Tetrahedron Vol. 42, No. 2, pp. 655 to 661, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

A STABLE DERIVATIVE OF CYCLOOCTATRIENYNE

SYNTHESIS AND CRYSTAL STRUCTURES OF 1,4,7,10-TETRAMETHYL-5,6-DIDEHYDRODIBENZO[*a,e*]CYCLOOCTENE AND 1,4,7,10-TETRAMETHYLDIBENZO[*a,e*]CYCLOOCTENE[1]

TZE-LOCK CHAN, THOMAS C. W. MAK,* CHI-DUEN POON and HENRY N. C. WONG*†
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

and

JIAN HUA JIA‡ and LI LI WANG‡
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

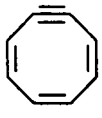
(*Received in Japan* 16 *January* 1985)

Abstract—A stable derivative of cyclooctatrienyne (**1**), namely 1,4,7,10-tetramethyl-5,6-didehydrodibenzo-[*a,e*]cyclooctene (**3**), has been synthesized and fully characterized. X-Ray crystallographic analyses indicate that **3** adopts a "butterfly" conformation intermediate between those of virtually planar 5,6-didehydrodibenzo-[*a,e*]cyclooctene (**2**) and tub-shaped 1,4,7,10-tetramethyldibenzo[*a,e*]cyclooctene (**16**). The methyl substituents effectively shield the otherwise rather exposed strained triple bond of **3** and kinetically stabilize it against dimerization and/or air oxidation.

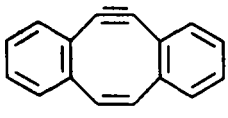
Presumably planar dehydro[8]annulenes are a family of extremely interesting compounds possessing very unusual properties owing to their highly strained structures.[2] The first dehydro[8]annulene, cyclooctatrienyne (**1**), was reported by Krebs as a transient intermediate.[3] A derivative of **1**, namely 5,6-didehydrodibenzo[*a,e*]cyclooctene (**2**), was later prepared and found to be relatively more stable. The monoyne **2** can be obtained in crystalline form, but the crystals quickly decompose after standing at room temperature for a few minutes.[4] Nevertheless, the structure of **2** was recently established by a low-temperature X-ray crystallographic study.[5]

Benzannelation tends to stabilize the fully-conjugated eight-membered carbocycle. Recently, Krebs and Wilke proposed that annelation of benzene rings to cyclooctatrienyne (**1**) would impede oligomerization reactions as well as kinetically stabilize the strained cycloalkyne.[6] Moreover, calculation of the *Q*-value[7,8] and MINDO/3 studies[9] on related compounds both suggested that in **2**, the bonds which are common to the eight-membered ring and the benzo groups should be slightly longer than normal carbon–carbon double bonds and other carbon–carbon bonds of the fused benzene rings. This bond elongation would ease the ring strain in the eight-membered carbocycle and therefore may be partly responsible for the relative stability of **2**. However, this bond lengthening effect has not been fully substantiated by X-ray crystallographic studies.[5,10]

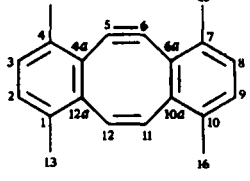
Although monoyne **2** is relatively more stable than **1**, it still decomposes easily in the crystalline state[4] due primarily to the exposure of the strained triple bond, thereby posing serious problems in its handling and characterization. We anticipated that appropriately placed alkyl substituents might sufficiently prevent molecule **2** from experiencing decomposition and/or oligomerization. 1,4,7,10 - Tetramethyl - 5,6 - didehydrodibenzo[*a,e*]cyclooctene (**3**), bearing methyl substituents at positions which would shield the reactive and strained alkyne group, thus appealed to us as a desirable target molecule.



1



2



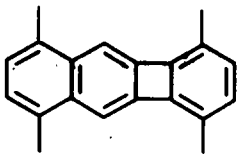
3

The synthesis of title compound **3** through an unexpected route was reported by us in 1978.[11] However, a low-temperature X-ray diffraction study[12] later demonstrated that the structure of the product obtained was in fact 1,4,6,9-tetramethylbenzo[*b*]biphenylene (**4**).§ We now wish to

† Also known as Nai Zheng Huang, to whom correspondence should be addressed.

‡ Undergraduate project participant from the Faculty of Pharmaceutical Science, Shanghai First Medical College, Shanghai, China.

