Dehydroannulenes. I. Synthesis and Properties of 1,5,10,14-Tetramethyl-6,8,15,17-tetrakisdehydro[18]annulene[1]

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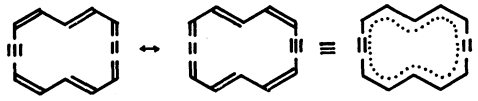
1,6,10,15-Tetramethyl-7,9,15,17-cyclooctadecatetraene-2,4,11,13-tetrayne-1,6-diol (VII), a 18-membered cyclic glycol, was synthesized by a stepwise reaction sequence starting from 3-methyl-2-penten-4-ynal (III). Treatment of the cyclic glycol (VII) with stannous chloride dihydrate in concentrated hydrochloric acid yielded tetramethyltetrakisdehydro[18]annulene (VIII). Examination of the NMR spectra clearly indicates that the tetrakisdehydro[18]annulene (VIII) containing formal diacetylene and hexapentaene units sustains a strong diamagnetic ring current and has a high conformational stability.

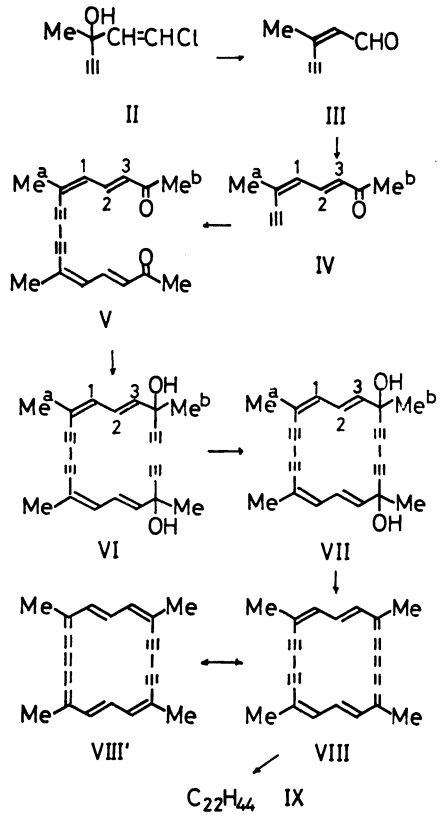
1,8-Bisdehydro[14]annulene (I) obtained by Sondheimer and Gaoni[2] holds an unique position in a wide variety of dehydroannulenes, *i.e.*, the annulene (I) contains formal acetylenic and cumulenic linkages in the



I I'

cyclic system, and equivalent Kekulé structures can be written in contrast to ordinary dehydroannulenes containing one or more acetylenic bonds in which no such type of equivalent resonance structures can be drawn. Bisdehydro[14]annulene (I) can be represented most properly by a symmetrical formula (I'). We have been interested in the synthesis and properties of such symmetrical dehydroannulenes containing linkages of sp-hybridized carbon atoms in the cyclic conjugated system. In this paper, we wish to report the synthesis and properties of tetramethyltetrakisdehydro[18]annulene (VIII) containing formal diacetylene and hexapentaene units in the conjugated ring.[3] The NMR spectrum of VIII provides a clear evidence for the existence of strong diamagnetic ring current in the 18π-electron system.

Ethynyl alcohol (II) prepared by the reaction of ethynylmagnesium bromide with β-chlorovinyl methyl ketone[4] in a high yield was treated with diluted sulfuric acid according to the reported method.[5] Examination of NMR spectrum of the resulting 2-penten-4-ynal reveals that the aldehyde largely consists of the *cis*-isomer (III) (*ca.* 95%) with respect to the ethynyl and the formyl groups consistent with the reported equilibration study of III in acidic conditions[6] being most suitable for the construction of desired 18-membered ring. The aldehyde without separating into pure *cis*-isomer (III) was condensed with acetone by the reported method[5b] with modification to give dieneyne ketone (IV). *trans*-Configuration of the newly formed double bond in IV was confirmed by IR and NMR spectroscopy. Oxidative coupling of IV by cupric acetate in pyridine[7] yielded diketone (V) in an almost quantitative



II III IV V VI VII VIII' VIII $C_{22}H_{44}$ IX

yield. Attempts of bis-ethynylation of the diketone using sodium, lithium or calcium acetylide[8] in liquid ammonia, ethynylmagnesium bromide in tetrahydrofuran and sodium acetylide in *N,N*-dimethylformamide[9] gave fruitless results. Finally, it was found that the diketone (V) can be ethynylated with lithium acetylide–ethylenediamine complex[10] in tetrahydrofuran. The product was chromatographed on alumina. The first substance to be eluted from the column was presumably monoethynylated derivative of V. Desired bis-ethynyl glycol (VI) was obtained from fractions eluted with benzene–ether (4: 6) and ether–ethyl acetate (6: 4) as a yellow viscous liquid in 63% yield. Oxidative coupling of the acyclic glycol (VI) by cupric acetate monohydrate in pyridine–methanol under high dilution conditions using ether as an entraining solvent resulted in a mixture of 18-membered cyclic glycol (VII) in a yield of 69.3%, which, upon chromatography on alumina, yielded a high melting isomer (VIIa) and a low melting isomer (VIIb) in a ratio of *ca.* 1.5: 1. The

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analytical and spectroscopic data, and the molecular weights determined by vapor osmometry were found to be identical. However, mixed melting point determination showed an appreciable depression. The isomerism can be reasonably attributed to *meso*- and *rac*-isomers. Recrystallization of the cyclic glycol (VIIa or VIIb) from acetone, methanol or ethyl acetate gave crystals containing solvent of crystallization in ratio of 1 : 1, 1 : 1 and 1 : 0.5, respectively. Formation of similar adducts has been reported for some 2,4-hexadiyne-1,6-diols and 2-butyne-1,4-diols.[11]

A solution of stannous chloride dihydrate in concentrated hydrochloric acid[12] was added to a vigorously stirred suspension of the cyclic glycol (VIIa or VIIb, or a mixture of them) at room temperature under nitrogen atmosphere. Instantaneous development of deep reddish color was observed. Chromatography of the product in benzene on alumina followed by elution with petroleum ether–benzene yielded a black purple crystalline powder, which gave black purple cubic crystals with metallic lustre upon recrystallization from benzene–petroleum ether (1 : 1) at a low temperature. The crystals gave a reddish purple solution similar to a permanganate solution. Full hydrogenation of the crystals in acetic acid over pre-reduced platinum oxide catalyst gave colorless crystals with low melting point. Absorption of 12.75 moles of hydrogen was observed (theoretical amount for the tetramethyltetrakisdehydro[18]-annulene is 13 moles). The elemental analysis, NMR spectrum and the appearance of molecular ion peak (M^+) at 308 in the mass spectrum provide the support that the low melting hydrocarbon should be tetramethylcycoloctadecane (IX, Mol. wt., 308), thus suggesting the black purple crystals is the desired 1,5,10,14-tetramethyl-6,8,15,17-tetradehydro[18]annulene (VIII). The tetrakisdehydro[18]annulene (VIII) was found to be rather unstable compound. Exposure of crystals of VIII to air and diffused daylight at room temperature caused a complete decomposition in a few hours. But a solution of VIII in benzene–petroleum ether could be kept for two weeks without decomposition in a refrigerator.

The measurement of NMR spectrum of the tetrakisdehydro[18]annulene (VIII) was encoutered by some difficulties owing to the poor solubility. As illustrated in Fig. 1, the NMR spectrum in deuteriotetrahydrofuran exhibited signals at τ 0.34 (d, J=16.0 Hz) and τ 7.42 (s), which could be assigned to the outer and the methyl protons, respectively. Although, the presence of high field signal due to the inner protons was expected in view of the appearance of the outer proton signal at a fairly low field, only a weak signal could be scarcely observed at an extremely high field. Therefore, high

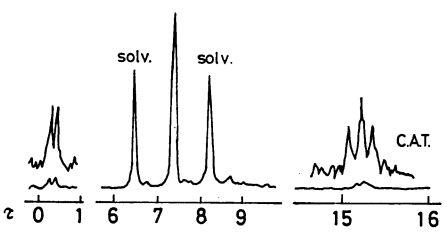


Fig. 1. 100 MHz NMR spectrum of VIII in THF-d_8.

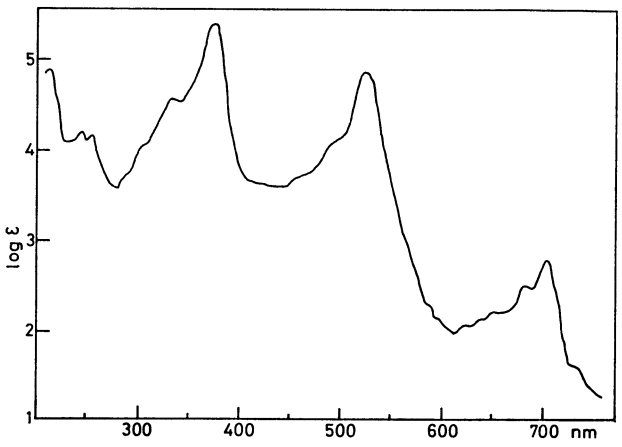


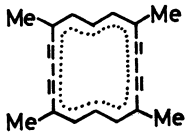
Fig. 2. Electronic spectrum of VIII in THF.

field portion of spectrum was scanned 10 times and treated with C.A.T. technique clearly revealing the presence of signal of the inner protons at a extremely high field (τ 15.24, t, J=16.0 Hz). The NMR spectrum clearly indicates that the tetrakisdehydro[18]-annulene (VIII) containing formal diacetylene and hexapentaene units sustains a strong diamagnetic ring current. Also, the NMR spectral pattern of VIII suggests the equivalence of the outer protons. The electronic spectrum of VIII in tetrahydrofuran, consisting of three main absorption bands, shows features characteristic of [4n+2]annulenes (Fig. 2). Consequently, the tetrakisdehydro[18]annulene (VIII) can be regarded as an aromatic system with delocalized 18π-electrons being resonance hybrid of two equivalent Kekulé structures (VIII and VIII'). In the other words, the tetrakisdehydro[18]annulene (VIII) can be represented most properly by a symmetrical formula (VIII").

Table 1. NMR spectral parameters of VIII in THF-d_8 (100 MHz, τ-values)

Temperature °C	Outer protons d	Methyl protons s	Inner protons t
−60	0.10	6.65	15.66
−40	0.15	6.81	15.56
−20	0.19	6.98	15.49
0	0.27	7.20	15.38
22.5	0.34	7.42	15.23
40	0.41	7.60	15.09
64	0.44	7.78	14.99

As summarized in Table 1, the NMR spectra of VIII were found to be essentially temperature independent over a range of −60 to +64 °C, reflecting a high conformational stability of the tetrakisdehydro[18]annulene skelton provided by the presence of straight linkages of diacetylene and hexapentaene units. Attempts to



VIII"

measure the spectrum at higher temperatures than 64 °C were failed owing to a rapid decomposition of VIII. Increase of diatropicity along with decrease of temperature can be reasonably attributed to an increase of planarity of the 18-membered ring due to diminishing vibration of ring carbon atoms about their equilibrium positions.

The tetrakisdehydro[18]annulene (VIII) forms 1:1 CT complex with 2,4,7-trinitrofluorenone. Attempt to nitrate VIII with cupric nitrate in acetic anhydride[13,14] or with tetranitromethane in pyridine–methanol[15] or with silver nitrate and benzoyl chloride[16] gave fruitless results. Also, no substituted product could be obtained on treatment of VIII with acetic anhydride in the presence of boron trifluoride etherate under various reaction conditions. Because it has been found that substituent is introduced to the carbon atom adjacent to sp-hydridized carbon atoms in electropholic substitution reactions of dehydroannulenes,[14,17] at least one of the causes of the failure of electrophilic substitution seems to be attributable to the fact that the reactive sites in VIII are blocked by the methyl groups. VIII gave no adduct with maleic anhydride.

In view of the strong diatropicity and high conformational stability found in the tetrakisdehydro[18]annulene (VIII), dehydro-annulenes of this type seems to have the most adequate structure for the study of aromaticity of macrocyclic system.

Experimental

All experiments were performed under nitrogen atmosphere under shielding from light. A high dilution appratus was used for the oxidative cyclization reactions of acyclic glycols. The intermediates were stored usually as diluted solutions in a refigerator to minimize decomposition. All melting and boiling points are uncorrected. Brockmann alumina (Act. II—III) was for chromatography, unless otherwise stated. The IR, UV and mass spectra were obtained on a Hitachi EPI-2, a Hitachi EPS-3 and a Hitachi RMU-7HR spectrometers, respectively. Shoulders in UV spectra are indicated by sh, and strong, medium and weak bands in IR spectra are denoted by S, M, and W, respectively. NMR spectra were measured with a Varian A-60 and JNM-RA-I Spectral Accumlator. The chemical shifts are recorded in τ-values with respect to TMS as an internal standard, and the coupling constants are given in Hz. A Hitachi-Perkin Elmer 115 vapor osmometer was used for the measurements of molecular weights.

1-Chloro-3-methyl-1-penten-4-yn-3-ol (II). To an ice-cooled solution of ethynylmagnesium bromide in tetrahydrofuran (305 ml), prepared from magnesium 12.12 g (0.50 mol) and ethyl bromide 60 g (0.56 mol),[18] was added a solution of β-chlorovinyl methyl ketone (35.2 g, 0.34 mol)[4] in the same solvent (120 ml) over 1.5 hr-period. After the mixture had been stirred overnight at room temperature, saturated ammonium chloride solution was added to the mixture under cooling. The organic layer and ethereal extracts of the aqueous layer were combined, and worked up in the usual way. Dark red liquid thus obtained was distilled under reduced pressure in the presence of a small amount of hydroquinone. Ethynyl alcohol (II) was obtained as a colorless liquid, bp 63—68 °C/1596 Pa, 25—30 g (55—66%). In a run performed under similar conditions, II was obtained in 81% yield.

The reaction of β-chlorovinyl methyl ketone with sodium acetylide in liquid ammonia[5b] gave less satisfactory result.

3-Methyl-2-penten-4-ynal (III). Anionotropic rearrangement of II was carried out with diluted sulfuric acid by the reported method.[5b] The aldehyde (III) was obtained as a pale yellow liquid, bp 45.5—51 °C/1463 Pa, 38.8 g, 86%, NMR (60 MHz, CCl_4): 7.87 (d, J=2, 3H, CH_3), 6.37 (s, 1H, -C≡CH), 3.78 (dd, J=8 and 2, 1H, olefinic H), −0.3 (d, J=8, 1H, -CHO). Weak signals of the *trans*-isomer could be observed at 7.68 (d, J=2, CH_3) and 6.5 (s, -C≡CH). The ratio of *cis*- and *trans*-isomers was estimated to be 95:5 on the basis of the relative intensities of the methyl proton signals.

6-Methyl-3,5-octadien-7-yn-2-one (IV). Diene ketone (IV) was prepared by the reported method[5b] with considerable modification. An ice-cooled mixture of 2.6% aqueous sodium hydroxide (27 ml) and ethanol (27 ml) was added in a portion to a stirred and ice-cooled solution of the aldehyde (III, 11.25 g, 0.119 mol) in acetone (54 ml) under nitrogen atmosphere. After being stirred for 1 hr at the same temperature, the reaction was quenched with 1 M sulfuric acid (11 ml). A dark red liquid obtained from ether extracts was distilled in the presence of hydroquinone under reduced pressure to give dieneyne ketone (IV, bp 42—48 °C/4 Pa, light yellow liquid, 7.39 g, 47%, NMR (60 MHz, CCl_4): 7.79 (d, J=2, 3H, Me^a), 7.78 (s, 3H, Me^b), 6.52 (s, 1H, -C≡CH), 3.97 (d, J=15, 1H, olefinic H^3), 3.62 (dd, J=11 and 2, 1H, olefinic H^1), 2.58 (dd, J=15 and 11, 1H, olefinic H^2).

6,11-Dimethyl-3,5,11,13-hexadecatetraene-7,9-diyne-2,15-dione (V). A solution of the dieneyne ketone (IV, 4.8 g, 0.036 mol) in methanol (51 ml) was added over 40 min-period at room temperature to a homogeneous mixture of cupric acetate monohydrate (14.7 g, 0.074 mol), methanol (149 ml) and pyridine (149 ml). The reaction mixture, after being stirred for 3 hr at the same temperature, was poured into 1 M sulfuric acid (1600 ml) under ice-cooling. The mixture containing fine yellow crystals was extracted with ether, and the extracts were washed with water and dried over sodium sulfate. The most part of the solvent was removed under reduced pressure. Further concentration under ordinary pressure yielded fairly pure diketone (V) as pale yellow crystals (4.734 g, 98.7%). The crystals were recrystallized 4 times from methanol to give an analytical specimen, mp 94—95 °C, IR (KBr-disk): 1650—1690 (triplet, C=O), 1590 (*trans* C=C), 980 (*cis* C=C) cm^{-1}, UV: λ_{max}^{EtOH} 248 sh (12700), 260 (17900), 298 (27500), 346 sh (30600), 364 (30900), 388 (24500), NMR (60 MHz, CCl_4): 7.92 (d, J=2, 6H, Me^a), 7.75 (s, 6H, Me^b), 3.97 (d, J=15, 2H, olefinic H^3), 3.45 (dd, J=11 and 2, 2H, olefinic H^1), 2.64 (dd, J=15 and 11, 2H, olefinic H^2).

Found: C, 81.27; H, 6.83%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

3,7,12,16-Tetramethyl-4,6,12,14-octadecatetraene-1,8,10,17-tetrayne-3,16-diol (VI). To a mixture of lithium acetylide-ethylenediamine complex[10] (6.5 g, 0.07 mol) and tetrahydrofuran (100 ml) saturated with acetylene was added at 35 °C a solution of the diketone (V, 3.1 g, 0.012 mol) in the same solvent (35 ml) over a period of 40 min under stirring and bubbling with acetylene. After the mixture had been stirred vigorously for further 3 hr at 30 °C under slow introduction of acetylene, cold water (30 ml) and saturated sodium chloride solution were added successively to the reaction mixture at 10 °C. The organic layer obtained by salting-out the mixture with sodium chloride was combined with ethereal extracts of the aqueous layer, and washed successively with 2 M hydrochloric acid (2 times), water (3 times) and saturated sodium chloride solution (3 times). The solvent was removed, after being dried over sodium sulfate, under reduced pressure to give a dark red liquid. The liquid dissolved in benzene was absorbed on alumina (Woelm, Grade I, 90 g) and eluted with

solvents with increasing polarity. The fractions eluted with benzene–ether–methanol gave bis-ethynyl diol, yellow viscous liquid, 2.32 g (63%). The bis-ethynylation was repeated in nearly the same scale as described above, and total 17 g of the diketone was converted into crude product. The crude product was chromatographed on alumina (Brockmann Act. I, 600 g). A mixture of starting material (V) and monoethynylated product was obtained from benzene–ether (19: 1—3: 2) eluates (1.296 g). Following fractions eluted with benzene–ether (3: 2—2: 3) yielded monoethynylated product (1.303 g). Elution with benzene–ether (2: 3) and ether–ethyl acetate (3: 2) gave desired VI (9.503 g). Although all attempts to crystallize VI were failed, the IR (neat): 3370 (broad, OH), 3330 (–C≡CH), 2190, 2050 (–C≡C–), 960 (*trans* C=C) cm^{-1}, NMR (60 MHz, CCl_4): 8.46 (s, 6H, Me^b), 8.05 (d, J=2, 6H, Me^a), 7.46 (s, 2H, –C≡CH), 6.90 (broad, 2H, OH, disappeared on addition of D_2O), 4.20 (d, J=15, 2H, H^3), 3.70 (dd, J=11 and 2, 2H, H^1), 3.07 (dd, J=15 and 11, 2H, H^2) and UV: λ_{max}^{MeOH} 232 sh, 239 sh, 253, 262, 276, 291, 308, 312, 336, 359 were found to be consistent with the assigned structure.

1,6,10,15-Tetramethyl-7,9,15,17-cyclooctadecatetraene-2,4,11,13-tetrayne-1,6-diol (VII). A solution of the acyclic glycol (VI, 2.003 g, 0.0063 mol) in ether (70 ml), methanol (70 ml) and pyridine (280 ml) was added over 9.5 hr-period to a stirred and refluxing mixture of cupric acetate monohydrate (5.04 g, 0.025 mol), pyridine (2000 ml) and ether (400 ml). After being refluxed for further 1 hr, the mixture was allowed to stand overnight at room temperature. The reaction mixture was concentrated to 200 ml under pressure on a water-bath kept below 50 °C. The concentrate was chilled and poured into 1M hydrochloric acid (2500 ml) under ice-cooling over 30 min-period. The mixture was extracted 5 times with ether, and the extracts were washed with saturated sodium chloride solution and dried over sodium sulfate. Dark brown oily residue obtained by evaporation of the extracts under reduced pressure below 25 °C was dissolved in benzene and chromatographed on alumina (500 g). Elution with ether–ethyl acetate (9: 1—1: 1) yielded a diastereomeric mixture of the cyclic glycol (VII, 1.376 g, 69.3%). The mixture of VII was chromatographed on alumina and careful elution with solvents with increasing polarity resulted in separation of diastereomers. Fractions eluted with ether–ethyl acetate (9: 1—3: 2) yielded a high melting isomer (VIIa, colorless cubes (from dichloromethane), mp 228—230 °C (dec.), IR (KBr-disk): 3360 (singlet, OH), 2190, 2150 (–C≡C–), 968 (*trans* C=C) cm^{-1}, UV: λ_{max}^{EtOH} 245 sh (28600), 254 (49400), 263.5 (61400), 292 (5120), 308 sh (6570), 327 (11600), 344 (18800), 368 (20100).

Found: C, 83.17; H, 6.22%, Mol. wt., 325 (vapor osmometry). Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%, Mol. wt., 316.

When VIIa was recrystallized from methanol, crystals containing 1 mol of methanol were obtained. Removal of the solvent of crystallization was found to be difficult even upon heating to 70 °C *in vacuo* for 39 hr.

Further elution with ether–ethyl acetate (1: 1) and ethyl acetate gave a low melting isomer (VIIb, colorless cubes (from dichloromethane), mp 220—223 °C (dec.), IR (KBr-disk): 3330, 3270 (doublet, OH), 2190, 2150 (–C≡C–), 972 (*trans* (C=C) cm^{-1}, UV: λ_{max}^{EtOH} 246 sh (27700), 254 (49500), 263 (63500), 292 (3330), 307 sh (5110), 326 (10500), 344 (17600), 369 (19300), NMR (60 MHz, DMSO-d_6): 8.53 (s, 6H, Me^b), 8.07 (d, J=2, 6H, Me^a), 6.67 (broad, 2H, disappeared on addition of D_2O), 4.07 (d, J=15, 2H, H^3), 3.34 (dd, J=11 and 2, 2H, H^1), 2.98 (dd, J=15 and 11, 2H, H^2).

Found: C, 83.61; H, 6.38%, Mol. wt., 312 (vapor osmometry). Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%, Mol. wt., 316.

VIIb forms crystals containing 1 mol of acetone and 1/2 mol of ethyl acetate. The acetone could be removed upon heating the crystals to 70 °C *in vacuo* for 23 hr.

Melting point of *ca.* 1: 1 mixture of VIIa and VIIb (203—210 °C) showed an appreciable depression.

1,5,10,14-Tetramethyl-6,8,15,17-tetrakisdehydro[18]annulene (VIII). To a vigorously stirred suspension of a diastereomeric mixture of VII (154 mg, 4.87×10^{-4} mol) in pentane (6 ml) and benzene (3 ml) was added at room temperature under nitrogen atmosphere a solution of stannous chloride dihydrate (270 mg, 1.19×10^{-3} mol) in concentrated hydrochloric acid (3 ml). After 10 min, benzene (15 ml) was added in 3 ml portions over 25 min-period. The reddish purple reaction mixture was poured into water (50 ml), and the organic layer was separated. The aqueous layer was extracted 4 times with ether. The combined organic layer and extracts, after being washed successively with water, aqueous sodium hydrogencarbonate and dried over magnesium sulfate for 3 hr, was concentrated to 50 ml under reduced pressure below 18 °C. Benzene was added to the concentrate and again concentrated under reduced pressure to give a benzene solution of the product (30 ml). The benzene solution thus obtained was passed through a column of alumina (50 g). Elution with benzene–petroleum ether gave VIII as a black purple crystalline powder (77 mg, 56%). Cyclic glycol (VII, 20 mg) was recovered from ether–ethyl acetate eluates. A solution of crude VIII in benzene–petroleum ether (1: 1) was kept in a refrigerator (−14 °C) to give pure VIII as black purple cubes with metallic lustre, which showed no melting point, but underwent color change to yellowish brown at *ca.* 180 °C, IR (KBr-disk): 2940 (M), 2910 (S), 2840 (M), 1535 (W), 1495 (W), 1485 (M, broad), 1365 (M), 1350 (M), 1277(M), 1265(W), 1150 (W), 1020(W), 953 (S), 880 (W, broad) cm^{-1}, UV: λ_{max}^{THF} 217.5 (78000), 237 (15200), 248.5 (14700), 259 sh (5150), 266 sh (4120), 272 sh (3670), 290 sh (4810), 306 sh (10400), 334.5 (35100), 371 (228000), 440 sh (2160), 452 (3230), 490 (11400), 520.5 (74200), 582 sh (185), 596 (124), 622 (121), 639 sh (129), 652 (164), 682 (318), 705 (614), 740 sh (37), NMR (60 MHz, CH_3, s): 6.37 (CCl_4), 6.73 (C_6D_6), 6.79 (DMSO-d_6).

Found: C, 93.56; H, 6.40%. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

The high and low melting isomers (VIIa and VIIb) gave VIII in almost the same yields as the case of diastereomeric mixture.

A solution of pure VIII could be kept for 2 weeks without any change under shielding from light at −14 °C, but as shown in Table 2, at room temperature, decrease of relative absorption intensity (ε_r) of the maximum at 520.5 nm of a solution of VIII in THF (15 mg/l) along with the elapse of time was observed.

Table 2. Decrease of relative absorption intensity

Time (day)	0	1	16	39	79
ε_r	1.00	0.89	0.83	0.61	0.06

Tetramethylcyclooctadecane (IX). VIII (16.618 mg, 5.885×10^{-3} mol) in acetic acid (10 ml) was reduced over pre-reduced platinum oxide catalyst ($PtO_2\cdot2H_2O$, 69.5 mg). Absorption of hydrogen ceased after 3.5 hr (12.75 mol, theoretical value, 13 mol). A solution of the reduction product in pentane was chromatographed on alumina, and eluted with pentane. The eluates were concentrated under reduced pressure to give colorless liquid, which was dissolved in ethyl

acetate–methanol (15:8). Crystals deposited on strong cooling of the solution were recrystallized from the same solvent to yield tetramethylcyclooctadecane (IX), colorless low melting crystals, IR (neat): 2950 (S), 2925 (S), 1460 (M), 1380 (M), 725 (W) cm^{-1}, NMR (60 MHz, CCl_4): 9.15 (CH_3), 8.73 (CH_2), 8.20 (CH).

Found: C, 85.60; H, 14.02%, M^+ 308. Calcd for $C_{22}H_{44}$: C, 85.63; H, 14.37%, Mol. wt., 308.

CT Complex of VIII with Trinitrofluorenone. A mixture of VIII (53 mg, 0.187 mmol), 2,4,7-trinitrofluorenone (80 mg, 0.253 mmol), benzene (4 ml) and methanol (3 ml) was refluxed for 5 min to give a homogeneous solution. The solution was kept at 0 °C overnight. Black purple needles deposited were collected and washed successively with petroleum ether and benzene to give pure 1:1 CT complex, which decomposed at 210 °C forming a grey material.

Found: C, 69.46; H, 3.86; N, 7.14%. Calcd for $C_{35}H_{23}N_3O_7$: C, 70.34; H, 3.88; N, 7.03%.

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