Bent Acenes: Synthesis and Molecular Structure of [6](1,4)Naphthalenophane and [6](1,4)Anthracenophane

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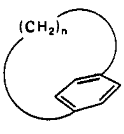
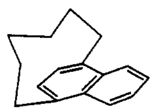
Abstract: The first total syntheses and structural studies of [6](1,4)naphthalenophane (**4**) and [6](1,4)anthracenophane (**5**), the smallest-bridged isolable cyclophanes with bent acene nuclei, are disclosed. The acenophanes **4** and **5** were successfully synthesized by the oxidative decarboxylation of the benzo- and naphtho-fused propellenecarboxylic acids **10** and **11** to give the bridgehead olefins **12** and **13** followed by subsequent treatment with potassium *tert*-butoxide. The acids **10** and **11** were obtained conveniently by the Diels–Alder reactions of the diene **7** followed by ring contraction. The electronic spectra and photoelectron spectra of **4** and **5** were measured and were compared with the corresponding 1,4-diethyl derivatives **14** and **15**. The bathochromic shift of the first transition in the UV spectrum, as well as the shift of the first ionization energies of **4** and **5** in comparison to **14** and **15**, respectively, can be ascribed mainly to the inductive effect of the hexamethylene chain and not to a bending of the π-system. The ^{1}H NMR chemical shifts of **4** and **5** as well as their dynamic NMR behavior suggest that the bridging methylene groups of **4** and **5** are more relaxed than that of **1**. The X-ray crystallographic structure analysis of **5** strongly supports these observations. The bent angle of the bridged aromatic ring of **5** is greater (by 1.5–1.6°) than those of the [6]paracyclophane derivatives **16** and **17**, whereas the deformation of the bridging methylene group of **5** is smaller than those of the latter.

The chemistry of small-bridged [*n*]paracyclophanes has been of keen interest during the last several years. [6]Paracyclophane (**1**), the smallest bridged [*n*]paracyclophane that has been isolated,[1] has been shown by Tochtermann[2] and by us[3] to possess an enormously bent benzene ring as well as remarkably stretched methylene bridges by X-ray structure studies of its derivatives. Moreover, unusual reactivities associated with the deformation in both the π-system and the bridge have been unveiled.[2,3] Contrary to the empirical and semiempirical calculations done for the next lower homologue, [5]paracyclophane (**2**), more sophisticated molecular orbital calculations predict that the out-of-plane bending of the benzene ring will be larger but not much different from those observed for the [6]paracyclophane derivatives.[4] However, although **2** and its derivatives have been successfully prepared and characterized by ^{1}H NMR and UV spectra at low temperature, they have thus far eluded isolation due to their lability.[5] The even smaller bridged [4]paracyclophane (**3**) has only been intercepted and characterized by UV spectra at 77 K by the groups of Bickelhaupt[6a] and Tsuji and Nishida.[6b,c] Although layered cyclophanes based on naphthalene and anthracene have been studied extensively,[7] bridged 1,4-naphthalenes and 9,10-anthracenes have been studied little and none are known with bridges smaller than six methylene units.[8] It is of critical interest to investigate the structure and properties of bent acenes with a small bridge having six or five methylene units. The reasons for this are (i) the higher π-bond order of the C(1)–C(2) bond of acene nuclei relative to benzene should lead to a severe distortion of the bridgehead double bond in the [*n*](1,4)acenophanes; (ii) there should be a lower ionization potential of acenes relative to benzene due to the higher HOMO levels of acenes; and (iii) the variety of reactivities inherent in both ground and excited states of acenes would be amplified in the acenophanes by the strain due to the short bridge. In this context, we disclose herein the synthesis and structural studies on [6](1,4)naphthalenophane (**4**) and [6](1,4)anthracenophane (**5**), which are the smallest bridged acenophanes yet isolated in each series.



1 n=6
2 n=5
3 n=4



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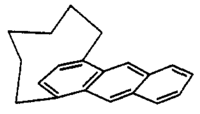

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The syntheses of **4** and **5** were successfully achieved by using the propellane to bridgehead olefin transformation[3a] as the crucial step of the synthesis. Toward this end, the diene **7** was prepared from the [2 + 2] photocycloadduct of the enone **6** with (*E*)-1,4-dichloro-2-butene followed by protection of the ketone and the subsequent 2-fold elimination of HCl in 40% overall yield. Diels–Alder reactions of the diene **7** with ethynyl tolyl sulfone[9]

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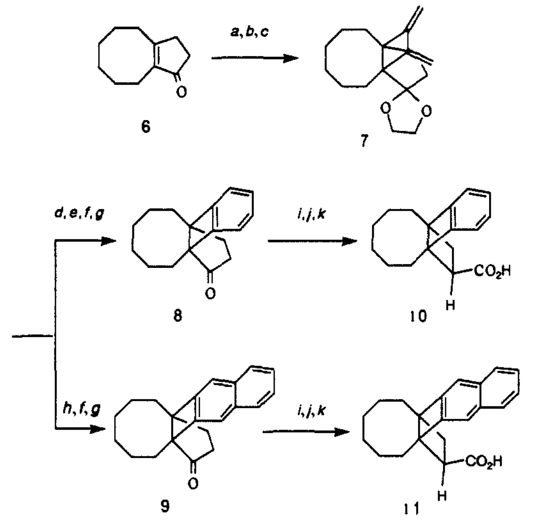
Scheme I[a]



[a] (a) (*E*)-1,4-Dichloro-2-butene, CH_2Cl_2, *hν*, Pyrex, room temperature. Only the major stereoisomer was used for the subsequent rections. (b) Ethylene glycol, TsOH, C_6H_6, 80 °C. (c) *t*-BuOK, DMSO, room temperature. (d) Ethynyl tolyl sulfone, C_6H_6, 80 °C. (e) $Na_2S_2O_4$, $NaHCO_3$, aqueous DMF, 120 °C. (f) DDQ, C_6H_6, room temperature. (g) HCl, aqueous THF, room temperature. (h) *o*-Dibromobenzene, BuLi, toluene, room temperature. (i) HCO_2Et, EtONa, C_6H_6, room temperature. (j) TsN_3, Et_3N, CH_2Cl_2, −10 °C to room temperature. (k) *hν* (λ > 350 nm), aqueous THF (1:1), 0 °C.

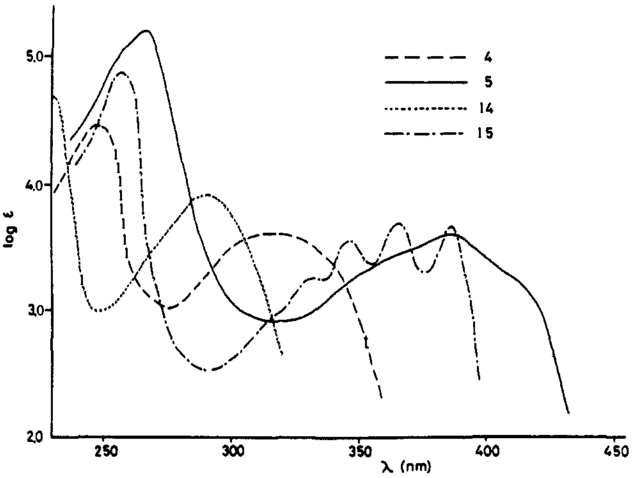
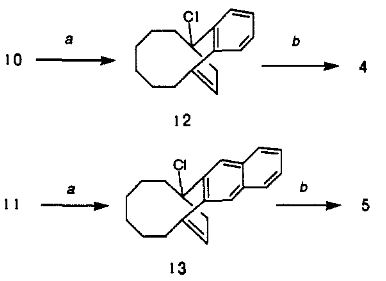


Figure 1. Electronic spectra of [6](1,4)naphthalenophane (**4**), [6](1,4)anthracenophane (**5**), 1,4-diethylnaphthalene (**14**), and 1,4-diethylanthracene (**15**) in cyclohexane.

and benzyne followed by dehydrogenation and deprotection gave the benzo- and naphtho-fused propellenones **8** and **9** in 45% and 62% overall yields, respectively. Propellenecarboxylic acids **10** and **11** were prepared (36% and 41% yields, respectively, for the three steps) by the ring contraction of the α-diazo ketones derived from the propellenones **8** and **9** (Scheme I). Since the products of the photo-Wolff rearrangement, especially **11**, were both thermally and photochemically unstable, the photolysis of the α-diazo ketones was carried out at 0 °C by using a filter to cut off the light of wavelength shorter than 350 nm. Oxidative decarboxylation of the acids **10** and **11** with lead tetraacetate in the presence of lithium chloride (5 equiv) in DMSO at room temperature gave the bridgehead chlorides **12** and **13** in 78% and 58% yields, respectively. The treatment of **12** and **13** with potassium *tert*-butoxide in DMSO furnished the air-sensitive acenophanes **4** (92%; colorless oil) and **5** (81%; yellow solid, mp 161-3 °C) (Scheme II).

Scheme II[a]



[a] (a) $Pb(OAc)_4$, LiCl, DMSO, room temperature. (b) *t*-BuOK, DMSO, room temperature.

Table I. Comparison between the Recorded Vertical Ionization Energies, $I_{v,j}$, of **4** and **14** as Well as **5** and **15**[a]

band	**4** $I_{v,j}$	**14** $I_{v,j}$	ΔI	assignment	**5** $I_{v,j}$	**15** $I_{v,j}$	ΔI	assignment
1	7.33	7.60	0.3	$1a_u$	6.95	7.16	0.2	$2b_{2g}$
2	8.44	8.56	0.1	$2b_{1u}$	8.28	8.30	0.0	$2b_{3g}$
3	9.20	9.35	0.15	$1b_{2g}$	8.5	8.70	0.2	$1a_u$
4	9.8	10.5	0.7	$1b_{3g}$	9.7	9.83	0.1	$1b_{2g}$

[a] All values in eV.

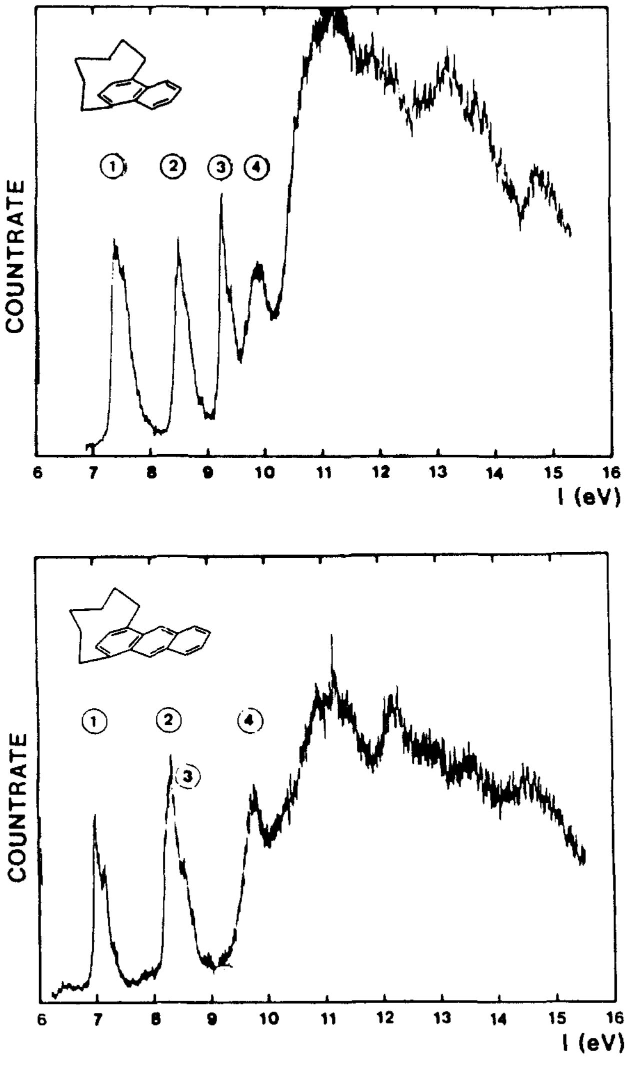


Figure 2. PE spectra of [6](1,4)naphthalenophane (**4**) and [6](1,4)anthracenophane (**5**).

The electronic spectra (in cyclohexane) of **4** (λ_{max} 314 (ε 3950), 246 (29 200) nm) and **5** (λ_{max} 385 (ε 3880), 266 (158000) nm) are shown in Figure 1. Both **4** and **5** exhibit distinct bathochromic shifts (25 and 20 nm, respectively) compared with 1,4-diethylnaphthalene (**14**)[10] and 1,4-diethylanthracene (**15**),[11] though the

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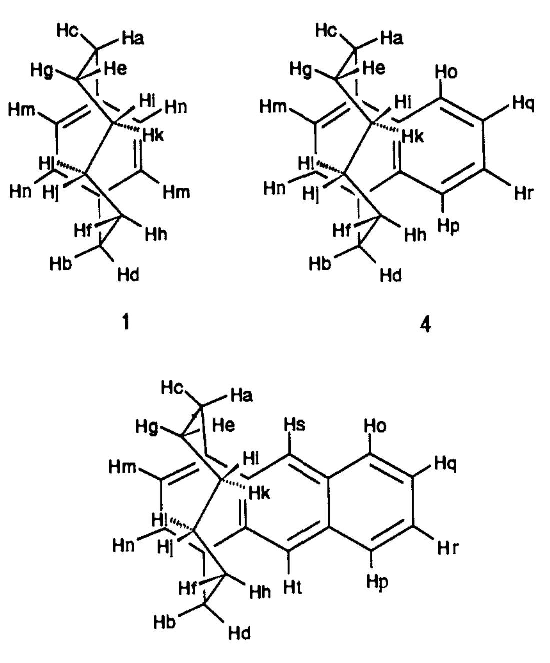


Figure 3. ^{1}H NMR assignments of [6]paracyclophane (**1**), [6](1,4)-naphthalenophane (**4**), and [6](1,4)anthracenophane (**5**) in CDCl$_3$ at -50 °C.

red shifts become less remarkable on going from [6]paracyclophane (**1**; 34 nm)[1a,31] to **4** and **5**. To elucidate the sequence of the π-MO's of **4** and **5** and to find out if there is any significant change in their electronic structure due to the bridging, we have recorded their He I photoelectron (PE) spectra. Both spectra are shown in Figure 2. In Table I the PE data of **4** and **5** are compared with those of **14** and **15**. The given assignments refer to the assignment of the PE bands of the parent systems, naphthalene[12] and anthracene.[12] It should be noted that the PE spectra of **4** and **5** are very similar to those of **14**, **15**, and the parent compounds. The comparison between the first three PE bands of **4** and **14** shows a shift of 0.1 eV for band 2 and shifts of 0.3 and 0.15 eV for bands 1 and 3, respectively. Similar shift differences are found when comparing the first four PE bands of **5** and **15** (see Table I). Both patterns are anticipated from first order perturbation theory if we take into account the π-AO coefficients at positions 1 and 4 in the highest occupied MO's of naphthalene and anthracene.

Our investigations of the PE spectra of **4** and **5** show that the effect of the bridge is mainly an inductive one. This finding is in line with investigations carried out on [6]paracyclophane (**1**)[13] and the corresponding dialkylbenzenes.[14] It is also in line with PE investigations on twisted ethylenes which reveal only small changes for a relative strong twisting.[15] The observed energy difference between the first PE band of **4** and that of **14** (ΔI_1 = 0.3 eV) as well as those between **5** and **15** (ΔI_1 = 0.2 eV) corresponds quite well to the energy difference of the first band in their respective UV spectra; The value for **4**/**14** amounts to ΔE_1 = 0.34 eV, for **5**/**15** ΔE_1 = 0.18 eV.

Table II. ^{1}H NMR Chemical Shifts of [6]Paracyclophane (**1**), [6](1,4)Naphthalenophane (**4**), and [6](1,4)Anthracenophane (**5**)[a]

	compound		
proton	**1**	**4**[b]	**5**[c]
Ha	1.97	2.86	3.00
Hb	1.97	2.27	2.36
Hc	2.79	3.01	3.08
Hd	2.79	3.49	3.58
He	1.58	1.74	1.77
Hf	1.58	1.58	1.60
Hg	0.51	0.71	0.80
Hh	0.51	0.34	0.38
Hi	1.06	0.79	0.71
Hj	1.06	1.11	1.14
Hk	-0.62	-1.84	-1.81
Hl	-0.62	-0.47	-0.31
Hm	7.22	7.41 (7.26)	7.33 (7.27)
Hn	7.13	7.34 (7.26)	7.27 (7.27)
Ho	-	7.96 (8.07)	8.00 (8.04)
Hp	-	8.08 (8.07)	8.00 (8.04)
Hq, Hr	-	7.46 (7.49)	7.48 (7.48)
Hs	-	-	8.45 (8.64)
Ht	-	-	8.58 (8.64)

[a] Measured at -50 °C in CDCl$_3$. Chemical shifts are in δ ppm. [b] Corresponding proton chemical shifts of 1,4-diethylnaphthalene (**14**) are given in parentheses. [c] Corresponding proton chemical shifts of 1,4-diethylanthracene (**15**) are given in parentheses.

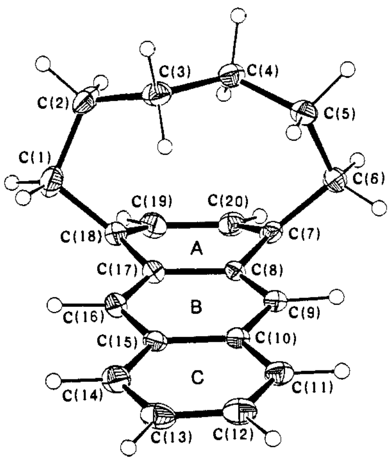
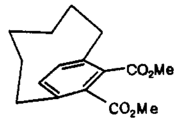


Figure 4. ORTEP drawing (side view) of [6](1,4)anthracenophane (**5**).

The assignment of the ^{1}H NMR signals of **4** and **5** (Figure 3 and Table II) taken at -50 °C was done by a combination of 2D NMR techniques (^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, and NOESY), taking into account the previous assignment for the ortho bis(methoxycarbonyl) substituted [6]paracyclophane **16**.[16] The chemical shifts of the aromatic rings of **4** and **5** are not much different from those of the reference compounds **14** and **15**, which indicates that the ring current of **4** and **5** is intact. The bridge protons (Hk) which are located above the interior of the aromatic ring of the acenophanes **4** and **5** exhibit significant up-field shift compared to that of [6]paracyclophane (**1**) because of the increase of the ring current at the interior of the aromatic rings of **4** and **5**. On the other hand, the protons (Hg and Hl) directing down toward the periphery of the aromatic ring are more deshielded in the order of **5** > **4** > **1**. Although chemical shifts are subject to many different effects, this deshielding is probably due to the increase of nonbonded distance between these protons and the aromatic ring which is in this order (**5** > **4** > **1**). Similarly, the barriers for the flipping of the bridge, which were estimated from



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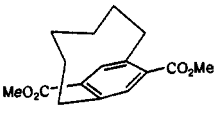

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Table III. Interatomic Bond Distances (Å) and Angles (deg) of [6](1,4)Anthracenophane (**5**)

	Bond Distances		
C(1)–C(2)	1.574 (6)	C(1)–C(18)	1.511 (5)
C(2)–C(3)	1.557 (6)	C(3)–C(4)	1.561 (5)
C(4)–C(5)	1.548 (5)	C(5)–C(6)	1.556 (5)
C(6)–C(7)	1.493 (5)	C(7)–C(8)	1.450 (4)
C(7)–C(20)	1.373 (5)	C(8)–C(9)	1.395 (5)
C(8)–C(17)	1.445 (5)	C(9)–C(10)	1.407 (5)
C(10)–C(11)	1.421 (5)	C(10)–C(15)	1.432 (5)
C(11)–C(12)	1.370 (5)	C(12)–C(13)	1.389 (6)
C(13)–C(14)	1.384 (6)	C(14)–C(15)	1.422 (5)
C(15)–C(16)	1.403 (5)	C(16)–C(17)	1.400 (5)
C(17)–C(18)	1.435 (5)	C(18)–C(19)	1.368 (5)
C(19)–C(20)	1.432 (5)		
	Bond Angles		
C(2)–C(1)–C(18)	106.1 (4)	C(1)–C(2)–C(3)	116.2 (4)
C(2)–C(3)–C(4)	115.8 (4)	C(3)–C(4)–C(5)	116.1 (3)
C(4)–C(5)–C(6)	116.4 (3)	C(5)–C(6)–C(7)	107.7 (3)
C(6)–C(7)–C(8)	119.3 (3)	C(6)–C(7)–C(20)	119.2 (3)
C(8)–C(7)–C(20)	117.6 (3)	C(7)–C(8)–C(9)	122.4 (3)
C(7)–C(8)–C(17)	117.7 (3)	C(9)–C(8)–C(17)	119.7 (3)
C(8)–C(9)–C(10)	121.2 (3)	C(9)–C(10)–C(11)	121.8 (4)
C(9)–C(10)–C(15)	119.5 (4)	C(11)–C(10)–C(15)	118.7 (3)
C(10)–C(11)–C(12)	120.5 (4)	C(11)–C(12)–C(13)	121.1 (4)
C(12)–C(13)–C(14)	120.5 (4)	C(13)–C(14)–C(15)	120.2 (4)
C(10)–C(15)–C(14)	118.8 (4)	C(10)–C(15)–C(16)	119.1 (4)
C(14)–C(15)–C(16)	122.0 (4)	C(15)–C(16)–C(17)	121.8 (4)
C(8)–C(17)–C(16)	118.7 (3)	C(8)–C(17)–C(18)	117.9 (3)
C(16)–C(17)–C(18)	123.4 (3)	C(1)–C(18)–C(17)	119.5 (3)
C(1)–C(18)–C(19)	118.3 (4)	C(17)–C(18)–C(19)	118.3 (4)
C(18)–C(19)–C(20)	119.4 (4)	C(7)–C(20)–C(19)	120.0 (4)

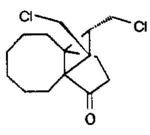
the coalescence temperatures for the AB patterns of Hm and Hn (400 MHz), decrease in the same order although the difference is subtle: **5** ($\Delta G_c^{\ddagger}(268)$ = 13.4 kcal/mol) < **4** ($\Delta G_c^{\ddagger}(273)$ = 13.6 kcal/mol) < **1** ($\Delta G_c^{\ddagger}(278)$ = 13.9 kcal/mol). These results may suggest that the bridges of **5** and **4** are slightly more relaxed than that of **1**.

The X-ray crystallographic structure analysis of **5** clearly reveals the structural features of this molecule (Figure 4). The bond lengths and angles are summarized in Table III. The bond length of the bridged aromatic ring (A) and the central ring (B) are almost normal for an anthracene derivative, suggesting little effect of the short bridge on the π-bond order of these aromatic rings. However, it is worth noting that the bond distances of the remote ring (C), especially C(12)–C(13) (1.389 Å), are rather short compared to those of anthracene itself.[17] The average out-of-plane flip angle (α) of the bridged aromatic ring (A) of **5** is 21.0° which is remarkably greater (by 1.5–1.6°) than those of the [6]paracyclophane derivatives **16**[2] and **17**,[3b] while the bending angle (β) of the benzyl carbons of **5** (19.5°) is only slightly smaller (0.4–0.7°) than those of **16** and **17**. On the other hand, the deformation of the methylene bridge is smaller in **5** than in **16** and **17**. The average bond angle of the benzyl carbons of **5** (106.9°) is larger by 0,4–0.9° while that of the rest of the methylenes (116,1°) is smaller by 0.7–1.4° than those of **16** and **17**. In summation, it is apparent that, in comparison with [6]paracyclophane (**1**), the out-of-plane bending of the aromatic ring of **5** is greater despite the higher π-bond order at the bridgeheads, whereas the bridge of **5** is less stretched because the aromatic ring of **5** can flex more easily than that of **1**. Work on the remarkable reactivities of **4** and **5** is in progress in our laboratories and will be reported shortly.

Experimental Section

NMR and mass spectra were taken with JEOL JMN-GSX-400 an JEOL JMS-DX303 spectrometers, respectively, at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. The X-ray crystal structure analysis of **5** was obtained with use of the facilities of the Crystallographic Research Center, Institute of Protein Research, Osaka University.

Bismethylene[6.3.2]propellanone Ethylene Ketal (7). A solution of 3.25 g (19.8 mmol) of the enone **6** and 24.5 g (200 mmol) of (*E*)-1,4-dichloro-2-butene in 50 mL of CH_2Cl_2 was irradiated through a Pyrex filter at room temperature with a 500-W high-pressure mercury lamp for 27 h. The solvent and the excess olefin were concentrated and the residue was chromatographed on silica gel with 3% ether in petroleum ether as the eluent to give 1.44 g (25%) of a mixture of two minor adducts and 3.51 g (61%) of a major adduct **18**. The major product **18** was recrystallized from ether: mp 86–88 °C; ^1H NMR ($CDCl_3$) δ 3.77 (dd, *J* = 5.9, 11.2 Hz, 1 H), 3.59 (dd, *J* = 9.8, 11.2 Hz, 1 H), 3.58 (d, *J* = 11.2 Hz, 1 H), 3.56 (d, *J* = 11.2 Hz, 1 H), 2.71 (ddd, *J* = 8.8, 10.7, 19.5 Hz, 1 H), 2.48 (ddd, *J* = 4.9, 10.7, 19.5 Hz, 1 H), 2.27 (ddd, *J* = 5.9, 9.8 Hz, 1 H), 2.17–1.96 (m, 3 H), 1.92–1.65 (m, 3 H), 1.61–1.39 (m, 6 H), 1.32–1.18 (m, 2 H), 1.03–0.93 (m, 1 H); IR (KBr) 1720, 1270, 720 cm^{-1}; MS *m/e* (relative intensity) 230 (M^+ + 2, 1) 288 (M^+, 1) 253 (13), 164 (100), 149 (35), 135 (35). Anal. Calcd for $C_{15}H_{22}OCl_2$: C, 62.29; H, 7.67. Found: C, 62.28; H, 7.66. The stereochemistry of the major adduct **18** was assumed to be cis-anti-trans in view of the stereoselectivity observed in the photoreaction of **6** and the related enones with 2-butenes.[18]



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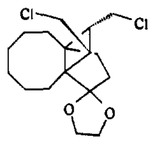
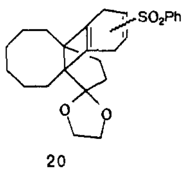


19

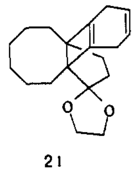
A mixture of 8.90 g (30.8 mmol) of the major photoadduct **18**, 16.8 mL (300 mmol) of ethylene glycol, and 570 mg (3.0 mmol) of *p*-toluenesulfonic acid monohydrate in 100 mL of benzene was heated under reflux for 9 days while water was removed with a Dean–Stark trap. The mixture was diluted with ether and washed with $NaHCO_3$ solution and water. The organic layer was dried ($MgSO_4$), and the solvent was evaporated. The residue was chromatographed on silica gel (elution with 3% ether/petroleum ether) to give 7.88 g (77%) of the ethylene ketal **19**. An analytical sample of **19** was obtained by recrystallization from ether/petroleum ether: mp 68–69 °C; ^1H NMR ($CDCl_3$) δ 3.99–3.88 (m, 4 H), 3.76 (dd, *J* = 5.5, 10.8 Hz, 1 H), 3.63 (dd, *J* = 5.9, 10.3 Hz, 1 H), 3.55 (dd, *J* = 9.7, 10.3 Hz, 1 H), 3.51 (dd, *J* = 10.7, 10.8 Hz, 1 H), 2.26 (ddd, *J* = 5.9, 9.4, 9.9 Hz, 1 H), 2.18 (ddd, *J* = 5.5, 9.6, 10.5 Hz, 1 H), 1.99–1.25 (m, 16 H); IR (KBr) 1145, 1040, 955, 940, 720 cm^{-1}; MS *m/e* (relative intensity) 334 (M^+ + 2, 1), 332 (M^+, 1), 297 (15), 261 (14), 209 (26), 99 (100), 86 (43). Attempted ketalization of the minor photoadducts was not successful which were recovered unreacted.

A solution of the ketal **19** (14.2 g, 42.6 mmol) in 33 mL of THF was added dropwise under nitrogen to a solution of 13.5 g (120 mmol) of potassium *tert*-butoxide in 97 mL of DMSO while the mixture was cooled with ice/water. The solution was stirred at room temperature for 2 h and then poured into ice/water and extracted with ether. The extract was washed with water and dried ($MgSO_4$), and the solvent was evaporated. The residue, after chromatography on silica gel (elution with 2% ether/petroleum ether), gave 10.5 g (95%) of the diene **7** as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 5.32 (s, 1 H), 5.21 (s, 1 H), 4.88 (s, 1 H), 4.67 (s, 1 H), 3.99–3.91 (m, 4 H), 1.93–1.76 (m, 3 H), 1.70–1.44 (m, 11 H), 1.40–1.32 (m, 2 H); IR (neat) 1035, 940, 870 cm^{-1}; MS *m/e* (relative intensity) 260 (M^+, 16), 99 (100).

Benzo[6.3.2]propellenone (8). A mixture of 19.8 g (7.6 mmol) of **7** and 14.0 g (7.8 mmol) of ethynyl tolyl sulfone[9] in 76 mL of benzene was heated under nitrogen at reflux for 7.5 h. The solvent was removed and the residue was chromatographed on silica gel (elution with 20% ether/petroleum ether) to give 31.4 g (94%) of the Diels–Alder adduct **20** as a viscous oil. ^1H NMR of the adduct indicated that the product consisted of a single isomer, though the orientation of the sulfonyl group was not determined: ^1H NMR ($CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.13 (m, 1 H), 3.93–3.77 (m, 4 H), 3.09–2.94 (m, 1 H), 2.85–2.61 (m, 3 H), 2.44 (s, 3 H), 1.85–1.26 (m, 16 H); IR (KBr) 1140, 1040, 940 cm^{-1}.



20



21

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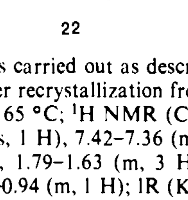
A mixture of **20** (10.0 g, 22.7 mmol), 14.8 g (68 mmol) of 80% $Na_2S_2O_4$, and 11.5 g (136 mmol) of $NaHCO_3$ in 230 mL of aqueous DMF (1:1 = v/v) was heated at 110–120 °C for 30 min. The mixture was diluted with water and extracted with ether. The same experiment was repeated three times, and the product was combined and chromatographed on silica gel. Elution with 5% ether/petroleum ether afforded 12.0 g (59%) of the desulfonylated product **21** as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.75 (m, 2 H), 3.94–3.83 (m, 4 H), 2.82–2.68 (m, 1 H), 2.59–2.46 (m, 3 H), 1.86–0.85 (m, 16 H); IR (neat) 1040, 940 cm^{-1}; MS *m/e* (relative intensity) 286 (M^+, 41), 245 (22), 214 (26), 187 (25), 99 (100).

To a solution of 15.4 g (53.8 mmol) of **21** in 216 mL of benzene was added 13.5 g (59.4 mmol) of dichlorodicyano-*p*-benzoquinone in portions. The mixture was stirred at room temperature for 4 h and then heated at reflux for 1 h. The mixture was filtered, and the filtrate was diluted with ether, washed with 10% NaOH solution and saturated NaCl solution, and then dried ($MgSO_4$). The solvent was removed to give a 15.8 g of a yellow oil which was dissolved in 540 mL of THF and 270 mL of 10% HCl. The solution was heated at 50 °C for 12 h and then diluted with ether. The organic layer was washed with $NaHCO_3$ solution and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (elution with 5% ether/petroleum ether) to yield 11.8 g (89%) of **8** as a white solid. Recrystallization from ether/petroleum ether afforded an analytical sample: mp 51.5–52.5 °C; ^1H NMR ($CDCl_3$) δ 7.25 (dt, *J* = 1.0, 7.3 Hz, 1 H), 7.18 (dt, *J* = 1.0, 7.3 Hz, 1 H), 7.09 (td, *J* = 1.0, 7.3 Hz, 1 H), 7.02 (td, *J* = 1.0, 7.3 Hz, 1 H), 2.51–2.23 (m, 4 H), 2.16 (ddd, *J* = 3.4, 4.9, 15.1 Hz, 1 H), 1.98–1.87 (m, 2 H), 1.77–1.51 (m, 6 H), 1.45–1.38 (m, 1 H), 1.27–1.18 (m, 1 H), 1.01–0.92 (m, 1 H); IR (KBr) 1710, 730 cm^{-1}; MS *m/e* (relative intensity) 240 (M^+, 34), 196 (98), 141 (100). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 85.06; H, 8.30.

Naphtho[6.3.2]propellenone (9). To a solution of 12.7 g (49.0 mmol) of **7** and 14.2 g (60.0 mmol) of *o*-dibromobenzene in 120 mL of toluene was added 40.0 mL (60.0 mmol) of 1.5 M butyllithium in hexane during 3.5-h period under argon atmosphere while the solution was cooled with water. The mixture was stirred at room temperature for 24 h and another portion of dibromobenzene (1.2 g, 5.0 mmol) and 3.0 mL of butyllithium (4.5 mmol) was added. After the solution was stirred for another 18 h, the mixture was diluted with ether, washed with water, and dried ($MgSO_4$). The solvent was removed to give a reddish brown oil which was dissolved in 100 mL of benzene. Dehydrogenation was carried out as described above and the subsequent chromatography (3% ether-/petroleum ether as eluent) gave 10.4 g (64%) of the ethylene ketal **22** as a viscous oil: ^1H NMR ($CDCl_3$) δ 7.82–7.77 (m, 2 H), 7.55 (s, 1 H), 7.40 (s, 1 H), 7.39–7.35 (m, 2 H), 4.22–3.89 (m, 4 H), 2.14–1.94 (m, 4 H), 1.84–1.42 (m, 7 H), 1.36–1.19 (m, 3 H), 1.10–1.01 (m, 1 H), 0.67–0.58 (m, 1 H); IR (neat) 1040, 940, 860, 740 cm^{-1}.

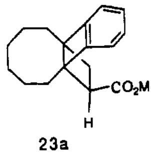


22

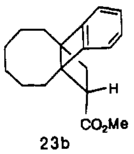
Deprotection of **22** was carried out as described above for **8** to give **9** in 98% yield, which after recrystallization from CH_2Cl_2/ether gave a colorless solid: mp 163–165 °C; ^1H NMR ($CDCl_3$) δ 7.80–7.72 (m, 2 H), 7.49 (2, 1 H), 7.44 (s, 1 H), 7.42–7.36 (m, 2 H), 2.49–2.20 (m, 5 H), 2.06–1.95 (m, 3 H), 1.79–1.63 (m, 3 H), 1.59–1.39 (m, 3 H), 1.27–1.17 (m, 1 H), 1.03–0.94 (m, 1 H); IR (KBr) 1730, 885, 755 cm^{-1}; MS *m/e* (relative intensity) 290 (M^+, 73), 262 (60), 248 (75), 246 (96), 233 (100), 205 (47), 191 (73). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.91; H, 7.62.

Benzo[6.2.2]propellenecarboxylic Acid (10). The α-diazo ketone of **8** was prepared by α-hydroxymethylation followed by diazo transfer in 91% yield as described previously[3a] except that benzene instead of ether was used as the solvent in the former reaction. The crude diazo ketone (2.85 g, 10.7 mmol) was dissolved in 240 mL of aqueous THF (1:1 = v/v), and the solution was irradiated through a filter solution of 0.05 M of 1,4-diphenylbutadiene in THF at 0 °C for 14 h. Most of THF was evaporated, and the residue was diluted with ether. The mixture was extracted with aqueous K_2CO_3 solution, and the extract was washed with ether, acidified with 10% HCl, and then extracted with ether. The organic layer was washed with water and dried ($MgSO_4$), and the solvent was evaporated to give 1.29 g (47%) of **10** as an almost colorless solid. An analytical sample of **10** was obtained by recrystallization from ether/petroleum ether: mp 134–135 °C; ^1H NMR ($CDCl_3$) δ 7.28–7.18 (m, 2 H), 7.11–7.06 (m, 2 H), 3.18 (dd, *J* = 7.3, 9.1 Hz, 1 H), 2.26–2.17 (m, 3 H), 2.10–2.01 (m, 2 H), 1.97–1.90 (m, 1 H), 1.93 (ddd, *J* = 3.7, 7.3, 15.4 Hz, 1 H), 1.63–1.51 (m, 2 H), 1.50–1.39 (m, 2 H), 1.36–1.21 (m, 2 H), 1.19–1.09 (m, 1 H), 1.07–0.97 (m, 1 H); IR (KBr) 3300–2500 (br), 1695, 1235, 750 cm^{-1}; MS *m/e* (relative intensity) 256 (M^+, 28), 211 (47), 155 (75), 141 (100). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.48; H, 7.84.

Treatment of **10** with ethereal diazomethane gave the corresponding methyl ester **23a** which was also obtained as a major product by photolysis of the α-diazo ketone of **8** in methanol (22% yield). While acid **10** was obtained as a single isomer, irradiation in methanol gave **23a** and its epimer **23b** (7%). **23a**: ^1H NMR ($CDCl_3$) δ 7.26–7.17 (m 2 H), 7.09–7.02 (m, 2 H), 3.53 (s, 3 H), 3.15 (dd, *J* = 2.0, 7.3 Hz, 1 H), 2.26–2.20 (m, 3 H), 2.09–2.02 (m, 2 H), 1.98–1.94 (m, 1 H), 1.63–1.52 (m, 2 H), 1.52–1.39 (m, 2 H), 1.36–1.23 (m, 2 H), 1.18–1.10 (m, 2 H); IR (neat) 1730, 1190, 1170, 740 cm^{-1}; MS *m/e* (relative intensity) 270 (M^+, 12), 211 (50), 155 (70), 141 (100). **23b**: ^1H NMR ($CDCl_3$) δ 7.27–7.23 (m, 2 H), 7.16–7.08 (m, 2 H), 3.74 (s, 3 H), 3.01 (dd, *J* = 5.8, 6.4 Hz, 1 H), 2.54 (dd, *J* = 6.4, 12.2 Hz, 1 H), 2.10–2.21 (m, 3 H), 1.98–1.93 (m, 1 H), 1.62–1.45 (m, 3 H), 1.44–1.31 (m, 2 H), 1.26–1.15 (m, 2 H), 1.08–0.97 (m, 1 H), 0.92–0.81 (m, 1 H); IR (neat) 1730, 1190, 1160, 745 cm^{-1}; MS *m/e* (relative intensity) 270 (M^+, 24), 211 (65), 155 (70), 141 (100).



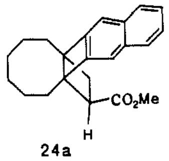
23a



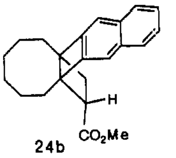
23b

Naphtho[6.2.2]propellenecarboxylic Acid (11). The α-diazo ketone of **9** was prepared as described above in 89% yield. Photolysis of 3.90 g (12.3 mmol) of the diazo ketone in aqueous THF (1:1 = v/v) yielded 1.77 g (47%) of acid **11**, which was recrystallized from ether/petroleum ether to give a colorless solid: mp 202–204 °C; ^1H NMR ($CDCl_3$) δ 7.80 (br d, *J* = 9.3 Hz, 1 H), 7.73 (br d, *J* = 9.4 Hz, 1 H), 7.49 (s, 1 H), 7.46 (s, 1 H), 7.42–7.36 (m, 2 H), 3.26 (dd, *J* = 7.5, 10.0 Hz, 1 H), 2.36–2.25 (m, 4 H), 2.17–196 (m, 4 H), 1.61–1.49 (m, 2 H), 1.29–1.19 (m, 2 H), 1.10 (m, 1 H), 0.95 (m, 1 H); IR (KBr) 3200–2400 (br), 1695, 1235, 930, 870, 755 cm^{-1}; MS *m/e* (relative intensity) 306 (M^+, 100), 261 (60), 249 (39), 236 (43), 205 (50), 191 (61). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.27; H, 7.19.

Photolysis of the α-diazo ketone of **9** in methanol gave esters **24a** and **24b** in 25% and 7% yields, respectively. **24a**: ^1H NMR ($CDCl_3$) δ 7.82–7.77 (m, 2 H), 7.47 (s, 2 H), 7.42–7.36 (m, 2 H), 3.53 (s, 3 H), 3.25 (dd, *J* = 6.8, 10.7 Hz, 1 H), 2.41 (dd, *J* = 6.1, 12.6 Hz, 1 H), 2.34 (dd, *J* = 10.7, 12.6 Hz, 1 H), 2.31 (ddd, *J* = 3.9, 5.9, 15.1 Hz, 1 H), 2.18–2.08 (m, 2 H), 2.01 (ddd, *J* = 3.9, 11.2, 15.1 Hz, 1 H), 1.65–1.45 (m, 4 H), 1.33–1.20 (m, 2 H), 1.15–1.05 (m, 1 H), 1.01–0.91 (m, 1 H); IR (neat) 1730, 1190, 1170, 865, 740 cm^{-1}; MS *m/e* (relative intensity) 320 (M^+, 100), 261 (82), 232 (62), 025 (59), 191 (71). **24b**: ^1H NMR ($CDCl_3$) δ 7.84–7.81 (m, 2 H), 7.56 (s, 1 H), 7.51 (s, 1 H), 7.43–7.41 (m, 2 H), 3.77 (s, 3 H), 3.13 (dd, *J* = 6.8, 7.8 Hz, 1 H), 2.66 (dd, *J* = 6.8, 12.2 Hz, 1 H), 2.17 (dd, *J* = 7.8, 12.2 Hz, 1 H), 2.16–2.11 (m, 2 H), 2.01–1.96 (m, 2 H), 1.65–1.39 (m, 4 H), 1.24–1.15 (m, 2 H), 1.13–0.95 (m, 1 H), 0.90–0.78 (m, 1 H); IR (neat) 1730, 1190, 1170, 960, 740 cm^{-1}; MS *m/e* (relative intensity) 320 (M^+, 100), 261 (93), 231 (48), 205 (58), 191 (72).



24a



24b

8-Chlorobenzobicyclo[6.2.2]dodeca-1(10),11-diene (12). To a solution of 256 mg (1.00 mmol) of **10** and 212 mg (5.00 mmol) of lithium chloride in 5.5 mL of DMSO was added 886 mg (2.00 mmol) of lead tetraacetate in one portion. The mixture was stirred at room temperature for 2.5 h and water was added followed by 10% HCl. The mixture was filtered, and the filtrate was extracted with ether. The extract was dried ($MgSO_4$) and the solvent evaporated. The residue was chromatgraphed on silica gel with petroleum ether as the eluent to give 193 mg (78%) of **4** as a colorless oil: ^1H NMR ($CDCl_3$, 50 °C) δ 7.83–7.79 (m, 1 H), 7.29–7.18 (m, 3 H), 5.94 (d, *J* = 7.0 Hz, 1 H), 3.16 (br d, *J* = 16.5 Hz, 1 H), 2.94–2.86 (m, 1 H), 2.73 (dd, *J* = 7.3, 16.5 Hz, 1 H), 2.27–2.11 (m, 2 H), 2.09–1.98 (m, 1 H), 1.67–1.38 (m, 6 H), 1.25 (br m, 1 H), 0.67 (br m, 1 H); ^{13}C NMR ($CDCl_3$, 50 °C) δ 140.5 (s), 137.5 (s), 135.5 (s), 127.7 (d), 127.5 (d), 126.8 (d), 124.1 (d), 122.5 (d), 76.1 (s), 48.0 (t), 40.1 (t), 33.9 (t), 29.2 (t), 28.4 (t), 22.6 (t), 26.1 (t); IR (neat) 910, 900, 815, 800, 790, 760, 750, 710 cm^{-1}; MS *m/e* (relative intensity) 248 (M$^+$ + 2, 10), 246 (M$^+$, 46), 211 (100), 141 (97); HR MS calcd for $C_{16}H_{19}Cl$ 246.1175, found 246.1178.

8-Chloronaphthobicyclo[6.2.2]dodeca-1(10),11-diene (13). Oxidative decarboxylation of 2.31 g (7.55 mmol) of **11** was carried out as described above to give 1.31 g (58%) of **5** as a pale yellow viscous oil: ^{1}H NMR (CDCl$_3$, 50 °C) δ 8.28 (s, 1 H), 7.86–7.79 (m, 2 H), 7.60 (s, 1 H), 7.46–7.40 (m, 2 H), 6.04 (br d, J = 5.5 Hz, 1 H), 3.19 (br d, J = 17.5 Hz, 1 H), 3.08–3.04 (m, 1 H), 2.80 (dd, J = 7.3, 16.0 Hz, 1 H), 2.38–2.24 (m, 2 H), 2.15–2.10 (m, 1 H), 1.68–1.43 (m, 6 H), 1.12 (br m, 1 H), 0.74 (br m, 1 H); ^{13}C NMR (CDCl$_3$, 50 °C) δ 139.5 (s), 137.7 (s), 133.8 (s), 133.0 (s), 132.9 (s), 128.1 (d), 127.6 (d), 126.3 (d), 126.1 (d), 125.9 (d), 125.0 (d), 121.1 (d), 76.0 (s), 48.9 (t), 40.4 (t), 34.0 (t), 29.1 (t), 28.2 (t), 26.4 (t), 25.1 (t); IR (neat) 1585, 940, 875, 805, 740 cm^{-1}; MS *m/e* (relative intensity) 298 (M$^+$ + 2, 38), 296 (M$^+$, 98), 261 (100), 191 (67); HR MS calcd for $C_{20}H_{21}Cl$ 296.1331, found 296.1332.

[6](1,4)Naphthalenophane (4). To a solution of 137 mg (1.22 mmol) of potassium *tert*-butoxide in 1.5 mL of DMSO was added 150 mg (0.61 mmol) of **12** in 1.0 mL of the same solvent under nitrogen atmosphere. The solution was stirred at room temperature for 15 min before water was added. The mixture was extracted quickly with ether and the extract was washed with saturated NaCl solution and dried (MgSO$_4$). The solvent was evaporated, and the residue was chromatographed on silica gel under nitrogen with use of deaerated solvent (2% ether/petroleum ether) to yield 110 mg (92%) of **4** as a colorless oil: ^{1}H NMR (CDCl$_3$, −50 °C) δ 8.08 (m, 1 H), 7.96 (m, 1 H), 7.46 (m, 2 H), 7.41 (d, J = 7.6 Hz, 1 H), 7.34 (d, J = 7.6 Hz, 1 H), 3.49 (dd, J = 5.6, 12.3 Hz, 1 H), 3.01 (dd, J = 7.0, 12.6 Hz, 1 H), 2.86 (ddd, J = 5.9, 11.7, 12.6 Hz, 1 H), 2.27 (ddd, J = 5.9, 12.0, 12.3 Hz, 1 H), 1.74 (m, 1 H), 1.58 (m, 1 H), 1.11 (m, 1 H), 0.79 (m, 1 H), 0.71 (m, 1 H), 0.34 (dddd, J = 6.2, 6.7, 12.6, 13.2 Hz, 1 H), −0.47, (ddd, J = 7.2, 7.2, 15.0 Hz, 1 H), −1.84 (ddd, J = 7.3, 7.6, 15.0 Hz, 1 H); ^{13}H NMR (CDCl$_3$, −50 °C) δ 140.9 (s), 139.5 (s), 138.9 (s), 134.9 (s), 130.8 (d), 126.8 (d), 125.1 (d), 124.7 (d), 124.3 (d), 123.9 (d), 36.8 (t), 36.0 (t), 33.9 (t), 32.0 (t), 26.9 (t), 24.9 (t); IR (neat) 1510, 810, 790, 780, 770, 750 cm^{-1}; MS *m/e* (relative intensity) 210 (M$^+$, 50), 167 (71), 154 (100); UV λ_{max} (cyclohexane) 314 (log ϵ 3.60), 246 (4.41) nm; HR MS calcd for $C_{16}H_{18}$ 210.1408, found 210.1396.

[6](1,4)Anthracenophane (5). Dehydrochlorination of 1.05 g (3.54 mmol) of **13** was carried out as described above to give 748 mg (81%) of **5** as a yellow solid. An analytical sample, obtained by recrystallization from petroleum ether under nitrogen, was a yellow solid: mp 161–163 °C; ^{1}H NMR (CDCl$_3$, −50 °C) δ 8.58 (s, 1 H), 8.45 (s, 1 H), 8.00 (m, 2 H), 7.48 (m, 2 H), 7.33 (d, J = 7.3 Hz, 1 H), 7.27 (d, J = 7.3 Hz, 1 H), 3.58 (dd, J = 5.2, 12.2 Hz, 1 H), 3.08 (dd, J = 7.0, 12.5 Hz, 1 H), 3.00 (ddd, J = 5.8, 11.3, 12.5 Hz, 1 H), 2.36 (ddd, J = 5.8, 12.2, 12.2 Hz, 1 H), 1.77 (m, 1 H), 1.60 (m, 1 H), 1.14 (m, 1 H), 0.80 (m, 1 H), 0.71 (m, 1 H), 0.38 (dddd, J = 6.2, 6.8, 12.8, 13.1 Hz, 1 H), −0.31 (ddd, J = 7.6, 7.6, 15.0 Hz, 1 H), −1.81 (ddd, J = 7.0, 7.6, 15.0 Hz, 1 H); ^{13}C NMR (CDCl$_3$, −50 °C) δ 141.1 (s), 139.1 (s), 138.7 (s), 134.4 (s), 131.0 (s), 130.5 (s), 130.1 (d), 128.0 (d, 2C), 126.3 (d), 125.1 (d), 125.0 (d), 122.3 (d), 121.9 (d), 37.0 (t), 36.5 (t), 34.5 (t), 31.7 (t), 27.2 (t), 24.9 (t); IR (KBr) 1530, 945, 890, 880, 855, 795, 785, 745, 730 cm^{-1}; MS *m/e* (relative intensity) 260 (M$^+$, 100), 217 (95), 204 (65), 202 (49), 191 (41); UV λ_{max} (cyclohexane) 385 (log ϵ 3.59), 266 (5.19). Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.92; H, 7.74.

X-ray Crystal Structure Analysis of 5. Crystal data: $C_{20}H_{20}$, M_r = 260.4, monoclinic, space group $P2_1/c$, a = 10.228 (1) Å, b = 19.851 (2) Å, c = 6.964 (1) Å, β = 94.889 (6)°, V = 1408.9 (2) Å^3, D_x = 1.226 g cm^{-3}, Z = 4. Diffraction intensities were measured on a Rigaku four-circle diffractometer by using nickel-filtered Cu Kα radiation. A total of 2087 reflections was collected up to 2θ = 120°, among which 1955 were observed reflections. The crystal structure was solved by the direct method (MULTAN-78)[19] and refined by the full-matrix least-squares (X-RAY SYSTEM)[20] to the R index of 0.122.

PE Spectroscopic Investigations. The PE spectra of **4**, **5**, **14**, and **15** have been recorded on a PS 18 spectrometer (Perkin-Elmer Ltd, Beaconsfield) at the following temperatures: **4**, 60 °C; **5**, 110 °C; **14**, 28 °C; **15**, 96 °C. Calibration was achieved with argon and xenon. A resolution of about 0.2 meV on the $^2P_{3/2}$ Ar line was obtained.

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Supplementary Material Available: Preparation and spectra of 1,4-diethylanthracene (**15**) and tables of fractional atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms for **5** (6 pages); observed and calculated structure factors for **5** (17 pages). Ordering information is given on any current masthead page.

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