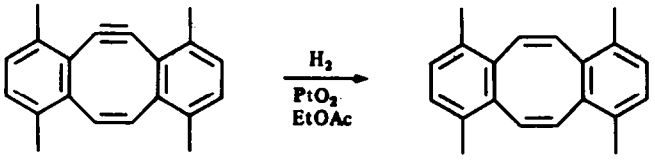
§ Physical and spectroscopic data of **4**: yellow prisms, m.p. 254–255°; electronic spectrum (n-hexane) λ_{max} 233 nm (sh, ε 16,100), 230 (sh, 13,900), 249 (sh, 11,600), 274 (66,300), 282 (95,700), 294 (28,500), 307 (38,800), 355 (3400), 375 (3500), 395 (3980); ^{1}H-NMR ($CDCl_3$): δ 2.13 (s, 6H), 2.39 (s, 6H), 6.50 (s, 2H), 6.80–6.89 (m, 4H); MS: M^+ at *m/e* 258.



4

report a conventional synthesis of monoyne 3 and its unambiguous characterization by X-ray crystallography as well as chemical and spectroscopic methods.

Monoyne 3 formed yellowish needles (from cold pentane) which decomposed at *ca* 88° in a sealed capillary upon rapid heating on an attempted melting point determination. The electronic spectrum of 3 is similar to that of 2.[4] The olefinic protons of 3 evince a 0.7 ppm upfield shift when compared with those of 16, which can be attributed to the paratropic effect manifested in the eight-membered ring of the presumably planar fully-conjugated molecule 3. The IR spectrum of 3 exhibits a weak absorption at 2240 cm^{-1}. The structure of 3 was most convincingly proved by X-ray crystallography (see following section) and by its



3 16

RESULTS AND DISCUSSION

Synthesis

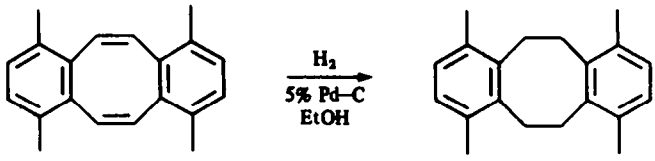
Scheme 1 outlines the preparation of 3. The endoxide 7 was obtained from the Diels–Alder cycloaddition of 2,5-dimethylfuran (5) and maleic anhydride (6). Conc sulfuric acid dehydration converted 7 to 3,6-dimethylphthalic anhydride (8).[13] The anhydride 8 underwent Friedel–Crafts acylation with *p*-xylene to yield 3,6-dimethyl-2-(2,5-dimethylbenzoyl)benzoic acid (9).[14] Spectroscopic data revealed that the pseudo-form 10[15] of 9 prevailed. On treatment with conc sulfuric acid, 10 furnished 1,4,5,8-tetramethylanthraquinone (11).[16] Reduction of 11 by zinc in acetic acid and pyridine gave 1,4,5,8-tetramethylanthracene (12).[16] Diels–Alder reaction between the anthracene 12 and dimethyl acetylenedicarboxylate (DMAD) provided 9,10-dihydro - 9,10 - (1',2' - dicarbomethoxy)etheno - 1,4,5,8 - tetramethylanthracene (13).[17] The ester 13, when subjected to saponification,[18] yielded the diacid 14, which was converted to 9,10 - dihydro - 9,10 - etheno - 1,4,5,8 - tetramethylanthracene (15) by copper-promoted decarboxylation.[18] Photorearrangement[19] of 15 in THF gave 1,4,7,10-tetramethyldibenzo[*a*,*e*]cyclooctene (16), whose structure was subsequently established by smooth hydrogenation in ethanol over 5% Pd–C to the known 1,4,7,10 - tetramethyl - 5,6,11,12 - tetrahydrodibenzo[*a*,*e*]cyclooctene (17),[11] as well as unequivocally by X-ray crystallography (see following section). Bromination[4] of 16 at 0° furnished 1,4,7,10 - tetramethyl - 5,6 - dibromodihydrodibenzo[*a*,*e*]cyclooctene (18). Dehydrobromination[4] of the dibromide 18 by KO^{t}Bu in THF, followed by usual work up,[4] gave 1,4,7,10 - tetramethyl - 5,6 - didehydrodibenzo[*a*,*e*]cyclooctene (3) in 50% yield.

ready absorption of one molar equivalent of hydrogen during hydrogenation over Adams' catalyst to provide 16 in 91% yield.

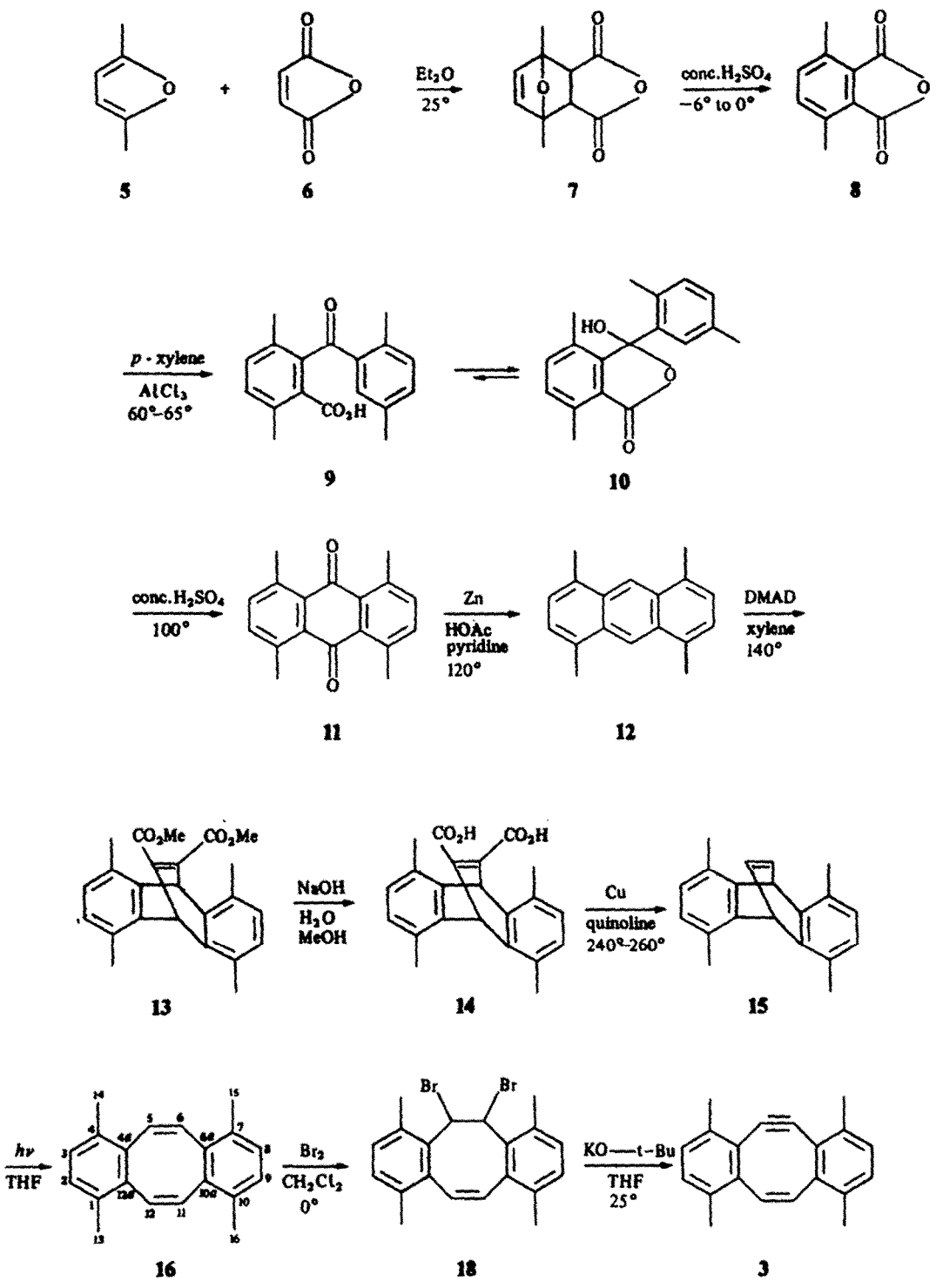
The monoyne 3, in its crystalline form, is remarkably stable and unreactive, which is in striking contrast with the property of its parent compounds 1 and 2. A sample of 3, which had been allowed to stand at room temperature (*ca* 28°) in its crystalline state without protection from air and light for a week showed only negligible decomposition, as revealed by its proton NMR spectrum. On the other hand, 3 is less stable and rather reactive in several solvents such as chloroform and diethyl ether. Insoluble white solids begin to precipitate as the original yellowish color of the solutions gradually fades and finally becomes colorless.

Molecular structure

A perspective view of 3 showing the molecular dimensions averaged according to idealized C_s symmetry is shown in Fig. 1. The bond lengths and angles involving the ethylenic and acetylenic C atoms in the central eight-membered ring are comparable to those in 2 [C=C, 1.333(8); C≡C, 1.211(8) Å; C—C=C, 145.0(5); C—C≡C, 154.0(5)°][5] and 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (19) [C≡C, 1.200(3) Å; C—C≡C, 155.8(2)°].[10] The acetylenic and ethylenic bridges have nearly the same span, 3.78 and 3.75 Å, respectively, between the benzene rings, as the difference in length of the double and triple bonds are compensated by their respective angular deviations from sp^2 and sp geometries. Molecule 16 conforms closely to idealized C_{2v} symmetry, and its average dimensions (Fig. 2) are in good agreement with corresponding values in dibenzo[*a*,*e*]cyclooctene (20).[20] In both 3 and 16, methyl substitution results in a



16 17


Et2O
25°
conc.H2SO4
−6° to 0°
p - xylene
AlCl3
60°-65°
CO2H
HO
conc.H2SO4
100°
Zn
HOAc
pyridine
120°
DMAD
xylene
140°
CO2Me
CO2Me
NaOH
H2O
MeOH
CO2H
CO2H
Cu
quinoline
240°-260°
hν
THF
Br2
CH2Cl2
0°
Br
Br
KO—t-Bu
THF
25°

Scheme 1.

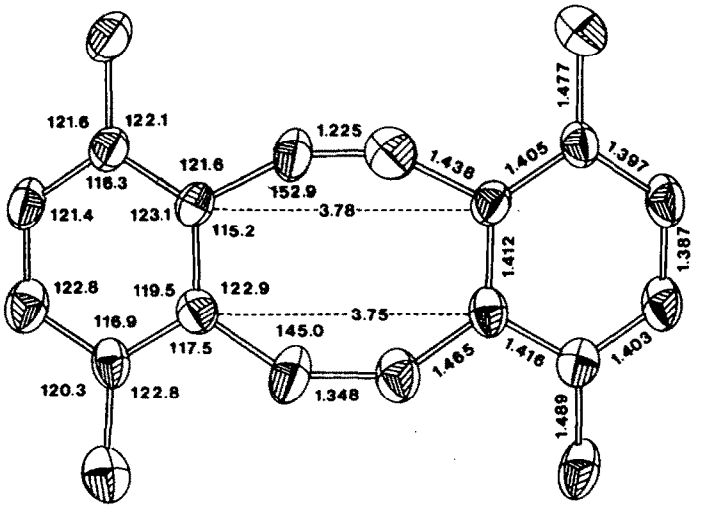
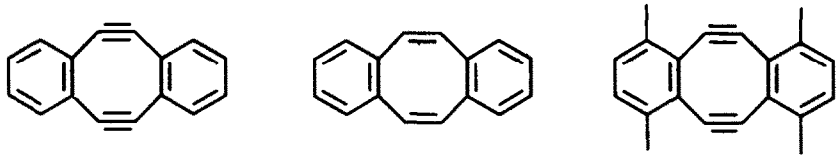


Fig. 1. Perspective view of 1,4,7,10-tetramethyl-5,6-didehydrodibenzo[*a,e*]cyclooctene (**3**) showing molecular dimensions averaged according to idealized C_s symmetry. Standard deviations: ~0.10 Å for C5—C6 and C11—C12, 0.08 Å for other bonds; ~0.6° for bond angles.

significantly smaller endocyclic valence angle at the substituted aromatic C atom.

Previous X-ray studies have established that diyne **19** is planar within 0.100 Å,[10] and that the two crystallographically independent molecules of **2** are planar within 0.031 and 0.174 Å, respectively.[5] In accordance with expectation, the molecular skeleton of **3** adopts a perceptibly "butterfly" shape as a consequence of the steric bulk of the methyl groups, which is also manifested by the inclination of the exocyclic C(aromatic)—C(methyl) bonds away from the central ring. It is convenient to describe the conformations of **3** and **16** quantitatively, relative to



19 **20** **21**

that of the unsubstituted **20**, in terms of the fold angles α and tilt angles β[21] in Table 1. Clearly tetramethyl substitution of **20** to give **16** results in a more folded conformation, and dehydrogenation of **16** to yield **3** corresponds to a flattening of the eight-membered ring. In this context it will be of interest to synthesize the hitherto unknown tetramethyl diyne **21** and investigate its relative stability and molecular structure.

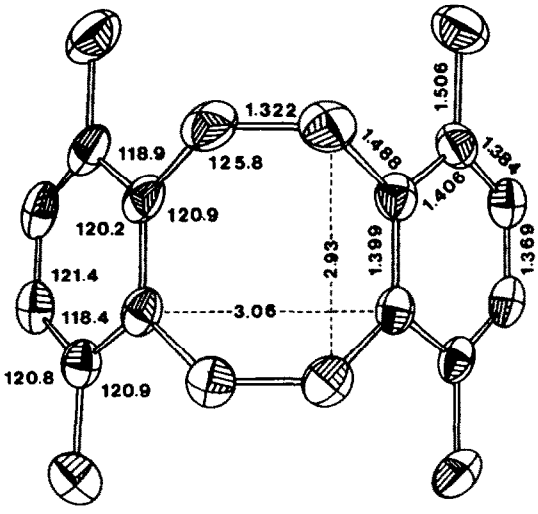


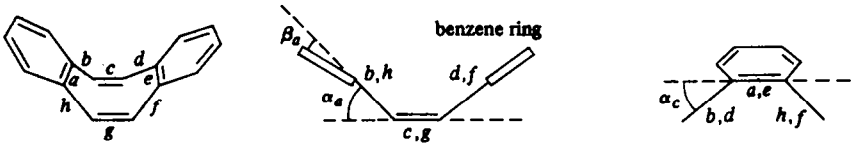
Fig. 2. Perspective view of 1,4,7,10-tetramethyldibenzo-[*a,e*]cyclooctene (**16**) showing molecular dimensions averaged according to idealized C_{2v} symmetry. Standard deviations: ~0.04 Å and 0.3° for bond lengths and angles, respectively.

EXPERIMENTAL

Microanalyses were performed by the microanalytical unit of the Shanghai Institute of Organic Chemistry. M.ps were determined on a hot-stage microscope apparatus unless otherwise stated, and are uncorrected. The electronic spectra were determined on a Perkin–Elmer 559 UV–VIS spectrophotometer. IR spectra were recorded on a Specord spectrophotometer or a Perkin–Elmer 680 spectrophotometer. ^{1}H-NMR spectra were determined on a Varian EM 360L (60 MHz) spectrometer in $CDCl_3$ unless stated otherwise, and the chemical shifts are reported as δ values in ppm downfield from Me_4Si as internal standard. High resolution mass spectra were recorded on a VG MM70-70F spectrometer or a Varian MAT 212 spectrometer. Other mass spectra were recorded on a Finnigan 4021 spectrometer or a Jeol JMS D300 spectrometer. All solvents were purified and dried by standard methods. All solvents were removed under reduced pressure. KO^{t}Bu was obtained from Fluka Chemical Ltd., Switzerland, and was used after purification by sublimation at high vacuum.

1,4 - *Dimethyl* - 7 - *oxabicyclo*[2.2.1]*hept* - 5 - *ene* - 2,3 - *dicarboxylic anhydride* (**7**).[13,22] To a stirred suspension of **6** (49

Table 1. Comparison of conformations[a] of some dibenzo[a,e]cyclooctenes



Molecule	α_a	β	α_c	α_g	Ref.
3	11.2	2.7	21.9	16.4	This work
16	47.0	1.3	50.7		This work
20	43.2	2.9	46.3		20

[a] The fold angle α and tilt angle β are defined as in Ref. 21. The subscript refers to the common edge of the six- and eight-membered rings. In the illustrated example, α_a is the dihedral angle between the plane containing bonds *b*, *a* and *h*, and the plane containing bonds *c* and *g*; β_a is the dihedral angle between the left benzene ring and the plane containing bonds *b*, *a* and *h*.

g, 0.5 mol) in anhyd Et_2O (50 ml) at room temp was added **5** (48 g, 0.5 mol). The mixture was stirred for an additional 2.5 hr after all the maleic anhydride had been dissolved. The resulting crystals were filtered off and washed with anhyd Et_2O (2 × 10 ml). The mother liquid was concentrated and the second crop of crystals were combined with those obtained previously. The total yield of **7** was 80.5 g (83%), m.p. 68–71° (lit.[13] m.p. 59–63°).

3,6-Dimethylphthalic anhydride (**8**).[13] The endoxide **7** (40 g, 0.2 mol) was added in small portions to conc H_2SO_4 (400 ml) cooled at −6°. The mixture was stirred vigorously and the temp of which was not allowed to rise above 0°. After all the endoxide **7** was added and the mixture became orange in color, it was allowed to rise slowly to 10° and was poured slowly onto crushed ice (2 kg). The resulting white crystals were collected on a Buchner funnel and washed with ice water. The crystals were then dissolved in a soln of NaOH (30 g) in H_2O (300 ml). Glacial AcOH (50 ml) was added to the soln. The soln was filtered to remove the insoluble materials and was acidified with 36% HCl (30 ml). The resulting ppt was collected and washed with H_2O until the washing was neutral. The ppt was added to benzene. Azeotropic distillation was performed until the distillate was clear in order to remove most of the water content. The benzene soln was filtered while hot and was concentrated to provide the anhydride **8** as light yellowish needles (21 g, 58%), m.p. 146–147° (lit.[13] m.p. 142–143°); ^{1}H-NMR 2.70 (s, 6H), 7.50 (s, 2H).

The pseudo form **10** *of 3,6-dimethyl-2-(2,5-dimethylbenzoyl)benzoic acid* (**9**).[14] The anhydride **8** (22.66 g, 0.13 mol) was dissolved in *p*-xylene (169 ml) at 0° with mechanical stirring. Anhyd $AlCl_3$ (80 g, 0.6 mol) was added slowly. The mixture was stirred at 60–65° until it became a red–brown homogeneous soln, it was then stirred at 60–65° for an additional 4 hr. It was allowed to cool and poured into ice water (300 ml) and then acidified to pH < 1. The two layers were separated. The aqueous layer was extracted with benzene (4 × 100 ml), and the benzene extracts were combined with the xylene layer. The combined organic layer was extracted with 5% NaOH aq (5 × 100 ml) and the NaOH extracts were treated with activated charcoal and filtered through a thin layer of celite. An equal volume of ice pieces was added to the NaOH aq and the mixture was acidified with 36% HCl (100 ml). The white ppt was collected and washed with warm water (< 40°) until the washings were neutral. The yield of **10** as a white powder was 27.8 g (76%), m.p. 145–147° (lit.[15] 150–152°); MS *m/e* 282 (M^+); ^{1}H-NMR 2.03 (s, 6H), 2.23 (s, 3H), 2.53 (s, 3H), 3.80 (br. s, 1H), 6.90–7.30 (m, 5H).

1,4,5,8-Tetramethylanthraquinone (**11**).[16] The phthalide **10** (10 g, 0.035 mol) and conc H_2SO_4 (70 ml) were heated at 100° for 1.5 hr. The resulting red–brown soln was poured into ice water and the ppt was extracted with hot benzene (60–70°) (5 × 100 ml). The benzene extracts were washed with sat Na_2CO_3 (3 × 150 ml), dried over $MgSO_4$ and concentrated to yield **11** as light yellow needles (4.3 g, 46%), m.p. 225° (lit.[16] 238°); MS *m/e* 264 (M^+); ^{1}H-NMR 2.63 (s, 12H), 7.20 (s, 4H).

1,4,5,8-Tetramethylanthracene (**12**).[16] To a mixture of **11** (5 g, 0.02 mol), activated Zn powder[23] (50 g, 0.7 mol) and pyridine (160 ml) heated at 120° was added dropwise 80% glacial AcOH (160 ml). The mixture was heated at 120° for 1.5 hr, and was poured into water (200 ml). Benzene (3 × 200 ml) was used to extract the organic substance. The benzene extracts were washed with 15% HCl (3 × 150 ml). The soln was evaporated to dryness. The yellowish residue was recrystallized from anhyd EtOH to give **12** as light-yellow needles (1.6 g, 36%), m.p. 215° (lit.[16] 221–222°); ^{1}H-NMR 2.36 (s, 12H), 7.03 (d, J = 2 Hz, 4H), 8.46 (s, 2H).

9,10-Dihydro-9,10-(1',2'-dicarbomethoxy)etheno-1,4,5,8-tetramethylanthracene (**13**). The anthracene **12** and dimethyl acetylenedicarboxylate (6 ml, 42 mmol) were heated at 140° until **12** was completely dissolved. The mixture was allowed to cool with stirring. The crystals formed were collected and washed with anhyd Et_2O (3 ml). The colorless crystals were recrystallized from MeOH to give **13** (3.99 g, 79.30%), m.p. 224–226°; MS *m/e* 376 (M^+); ^{1}H-NMR 2.36 (s, 12H), 3.70 (s, 6H), 5.85 (s, 2H), 6.63 (s, 4H). (Found: C, 76.58; H, 6.38. Calc for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43%.)

9,10-Dihydro-9,10-etheno-1,4,5,8-tetramethylanthracene (**15**). The diester **13** (1.08 g, 2.87 mmol) and NaOH (30 g, 0.75 mol) were refluxed at 100° in 50% aqueous MeOH (300 ml) for 2.5 hr. The resulting mixture was extracted with $CHCl_3$ (3 × 50 ml), and the aqueous soln was then acidified with 36% HCl (100 ml). The acidic aqueous soln was extracted with $CHCl_3$ (3 × 100 ml), and the $CHCl_3$ soln was dried ($MgSO_4$) and evaporated to give the residual **14** (0.85 g, 83.7%), m.p. 245–247° (from EtOH); MS *m/e* 348 (M^+). Diacid **14** could be used immediately without further purification. Diacid **14** (2.28 g, 6.55 mmol), Cu powder (3.26 g, 50 mmol) and quinoline (120 ml) were heated at 240–260° for 30 min. $CHCl_3$ (120 ml) was added to dilute the mixture, which was washed with 10% HCl to remove quinoline. The residue after evaporation was chromatographed on a silica gel column (40 g), eluted with pentane to give colorless crystals **15** (1.25 g, 73%), m.p. 173° (from EtOH); MS *m/e* 264 (M^+); ^{1}H-NMR (CCl_4) 2.41 (s, 12H), 5.49–5.62 (q, J = 3, 4 Hz, 2H), 6.60 (s, 4H), 6.88–6.99 (q, J = 3, 4 Hz, 2H). (Found: C, 92.08; H, 7.74. Calc for $C_{20}H_{20}$: C, 92.26; H, 7.74%.)

1,4,7,10-Tetramethyldibenzo[a,e]cyclooctene (**16**). Compound **15** (1 g, 3.9 mmol) in THF (250 ml) was irradiated with a medium pressure mercury lamp (125 W) for 26 hr. THF was evaporated and the residue was extracted with hot pentane (100 ml). The pentane extract was evaporated and the residue was recrystallized from EtOH to give **16** as colorless needles (0.65 g, 50%), m.p. 169–171°; MS *m/e* 260 (M^+); ^{1}H-NMR 2.18 (s, 12H), 6.63 (s, 4H), 6.85 (s, 4H). (Found: C, 92.05; H, 7.72. Calc for $C_{20}H_{20}$: C, 92.26; H, 7.74%.)

Catalytic hydrogenation of **16** *to 1,4,7,10-tetramethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene* (**17**). Compound **16** (23.3 mg, 0.089 mmol) was hydrogenated at room temp and

Table 2. Data collection and processing parameters

Compound	3	16
Molecular formula	$C_{20}H_{18}$	$C_{20}H_{20}$
Molecular weight	258.36	260.38
Cell constants	$a = 5.011(2)$ Å	$a = 7.519(2)$ Å $\alpha = 100.76(2)°$
	$b = 13.228(4)$	$b = 10.689(3)$ $\beta = 108.67(2)$
	$c = 22.245(6)$	$c = 10.830(3)$ $\gamma = 104.92(2)$
	$V = 1474.5(5)$ Å^3	$V = 761.6(3)$ Å^3 $Z = 2$
	$Z = 4$	
Density (exptl)	1.15 g cm^{-3}	1.13 g cm^{-3}
Density (calc)	1.164 g cm^{-3}	1.135 g cm^{-3}
Space group	$P2_12_12_1$	$P\bar{1}$
Absorption coefficient	0.61 cm^{-1}	0.59 cm^{-1}
Crystal size	0.40 × 0.24 × 0.14 mm	0.42 × 0.36 × 0.22 mm
Scan type and speed	$\omega-2\theta$; 2.02–8.37 deg min^{-1}	
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$	
Background counting	stationary counts for one-half of scan time at each end of scan	
Collection range	$h, k, \pm l$; $2\theta_{max} = 42°$	$h, \pm k, \pm l$; $2\theta_{max} = 54°$
Unique data measured	1387	2900
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	1195	1793
Number of variables, p	193	193
$R_F = \Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.108	0.071
Weighting scheme	$w = [\sigma^2(F_o)+0.0025\lvert F_o\rvert^2]^{-1}$	
$R_G = [\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.130	0.092
$S = [\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(n-p)]^{1/2}$	2.076	1.321
Residual extrema in final difference map	+0.55 to −0.40 e Å^{-3}	+0.19 to −0.24 e Å^{-3}

at atmospheric pressure over 5% Pd–C (40 mg) in abs EtOH (10 ml). The uptake of H_2 was 4.3 ml. The mixture was filtered through a thin layer of celite and evaporated. The residue was recrystallized from anhyd MeOH to give **17** as colorless crystals (23.5 mg, quantitative), m.p. 146° (lit.[11] 148–150°); MS *m/e* 264 (M^+); ^{1}H-NMR 2.20 (s, 12H), 3.03 (s, 8H), 6.55 (s, 4H).

1,4,7,10 - *Tetramethyl* - 5,6 - *dibromo* - 5,6 - *dihydrodibenzo[a,e]cyclooctene* (**18**). To a soln of **16** (514 mg, 1.98 mmol) in CH_2Cl_2 (5 ml) was added dropwise a soln of Br_2 (480 mg, 3 mmol) in CH_2Cl_2 (2 ml) at 0°. After Br_2 addition, the mixture was stirred for an additional 20 min. It was then evaporated and the residue was recrystallized from cyclohexane–CCl_4 to give **18** as light-yellow crystals (716 mg, 86%), m.p. 175–183°; MS *m/e* 418 (M^+); ^{1}H-NMR 2.06 (s, 3H), 2.13 (s, 3H), 2.38 (s, 3H), 2.54 (s, 3H), 5.94–6.60 (ABq centred at 6.24, J = 10 Hz, 2H), 6.82 (s, 4H), 7.04 (d, J = 2 Hz, 2H). (Found: C, 57.18; H, 4.76; Br, 38.78. Calc for $C_{20}H_{20}Br_2$: C, 57.17; H, 4.80; Br, 38.02%.)

1,4,7,10 - *Tetramethyl* - 5,6 - *didehydrodibenzo[a,e]cyclooctene* (**3**). The dibromide **18** (98 mg, 0.23 mmol) in anhyd THF (2 ml) was added dropwise to KO^{t}Bu (150 mg, 1.34 mmol) in anhyd THF (5 ml). The mixture was stirred for an additional 30 min. 1 N HCl (15 ml) was added and was followed by ether extraction (20 ml). The ethereal extract was washed with H_2O (3 × 75 ml), dried ($MgSO_4$) and evaporated. The residue was chromatographed on an alumina column (30 g, Grade III) eluted with pentane. The collected pentane soln was evaporated to give **3** as yellowish crystals (31 mg, 50%). The crystals can be recrystallized by dissolving in a minimum amount of pentane and **3** crystallized as yellow needles when the pentane soln was kept at −20°, m.p. 88° (dec); MS *m/e* 258; ^{1}H-NMR 2.16 (s, 12H), 5.97 (s, 2H), 6.73 (s, 4H); UV (n-hexane) λ_{max} 272 nm (ε 80,500), 282 (87,500), 358 (3540), 369 (sh, 3480), 388 (sh, 2040); exact mass calc for $C_{20}H_{18}$ 258.1408, found 258.1408.

Catalytic hydrogenation of **3** *to* 1,4,7,10-*tetramethyldibenzo[a,e]cyclooctene* (**16**). Adams' catalyst (PtO_2) (9.7 mg) in EtOAc (10 ml) was hydrogenated at room temp and atmospheric pressure to Pt. A soln of **3** (13 mg, 0.05 mmol) in EtOAc (2 ml) was added. Hydrogenation was carried out for 5 hr until the yellow color of the soln disappeared. The uptake of H_2 was 1.5 ml (0.07 mmol). Pt was removed and the solvent was evaporated to give **16** (11.9 mg, 91%). The physical data of **16** were identical to those of an authentic sample of **16**.

X-ray crystallography. Considerable difficulty was experienced in growing crystals of acceptable quality for monoyne **3**, and eventually a wedge-shaped protrusion was cleaved off a crystalline mass. Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo$K\alpha$ radiation, $\lambda = 0.71069$ Å), and determination of the crystal class, orientation matrix, and accurate unit-cell parameters were performed according to established procedures.[24] Intensities were recorded at 22° and processed with the learnt-profile procedure.[25] Data collection and processing parameters for compounds **3** and **16** are summarized in Table 2.

Structure soln was achieved by direct phase determination employing negative quartets.[26] All C atoms were varied anisotropically in subsequent refinement. The Me groups were treated as rigid bodies, and the aromatic and ethylenic (for **16** only) H atoms generated geometrically and allowed to ride on their respective parent C atoms. The protons bonded to C11 and C12 in **3** were located directly from a difference Fourier map. All H atoms were assigned isotropic temperature factors in structure factor calculations.

All calculations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL[27] program package. Analytic expressions of atomic scattering factors[28] were used, and the weighting scheme employed for the blocked-cascade[29] least-squares refinement and analysis of variance was $w = [\sigma^2(\lvert F_o\rvert)+0.0025\lvert F_o\rvert^2]^{-1}$. The R indices and other parameters at convergence are listed in Table 2.†

† The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

Supplementary data deposited with the British Library, Lending Division: bond distances and angles, hydrogen coordinates, anisotropic thermal parameters, and structure factors (27 pages). See Notice to Authors, *Tetrahedron* **40**(2), ii (1984).

Acknowledgement—We thank Mr Y. H. Law for measuring the exact masses for all new compounds. This work was partially supported by a research grant administered by the Royal Society of Chemistry, U.K., as well as by a Messrs. Ho Tim and Ho Yin Research Grant administered by the Chinese University of Hong Kong.

REFERENCES

[1] The preliminary communication of this work has appeared, see N. Z. Huang, J. H. Jia, L. L. Wang, T.-L. Chan and T. C. W. Mak, *Tetrahedron Lett.* **23**, 4797 (1982).
[2] N. Z. Huang and F. Sondheimer, *Accts Chem. Res.* **15**, 96 (1982).
[3] A. Krebs, *Angew. Chem.* **77**, 966 (1965); *Ibid. Int. Ed. Engl.* **4**, 953 (1965); A. Krebs and D. Byrd, *Justus Liebigs Annln Chem.* **707**, 66 (1967).
[4] H. N. C. Wong, P. J. Garratt and F. Sondheimer, *J. Am. Chem. