotational operations in the Patterson function with the idealized model structure constructed by referencing the structure of a similar compound, [2.2](9,10)anthracenophane.[7] The position of one of the two independent molecules (A molecule) in an asymmetric unit could be deduced. The other molecule (B molecule) was located on the Fourier map computed by using atomic parameters of carbon atoms of the A molecule. Hydrogen atoms of the two molecules were located by geometrical consideration, and they were refined isotropically. Final R index was 0.053 for observed reflections. The weighting scheme used at the final stage of the refinement was $w=\{\sigma^2(F_o)+0.04756|F_o|+0.00017|F_o|^2\}^{-1}$, where σ is the standard deviation obtained from the counting statics. The final atomic parameters are listed in Table.††††

Photoisomer: From the Wilson plot average temperature factor and scale factor were obtained. The $\sum_2$ formula was applied to 795 normalized structure factor magnitudes $|E|$'s($|E| \leqq 1.2$) in order to establish the phase relationship by the symbolic addition method.[9] One of the two E maps, respectively synthesized by two possible sets of signs of 277 reflections, could locate the 32 carbon atoms. The structure was first refined isotropically. Anisotropic temperature factors were then assigned for the carbon atoms, and the structure was refined with unit weight. Hydrogen atoms located on the difference Fourier map was in-

††††Tables of observed and calculated structure factors and anisotropic thermal parameters are kept at the Chemical Society of Japan, Document No. 8541.

Table 1. Final atomic coordinates of *syn*-[2.2](1,4)-anthracenophane with their estimated standard deviations in parentheses

a) Carbon atoms

Atom	x	y	z	B_{eq}/Å²[8]
1C(1)	0.34434(14)	1.3132(5)	0.33565(17)	2.0
1C(2)	0.39834(14)	1.2430(5)	0.33140(18)	1.8
1C(3)	0.44068(15)	1.2253(5)	0.38840(18)	2.0
1C(4)	0.48142(14)	1.1033(5)	0.39351(18)	2.1
1C(5)	0.47983(13)	1.0001(5)	0.34089(18)	1.8
1C(6)	0.50651(15)	0.8313(5)	0.35561(18)	2.1
1C(7)	0.44529(14)	1.0426(5)	0.27460(17)	1.7
1C(8)	0.44964(14)	0.9668(5)	0.21576(19)	2.1
1C(9)	0.41507(14)	1.0063(5)	0.15174(18)	1.9
1C(10)	0.41999(15)	0.9317(5)	0.09131(20)	2.4
1C(11)	0.38644(16)	0.9751(6)	0.03029(20)	2.6
1C(12)	0.34552(15)	1.0947(6)	0.02559(18)	2.3
1C(13)	0.33909(14)	1.1692(5)	0.08213(19)	2.1
1C(14)	0.37345(14)	1.1284(5)	0.14715(18)	1.9
1C(15)	0.36918(14)	1.2036(5)	0.20664(19)	2.0
1C(16)	0.40378(14)	1.1654(5)	0.27024(17)	1.7
2C(1)	0.30823(15)	1.1841(6)	0.36180(21)	2.6
2C(2)	0.33370(14)	1.0158(6)	0.37244(20)	2.4
2C(3)	0.36721(16)	0.9736(6)	0.43398(20)	2.7
2C(4)	0.40771(16)	0.8533(6)	0.44054(19)	2.6
2C(5)	0.41612(15)	0.7737(5)	0.38504(19)	2.2
2C(6)	0.47157(15)	0.7064(5)	0.38660(19)	2.3
2C(7)	0.37414(14)	0.7865(5)	0.32266(19)	2.1
2C(8)	0.37439(15)	0.6909(5)	0.26684(19)	2.2
2C(9)	0.33597(15)	0.7094(5)	0.20368(19)	2.2
2C(10)	0.33774(15)	0.6169(6)	0.14577(20)	2.4
2C(11)	0.29984(17)	0.6386(6)	0.08531(19)	2.7
2C(12)	0.25813(16)	0.7580(6)	0.07823(20)	2.8
2C(13)	0.25560(15)	0.8510(5)	0.13250(20)	2.5
2C(14)	0.29393(14)	0.8316(5)	0.19710(20)	2.2
2C(15)	0.29250(15)	0.9263(6)	0.25312(21)	2.4
2C(16)	0.33192(14)	0.9098(5)	0.31597(20)	2.1
3C(1)	0.22445(13)	0.8118(5)	0.41690(17)	1.7
3C(2)	0.20205(13)	0.6419(5)	0.42137(16)	1.5
3C(3)	0.18701(14)	0.5980(5)	0.47816(16)	1.7
3C(4)	0.14626(14)	0.4789(5)	0.47577(16)	1.7
3C(5)	0.11935(13)	0.4026(5)	0.41635(17)	1.6
3C(6)	0.06214(14)	0.3389(5)	0.40717(17)	1.9
3C(7)	0.14425(13)	0.4128(5)	0.36095(16)	1.4
3C(8)	0.12787(13)	0.3112(5)	0.30399(17)	1.6
3C(9)	0.15190(13)	0.3192(5)	0.25049(16)	1.5
3C(10)	0.13452(14)	0.2177(5)	0.19206(17)	1.8
3C(11)	0.15882(15)	0.2291(5)	0.14078(17)	2.0
3C(12)	0.20230(15)	0.3422(5)	0.14500(17)	2.0
3C(13)	0.21965(14)	0.4422(5)	0.19980(17)	1.8
3C(14)	0.19468(13)	0.4349(5)	0.25429(16)	1.5
3C(15)	0.21092(13)	0.5396(5)	0.31032(17)	1.6
3C(16)	0.18644(13)	0.5323(5)	0.36393(16)	1.4
4C(1)	0.18238(13)	0.9531(5)	0.41925(16)	1.6
4C(2)	0.12441(13)	0.8899(5)	0.40495(16)	1.5
4C(3)	0.09974(14)	0.8702(5)	0.45540(17)	1.8
4C(4)	0.05865(14)	0.7510(5)	0.45137(17)	1.9
4C(5)	0.04143(13)	0.6501(5)	0.39648(16)	1.6
4C(6)	0.01851(13)	0.4822(5)	0.40222(17)	1.9
4C(7)	0.05659(13)	0.6936(5)	0.33557(16)	1.5
4C(8)	0.03466(13)	0.6125(5)	0.27435(17)	1.6
4C(9)	0.05411(13)	0.6408(5)	0.21774(16)	1.5
4C(10)	0.03438(14)	0.5500(5)	0.15632(17)	1.9
4C(11)	0.05653(15)	0.5731(5)	0.10385(17)	2.0
4C(12)	0.09982(15)	0.6869(5)	0.10900(17)	2.1
4C(13)	0.11950(14)	0.7760(5)	0.16635(18)	1.8
4C(14)	0.09690(13)	0.7579(5)	0.22268(16)	1.6
4C(15)	0.11767(13)	0.8421(5)	0.28337(17)	1.6

Table 1. (continued)

a) Carbon atoms Atom	x	y	z	B_{eq}/Å^2 [28]
4C(16)	0.09869(13)	0.8135(5)	0.34022(16)	1.4

b) Hydrogen atoms Atom	x	y	z	B/Å^2
1H(1)	0.3205(14)	1.352(5)	0.2908(17)	2.0(8)
1H(1)	0.3481(15)	1.403(6)	0.3637(18)	2.2(8)
1H(3)	0.4381(14)	1.285(5)	0.4288(17)	1.8(8)
1H(4)	0.5072(14)	1.075(6)	0.4400(17)	2.1(8)
1H(6)	0.5438(15)	0.845(6)	0.3906(18)	2.0(8)
1H(6)	0.5117(15)	0.783(6)	0.3162(18)	2.4(9)
1H(8)	0.4783(14)	0.881(6)	0.2188(17)	2.0(8)
1H(10)	0.4496(15)	0.848(6)	0.0954(19)	2.6(9)
1H(11)	0.3946(17)	0.917(6)	−0.0082(20)	3.2(10)
1H(12)	0.3228(16)	1.125(6)	−0.0200(19)	2.8(9)
1H(13)	0.3076(15)	1.237(6)	0.0773(18)	2.2(9)
1H(15)	0.3403(14)	1.285(5)	0.2038(17)	1.9(8)
2H(1)	0.2688(15)	1.192(6)	0.3288(18)	2.5(9)
2H(1)	0.3014(15)	1.216(6)	0.4059(18)	2.6(9)
2H(3)	0.3687(16)	1.045(6)	0.4734(19)	2.6(9)
2H(4)	0.4370(15)	0.838(6)	0.4862(18)	2.6(9)
2H(6)	0.4956(15)	0.678(6)	0.4358(18)	2.4(9)
2H(6)	0.4697(15)	0.589(6)	0.3610(18)	2.1(8)
2H(8)	0.4052(15)	0.615(6)	0.2684(18)	2.2(8)
2H(10)	0.3679(16)	0.539(6)	0.1504(19)	2.7(9)
2H(11)	0.2990(16)	0.570(6)	0.0436(19)	3.0(10)
2H(12)	0.2286(16)	0.777(6)	0.0288(19)	3.1(10)
2H(13)	0.2245(16)	0.936(6)	0.1244(19)	2.6(9)
2H(15)	0.2633(15)	1.009(6)	0.2466(18)	2.4(9)
3H(1)	0.2343(13)	0.823(5)	0.3715(16)	1.5(7)
3H(1)	0.2564(14)	0.825(5)	0.4537(17)	1.5(8)
3H(3)	0.2001(14)	0.660(5)	0.5220(17)	1.8(8)
3H(4)	0.1293(14)	0.461(5)	0.5132(17)	1.8(8)
3H(6)	0.0588(14)	0.270(6)	0.4448(17)	1.9(8)
3H(6)	0.0514(14)	0.266(5)	0.3656(17)	2.0(8)
3H(8)	0.0972(14)	0.231(5)	0.3006(17)	1.6(8)
3H(10)	0.1017(14)	0.137(5)	0.1895(17)	1.6(8)
3H(11)	0.1425(15)	0.167(6)	0.1005(17)	2.0(8)
3H(12)	0.2184(14)	0.358(5)	0.1079(17)	2.0(8)
3H(13)	0.2505(14)	0.520(6)	0.2021(17)	1.8(8)
3H(15)	0.2400(14)	0.617(5)	0.3102(17)	1.6(8)
4H(1)	0.1875(14)	1.034(5)	0.3868(17)	1.5(8)
4H(1)	0.1953(14)	1.000(6)	0.4654(17)	1.7(8)
4H(3)	0.1171(14)	0.904(5)	0.5009(17)	1.6(8)
4H(4)	0.0490(14)	0.708(6)	0.4916(17)	1.8(8)
4H(6)	0.0058(14)	0.484(6)	0.4444(17)	2.0(8)
4H(6)	−0.0108(14)	0.453(5)	0.3670(17)	1.8(8)
4H(8)	0.0040(15)	0.533(6)	0.2693(16)	1.8(8)
4H(10)	0.0028(14)	0.478(5)	0.1528(17)	1.7(8)
4H(11)	0.0395(15)	0.513(6)	0.0619(17)	1.9(8)
4H(12)	0.1135(15)	0.702(6)	0.0718(18)	2.0(8)
4H(13)	0.1477(14)	0.852(5)	0.1691(17)	1.6(8)
4H(15)	0.1465(14)	0.919(5)	0.2886(17)	1.5(8)

cluded in the refinement with isotropic temperature factors. Finally, the refinement converged with R= 0.043 for non-zero reflections. The atomic parameters are given in Table 2.††††

Atomic scattering factors for the carbon and hydrogen atoms were first taken from those of T. Suzuki[10] and at the final stage from International Tables for X-Ray Crystallography.[11] Computations were done mainly on a NEAC 2200-700 computer at the Computation Center, Osaka University. At the final stage, an ACOS 850 computer was used at the Crystallographic

Table 2. Final atomic coordinates of photoisomer with their estimated standard deviations in parentheses

a) Carbon atoms Atom	x	y	z	B_{eq}/Å^2 [28]
1C(1)	0.5658(5)	0.6523(3)	0.18364(18)	4.3
1C(2)	0.6090(5)	0.5722(3)	0.23769(17)	3.5
1C(3)	0.6838(5)	0.4802(3)	0.21957(18)	4.1
1C(4)	0.7840(5)	0.4260(3)	0.26534(19)	4.1
1C(5)	0.8091(5)	0.4631(3)	0.33203(17)	3.5
1C(6)	0.9665(5)	0.4346(3)	0.37175(19)	4.2
1C(7)	0.7095(4)	0.5435(3)	0.35370(16)	3.1
1C(8)	0.7413(4)	0.5932(3)	0.42317(16)	3.2
1C(9)	0.5854(4)	0.6405(3)	0.44930(17)	3.1
1C(10)	0.5401(5)	0.6327(3)	0.51739(18)	3.7
1C(11)	0.3995(5)	0.6817(3)	0.5391(2)	4.6
1C(12)	0.3022(5)	0.7379(3)	0.4932(3)	4.8
1C(13)	0.3448(5)	0.7440(3)	0.4250(2)	4.0
1C(14)	0.4870(4)	0.6959(3)	0.40282(18)	3.3
1C(15)	0.5435(4)	0.7020(3)	0.33049(17)	3.2
1C(16)	0.6081(4)	0.5982(3)	0.30726(17)	3.0
2C(1)	0.7089(5)	0.7356(3)	0.17642(18)	4.2
2C(2)	0.8556(5)	0.7151(3)	0.22452(17)	3.5
2C(3)	0.9896(5)	0.6583(3)	0.20284(18)	4.2
2C(4)	1.0902(5)	0.6048(3)	0.24955(18)	4.1
2C(5)	1.0571(4)	0.6070(3)	0.31902(17)	3.5
2C(6)	1.1120(5)	0.5171(3)	0.36365(19)	4.2
2C(7)	0.9419(4)	0.6786(3)	0.34201(16)	3.06
2C(8)	0.8879(4)	0.6785(3)	0.41543(16)	3.1
2C(9)	0.8322(4)	0.7850(3)	0.43581(17)	3.2
2C(10)	0.8700(5)	0.8283(3)	0.49908(18)	3.8
2C(11)	0.8150(5)	0.9267(3)	0.5147(2)	4.7
2C(12)	0.7206(5)	0.9815(3)	0.4676(3)	5.0
2C(13)	0.6830(5)	0.9383(3)	0.4043(2)	4.3
2C(14)	0.7351(4)	0.8400(3)	0.38880(17)	3.2
2C(15)	0.6921(4)	0.7867(3)	0.32211(17)	3.3
2C(16)	0.8408(4)	0.7330(3)	0.29429(17)	3.1

b) Hydrogen atoms Atom	x	y	z	B/Å^2
1HA(1)	0.455(5)	0.690(3)	0.1938(18)	3.6(9)
1HB(1)	0.559(5)	0.615(3)	0.1388(18)	3.4(9)
1H(3)	0.691(5)	0.457(3)	0.1685(17)	3.1(9)
1H(4)	0.852(5)	0.366(3)	0.2484(19)	4.0(10)
1HA(6)	1.012(5)	0.369(3)	0.3561(18)	3.7(10)
1HB(6)	0.943(5)	0.424(3)	0.4238(18)	3.5(9)
1H(8)	0.788(4)	0.537(3)	0.4571(16)	2.4(8)
1H(10)	0.613(5)	0.592(3)	0.5510(18)	3.4(9)
1H(11)	0.374(5)	0.674(3)	0.5893(19)	3.8(10)
1H(12)	0.193(5)	0.773(3)	0.5077(19)	4.0(10)
1H(13)	0.271(5)	0.780(3)	0.3895(17)	3.0(9)
1H(15)	0.440(4)	0.723(3)	0.3004(16)	2.1(8)
2HA(1)	0.753(5)	0.737(3)	0.1283(17)	3.0(9)
2HB(1)	0.658(5)	0.807(3)	0.1865(17)	3.0(9)
2H(3)	1.003(5)	0.649(3)	0.1526(18)	3.2(9)
2H(4)	1.180(5)	0.559(3)	0.2338(18)	3.8(10)
2HA(6)	1.225(5)	0.483(3)	0.3436(19)	4.1(10)
2HB(6)	1.149(5)	0.542(3)	0.4125(19)	3.8(10)
2H(8)	0.985(4)	0.656(3)	0.4486(16)	1.8(8)
2H(10)	0.939(5)	0.786(3)	0.5341(18)	3.2(9)
2H(11)	0.832(5)	0.958(3)	0.5625(19)	4.8(11)
2H(12)	0.677(5)	1.052(3)	0.4813(19)	4.5(11)
2H(13)	0.619(5)	0.977(3)	0.3668(18)	3.7(10)
2H(15)	0.643(5)	0.839(3)	0.2878(17)	2.9(9)

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Results and Discussion

Molecular Structure. Perspective views (*ORTEP* drawing)[12] of *syn*-anthracenophane and photoisomer molecules with atom labelling, are shown in Figs. 1 and 2, respectively. Bond distances and bond angles of both compounds are listed in Table 3.

syn-*Anthracenophane*: As seen in Fig. 1, the feature of the molecular structure is that two anthracene nuclei are closely placed in nearly parallel. All of the four anthracene nuclei in two crystallographically independent A and B molecules have normal bond distances and bond angles. However, each of the ethylene-bridged benzene rings is boat-shaped as those in [2.2]paracyclophane[13] and layered paracyclophanes.[14]

The four C_{sp^3}–C_{sp^3} bonds of ethylene bridges, 1Cl–2Cl [1.588(6)Å], 1C6–2C6[1.597(6)Å], 3Cl–4Cl[1.585(5)Å], and 3C6–4C6[1.598(5)Å] are elongated by 0.02 to 0.04 Å than the corresponding bonds of [2.2](9,10)anthracenophane[7] and [2.2]paracyclophane.[13]

As side view of each molecule is presented in Fig. 3, in which nonbonded intramolecular atomic distances between anthracene nuclei are given. As shown in Figs. 1 and 3 the structure of the present compound demonstrates that all the anthracene nuclei are approximately in parallel position suitable for forming an excimer and that two anthracene nuclei are mutually overlapped well in the A molecule whereas less in the B molecule. The nonbonded interatomic distances between the two pairs of active sites, C8 and C15 in the largely overlapped A molecule [1C8····2C8= 3.312(6) and 1C15····2C15=3.301(6)Å] are shorter than the van der Waals contact. On the other hand, the less overlapped B molecule shows slightly longer interatomic distances between the corresponding carbon atoms, 3C8····4C8[3.357(6)Å] and 3C15····4C15 [3.366(5) Å], which are longer than the 3C7····4C8[3.302(5) Å] and 3C16····4C15[3.256(5)Å], owing to larger mutual displacement of the two anthracene nuclei along their longer axis. However, all of them are longer than the corresponding ones of [2.2](9,10)anthracenophane [both 2.772(3)Å][7] but shorter than that of anthracenophane excimer [~3.5 Å].[2] These nonbonded distances between two sp^2 carbon atoms are relatively shorter than the van der Waals distance, which shows considerable overlap between the two $2p_x$ orbitals easy to form a covalent bond. It can be said that the *syn*-anthracenophane molecule has the structure ready for the isomerization to their photoisomers, and *vice versa*.

Photoisomer: The feature of the structure is that, in addition to the ethylene bridge, the 1C8–2C8 and 1C15–2C15 bonds connect the upper and lower dihydroanthracene nuclei tightly, and the end benzene rings are not in parallel (Fig. 4). The 1C8–2C8 and

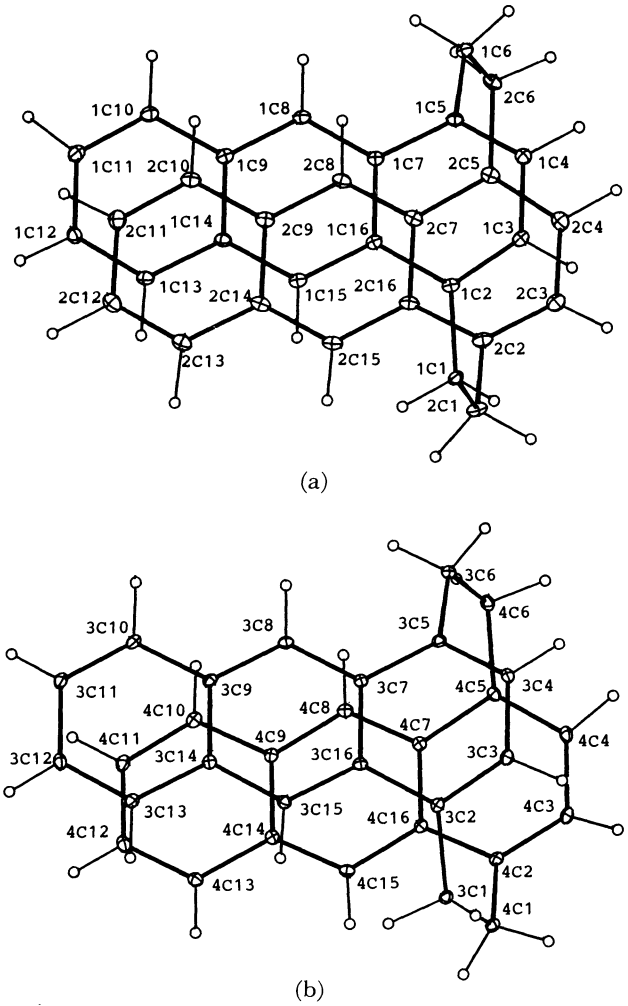

Fig. 1. A. perspective view(*ORTEP* drawing)[12] of *syn*-[2.2](1,4) anthracenophane molecules.
(a): A molecule, (b): B molecule
Non-hydrogen atoms are expressed by thermal ellipsoids with 10% probability level. Hydrogen atoms are drawn as spheres with B=1 Å^2.

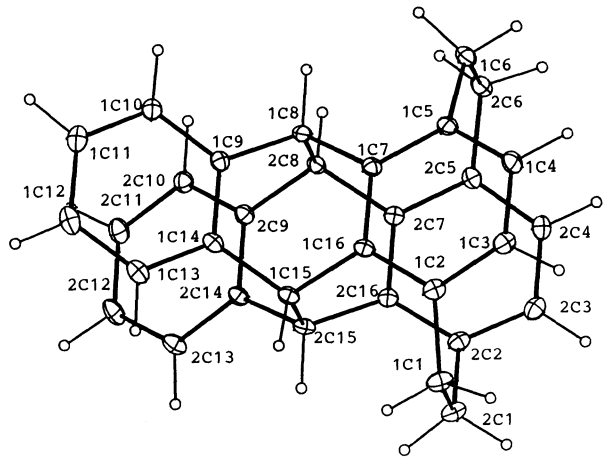

Fig. 2. A perspective view[12] of *syn*-[2.2](1,4) anthracenophane photoisomer molecule.
Non-hydrogen atoms are expressed by thermal ellipsoids with 10% probability level. Hydrogen atoms are drawn as spheres with B=1 Å^2.

Table 3. Bond distances and bond angles of *syn*-anthracenophane and photoisomer with their estimated standard deviations in parentheses

	Syn-anthracenophane			Photoisomer	
	A molecule		B molecule		
Bond distances[l/Å]					
1C2–1C3	1.365(5)	3C2–3C3	1.374(5)	1C2–1C3	1.387(5)
1C3–1C4	1.422(5)	3C3–3C4	1.414(5)	1C3–1C4	1.383(5)
1C4–1C5	1.363(5)	3C4–3C5	1.374(5)	1C4–1C5	1.401(5)
1C5–1C7	1.446(5)	3C5–3C7	1.452(5)	1C5–1C7	1.389(5)
1C7–1C16	1.442(5)	3C7–3C16	1.441(5)	1C7–1C16	1.400(5)
1C2–1C16	1.448(5)	3C2–3C16	1.447(5)	1C2–1C16	1.404(5)
2C2–2C3	1.361(6)	4C2–4C3	1.364(5)	2C2–2C3	1.383(5)
2C3–2C4	1.405(6)	4C3–4C4	1.416(5)	2C3–2C4	1.392(5)
2C4–2C5	1.380(6)	4C4–4C5	1.367(5)	2C4–2C5	1.393(5)
2C5–2C7	1.430(5)	4C5–4C7	1.453(5)	2C5–2C7	1.396(5)
2C7–2C16	1.453(5)	4C7–4C16	1.436(5)	2C7–2C16	1.412(5)
2C2–2C16	1.438(6)	4C2–4C16	1.452(5)	2C2–2C16	1.394(5)
1C1–1C2	1.517(5)	3C1–3C2	1.511(5)	1C1–1C2	1.517(5)
1C5–1C6	1.528(5)	3C5–3C6	1.513(5)	1C5–1C6	1.518(5)
2C1–2C2	1.508(6)	4C1–4C2	1.518(5)	2C1–2C2	1.520(5)
2C5–2C6	1.511(6)	4C5–4C6	1.506(5)	2C5–2C6	1.518(5)
1C1–2C1	1.588(6)	3C1–4C1	1.585(5)	1C1–2C1	1.589(5)
1C6–2C6	1.597(6)	3C6–4C6	1.598(5)	1C6–2C6	1.599(5)
1C7–1C8	1.390(5)	3C7–3C8	1.401(5)	1C7–1C8	1.521(5)
1C8–1C9	1.405(5)	3C8–3C9	1.401(5)	1C8–1C9	1.500(4)
1C14–1C15	1.399(5)	3C14–3C15	1.402(5)	1C14–1C15	1.501(5)
1C15–1C16	1.396(6)	3C15–3C16	1.411(5)	1C15–1C16	1.516(4)
2C7–2C8	1.389(5)	4C7–4C8	1.395(5)	2C7–2C8	1.513(4)
2C8–2C9	1.403(6)	4C8–4C9	1.405(5)	2C8–2C9	1.509(4)
2C14–2C15	1.396(6)	4C14–4C15	1.394(5)	2C14–2C15	1.510(5)
2C15–2C16	1.408(6)	4C15–4C16	1.403(5)	2C15–2C16	1.501(4)
1C8···2C8	3.312(6)	3C8···4C8	3.357(5)	1C8–2C8	1.628(4)
1C15···2C15	3.301(6)	3C15···4C15	3.366(5)	1C15–2C15	1.637(5)
1C9–1C10	1.420(6)	3C9–3C10	1.425(5)	1C9–1C10	1.395(5)
1C10–1C11	1.357(6)	3C10–3C11	1.366(5)	1C10–1C11	1.376(5)
1C11–1C12	1.413(6)	3C11–3C12	1.428(5)	1C11–1C12	1.385(6)
1C12–1C13	1.361(6)	3C12–3C13	1.362(5)	1C12–1C13	1.390(6)
1C13–1C14	1.421(5)	3C13–3C14	1.435(5)	1C13–1C14	1.385(5)
1C9–1C14	1.440(5)	3C9–3C14	1.429(5)	1C9–1C14	1.391(5)
2C9–2C10	1.421(6)	4C9–4C10	1.430(5)	2C9–2C10	1.387(5)
2C10–2C11	1.360(6)	4C10–4C11	1.362(5)	2C10–2C11	1.386(5)
2C11–2C12	1.420(6)	4C11–4C12	1.425(5)	2C11–2C12	1.378(6)
2C12–2C13	1.366(6)	4C12–4C13	1.358(5)	2C12–2C13	1.387(6)
2C13–2C14	1.425(6)	4C13–4C14	1.437(5)	2C13–2C14	1.378(5)
2C9–2C14	1.443(6)	4C9–4C14	1.433(5)	2C9–2C14	1.390(5)
Bond angles[ϕ/°]					
1C2–1C1–2C1	113.1(4)	3C2–3C1–4C1	113.2(3)	1C2–1C1–2C1	111.9(3)
1C1–1C2–1C3	120.5(4)	3C1–3C2–3C3	119.4(4)	1C1–1C2–1C3	120.3(3)
1C1–1C2–1C16	121.4(4)	3C1–3C2–3C16	122.7(4)	1C1–1C2–1C16	120.4(3)
1C3–1C2–1C16	117.1(4)	3C3–3C2–3C16	117.0(4)	1C3–1C2–1C16	117.9(3)
1C2–1C3–1C4	121.9(4)	3C2–3C3–3C4	121.7(4)	1C2–1C3–1C4	121.5(3)
1C3–1C4–1C5	120.8(4)	3C3–3C4–3C5	121.6(4)	1C3–1C4–1C5	119.8(4)
1C4–1C5–1C6	119.0(4)	3C4–3C5–3C6	119.7(4)	1C4–1C5–1C6	119.5(3)
1C4–1C5–1C7	118.5(4)	3C4–3C5–3C7	116.9(4)	1C4–1C5–1C7	118.1(4)
1C6–1C5–1C7	121.7(4)	3C6–3C5–3C7	122.6(4)	1C6–1C5–1C7	120.6(3)
1C5–1C6–2C6	112.6(4)	3C5–3C6–4C6	112.9(3)	1C5–1C6–2C6	113.1(3)
1C5–1C7–1C8	122.6(4)	3C5–3C7–3C8	121.9(4)	1C5–1C7–1C8	120.4(3)
1C5–1C7–1C16	118.1(4)	3C5–3C7–3C16	119.3(3)	1C5–1C7–1C16	120.9(3)
1C7–1C8–1C9	122.2(4)	3C7–3C8–3C9	122.3(4)	1C7–1C8–1C9	110.8(3)
				1C7–1C8–2C8	108.1(3)
				1C9–1C8–2C8	111.8(3)
1C8–1C9–1C10	122.5(4)	3C8–3C9–3C10	122.2(4)	1C8–1C9–1C10	122.6(3)
1C8–1C9–1C14	118.8(4)	3C8–3C9–3C14	118.8(4)	1C8–1C9–1C14	117.1(3)
1C10–1C9–1C14	118.7(4)	3C10–3C9–3C14	119.0(4)	1C10–1C9–1C14	120.3(3)
1C9–1C10–1C11	120.8(4)	3C9–3C10–3C11	120.6(4)	1C9–1C10–1C11	119.9(4)
1C10–1C11–1C12	120.7(5)	3C10–3C11–3C12	120.5(4)	1C10–1C11–1C12	120.0(4)
1C11–1C12–1C13	120.7(4)	3C11–3C12–3C13	120.5(4)	1C11–1C12–1C13	120.3(4)

Table 3. (continued)

Syn-anthracenophane				Photoisomer	
A molecule		B molecule			
1C12-1C13-1C14	120.7(4)	3C12-3C13-3C14	120.5(4)	1C12-1C13-1C14	120.1(4)
1C13-1C14-1C15	122.9(4)	3C13-3C14-3C15	121.5(4)	1C13-1C14-1C15	123.1(4)
1C9-1C14-1C13	118.4(4)	3C9-3C14-3C13	118.9(4)	1C9-1C14-1C13	119.4(4)
1C9-1C14-1C15	118.7(4)	3C9-3C14-3C15	119.7(4)	1C9-1C14-1C15	117.6(3)
1C14-1C15-1C16	122.6(4)	3C14-3C15-3C16	121.5(4)	1C14-1C15-1C16	110.6(3)
				1C14-1C15-2C15	111.7(3)
				1C16-1C15-2C15	107.9(3)
1C2-1C16-1C7	119.6(4)	3C2-3C16-3C7	119.1(3)	1C2-1C16-1C7	119.5(3)
1C2-1C16-1C15	121.9(4)	3C2-3C16-3C15	122.0(4)	1C2-1C16-1C15	120.9(3)
1C7-1C16-1C15	118.5(4)	3C7-3C16-3C15	118.9(4)	1C7-1C16-1C15	117.0(3)
1C1-2C1-2C2	112.6(4)	3C1-4C1-4C2	112.3(3)	1C1-2C1-2C2	112.5(3)
2C1-2C2-2C3	120.0(4)	4C1-4C2-4C3	121.6(4)	2C1-2C2-2C3	120.4(3)
2C1-2C2-2C16	120.9(4)	4C1-4C2-4C16	119.6(3)	2C1-2C2-2C16	119.7(3)
2C3-2C2-2C16	118.1(4)	4C3-4C2-4C16	117.4(4)	2C3-2C2-2C16	118.4(4)
2C2-2C3-2C4	121.5(4)	4C2-4C3-4C4	121.8(4)	2C2-2C3-2C4	120.7(4)
2C3-2C4-2C5	121.8(4)	4C3-4C4-4C5	121.7(4)	2C3-2C4-2C5	120.5(4)
2C4-2C5-2C6	120.8(4)	4C4-4C5-4C6	121.7(4)	2C4-2C5-2C6	119.1(3)
2C4-2C5-2C7	117.3(4)	4C4-4C5-4C7	117.6(4)	2C4-2C5-2C7	118.3(3)
2C6-2C5-2C7	120.8(4)	4C6-4C5-4C7	119.4(4)	2C6-2C5-2C7	120.8(3)
1C6-2C6-2C5	112.6(4)	3C6-4C6-4C5	113.0(4)	1C6-2C6-2C5	111.6(3)
2C5-2C7-2C8	121.8(4)	4C5-4C7-4C8	121.7(4)	2C5-2C7-2C18	121.0(3)
2C5-2C7-2C16	119.2(4)	4C5-4C7-4C16	118.8(4)	2C5-2C7-2C16	119.7(3)
2C7-2C8-2C9	122.9(4)	4C7-4C8-4C9	121.6(4)	2C7-2C8-2C9	110.2(3)
				1C8-2C8-2C7	108.5(3)
				1C8-2C8-2C9	112.0(3)
2C8-2C9-2C10	122.9(4)	4C8-4C9-4C10	121.8(4)	2C8-2C9-2C10	123.2(3)
2C8-2C9-2C14	118.3(4)	4C8-4C9-4C14	119.2(4)	2C8-2C9-2C14	117.4(3)
2C10-2C9-2C14	118.8(4)	4C10-4C9-4C14	118.9(4)	2C10-2C9-2C14	119.4(3)
2C9-2C10-2C11	121.2(4)	4C9-4C10-4C11	120.4(4)	2C9-2C10-2C11	120.3(4)
2C10-2C11-2C12	120.5(4)	4C10-4C11-4C12	121.0(4)	2C10-2C11-2C12	120.1(4)
2C11-2C12-2C13	120.0(4)	4C11-4C12-4C13	120.4(4)	2C11-2C12-2C13	119.6(4)
2C12-2C13-2C14	121.6(4)	4C12-4C13-4C14	120.7(4)	2C12-2C13-2C14	120.6(4)
2C13-2C14-2C15	122.7(4)	4C13-4C14-4C15	122.2(4)	2C13-2C14-2C15	123.3(4)
2C9-2C14-2C13	117.8(4)	4C9-4C14-4C13	118.6(4)	2C9-2C14-2C13	119.9(4)
2C9-2C14-2C15	119.5(4)	4C9-4C14-4C15	119.1(4)	2C9-2C14-2C15	116.8(3)
2C14-2C15-2C16	122.0(4)	4C14-4C15-4C16	122.0(4)	2C14-2C15-2C16	111.0(3)
				1C15-2C15-2C14	111.9(3)
				1C15-2C15-2C16	108.6(3)
2C2-2C16-2C7	118.8(4)	4C2-4C16-4C7	119.6(4)	2C2-2C16-2C7	120.2(3)
2C2-2C16-2C15	122.6(4)	4C2-4C16-4C15	121.3(4)	2C2-2C16-2C15	121.4(3)
2C7-2C16-2C15	118.5(4)	4C7-4C16-4C15	118.8(4)	2C7-2C16-2C15	116.4(3)

1C15-2C15 bond distances are 1.628(4) and 1.637(5) Å, which are very long and comparable to that in [9′,10′]-dihydroanthraceno[9,10]dihydroanthracene[1.61(2) Å].[14]

In the [2.2]paracyclophane moiety at one end of the molecule, the C2-C16[1.404(5) and 1.394(5) Å], C5-C7[1.389(5) and 1.396(5) Å], and C7-C16[1.400(5) and 1.412(5) Å] bond distances are clearly shorter than those in *syn*-anthracenophane. Two benzene rings in this moiety deformed in boat form as in *syn*-anthracenophane and other related compounds. The central C_{sp^3}-C_{sp^3} bonds of the ethylene bridges are equal to those in *syn*-anthracenophane.

In the third benzene rings of the dihydroanthracene nuclei, the C9-C10, C11-C12, C13-C14, and C9-C14 bond distances are respectively shorter, whereas the C10-C11 and C12-C13 distances are longer, than the corresponding distances in *syn*-anthracenophane (Table 3). The bond distances [av. 1.387 and 1.384 Å] and bond angles [av. 120 and 120°] in the third benzene rings are contracted to normal values of the benzene molecule by the photoisomerization.

A side view of the molecule, which can be compared with those of *syn*-anthracenophane (Fig. 3), is depicted in Fig. 4 with nonbonded intramolecular atomic distances. The left half of the present molecule, namely the [2.2]orthocyclophane skeleton, has a similar structure as a half of the [9′,10′]dihydroanthraceno-[9,10] dihydroanthracene. The dihedral angle formed by the end benzene rings is 46.6°, which is equal to that of [9′,10′]dihydroanthraceno[9,10]dihydroanthracene [46°]. In the right half of the molecule, namely the tetra-bridged cyclophane skeleton, the nonbonded 1C7····2C[2.580(4) Å] and 1C16····2C16[2.581(4) Å] distances are shorter by about 0.04 Å than that between the upper and lower benzene rings in [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane[2.624 Å], the closest

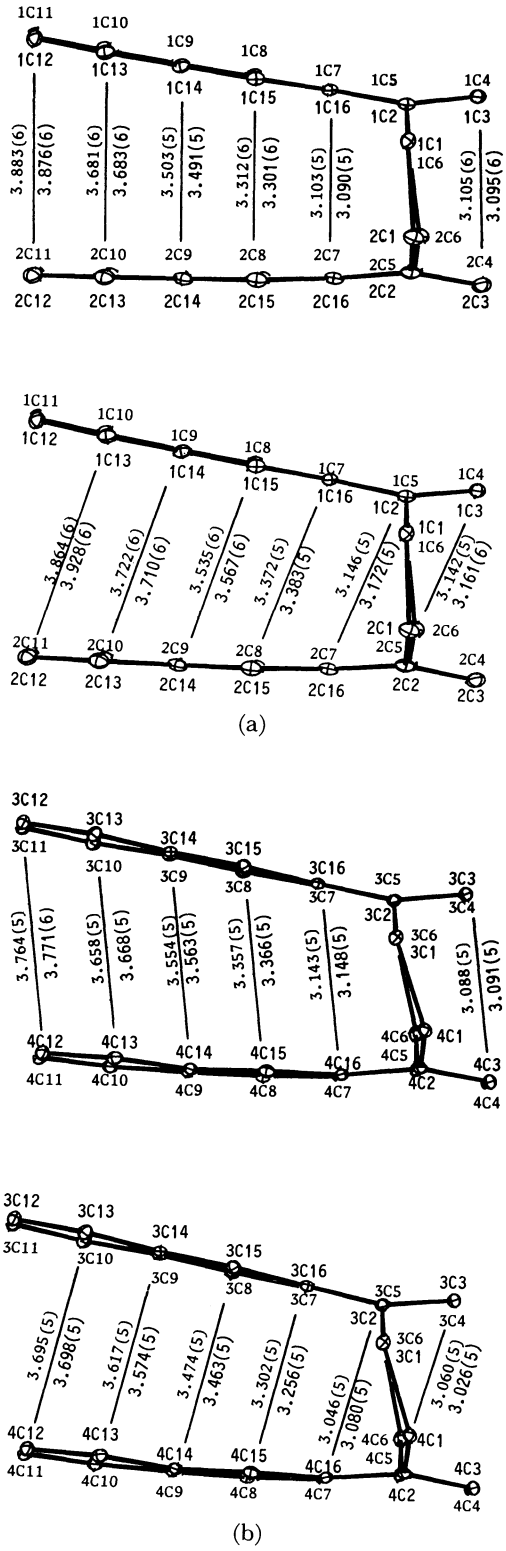

Fig. 3. A side view of *syn*-anthracenophane molecules.[12]
(a): A molecule, (b): B molecule
Hydrogen atoms are omitted for clarity. Nonbonded atomic distances(l/Å) are given with their estimated standard deviations in parentheses.

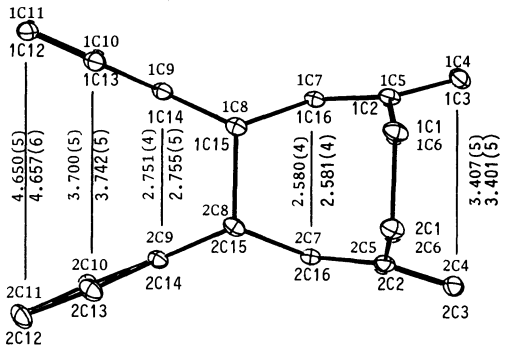

Fig. 4. A side view of *syn*-anthracenophane photoisomer molecules.[12]
Hydrogen atoms are omitted for clarity. Nonbonded atomic distances(l/Å) are given with their estimated standard deviations in parentheses.

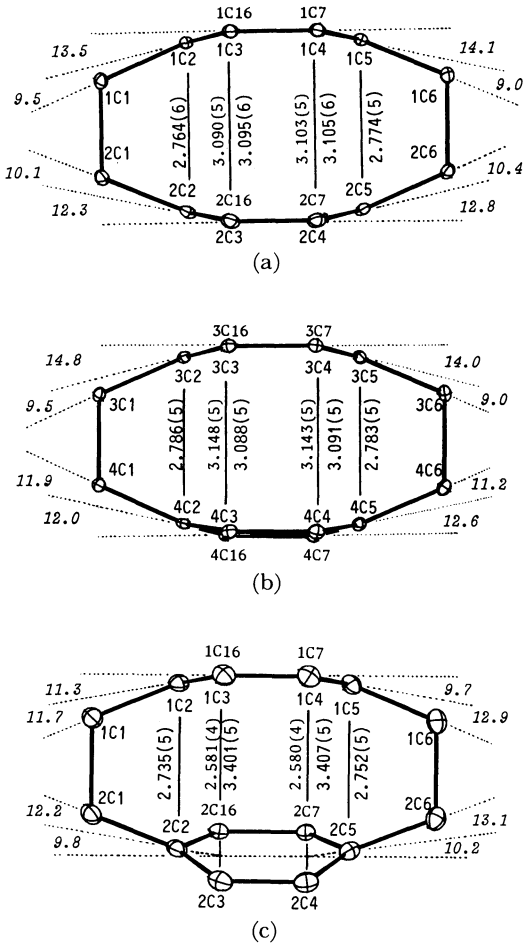

Fig. 5. A comparison of [2.2]paracyclophane moieties in *syn*-anthracenophane and its photoisomer.[12]
Selected interatomic distances [l/Å] are given with their estimated standard deviations in parentheses.
(a): *syn*-Anthracenophane, A molecule, (b): *syn*-Anthracenophane, B molecule, (c): Photoisomer.

distance reported so far. This fact suggests an existence of large strain in the present molecule. One of the chemical proof is that, against the Woodward-Hoffmann rule, by thermal fission of the 1C8–2C8

and 1C15–2C15 bonds the present compound is easily isomerized to *syn*-anthracenophane.

A side view of the [2.2]paracyclophane moiety in the present photoisomer is compared with those of *syn*-anthracenophane in Fig. 5. In the *syn*-anthracenophane the upper and lower benzene rings of this part of the A molecule are parallel and mutually overlapped well (Figs. 3a and 5a), while those of the B molecule not so parallel and not so overlapped well (Figs. 3b and 5b); this difference is caused by a conformational change at ethylene bridges as seen in Fig. 3. Whereas, the [2.2]paracyclophane moiety in the photoisomer shows a large distortion due to the 1C8–2C8 and 1C15–2C15 bonds formation (Figs. 4 and 5c).

Crystal Structure: The packing of molecules in crystals of *syn*-anthracenophane and its photoisomer are respectively given in Figs. 6 and 7 (*ORTEP* drawing).[12] Close intermolecular atomic contacts in these crystals are listed in Table 4.

syn-*Anthracenophane*: Molecules are packed densely. The closest distance between A molecules is 3.400(6) Å and that between B molecules 3.399(5)Å. However, the shortest contact between A and B molecules is 3.539(6)Å, which is slightly longer than the former two.

Photoisomer: A comparatively loose packing of molecules is observed. The closest intermolecular atomic contact is 3.563(7)Å.

The authors are grateful to Miss Nobuko Kanehisa who helped them at the final stage of the computation and for *ORTEP* drawing.

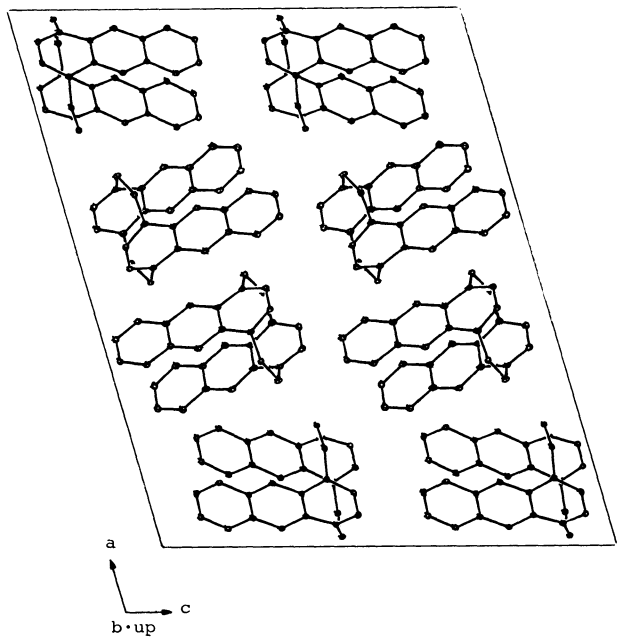

Fig. 6. Crystal structure of *syn*-anthracenophane.[12] Hydrogen atoms are omitted.

TABLE 4. CLOSE INTERMOLECULAR ATOMIC CONTACT[*l*/Å] LESS THAN 3.6 Å WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

syn-Anthracenophane					
1C1····2C8[a]	3.560(6)	key: a,	*x*,	1+*y*,	*z*;
1C12···2C4[b]	3.400(6)	b,	*x*,	0.5+*y*,	−0.5+*z*;
2C12···3C4[b]	3.539(6)	c,	−*x*,	−0.5+*y*,	0.5−*z*;
3C6····4C10[c]	3.399(6)				
Photoisomer					
1C5····1C11[a]	3.597(5)	key: a,	1−*x*,	1−*y*,	1−*z*.
1C10···1C10[a]	3.563(7)				

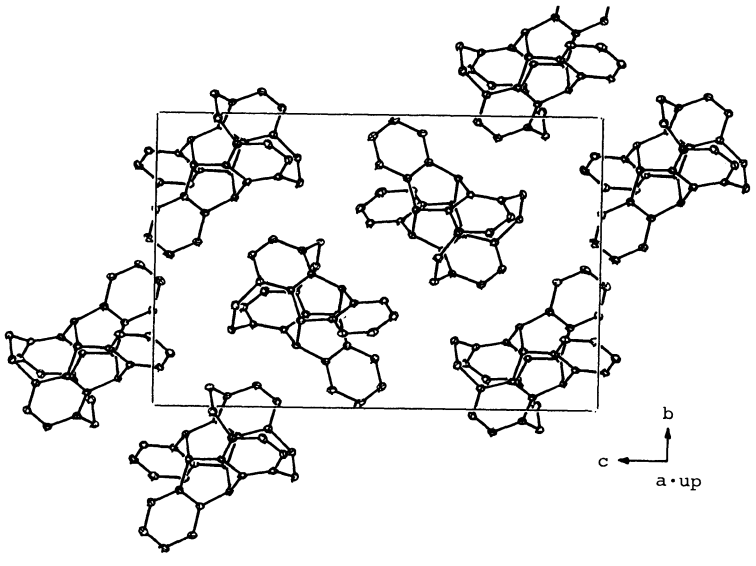

Fig. 7. Crystal structure of *syn*-anthracenophane photoisomer.[12] Hydrogen atoms are omitted.

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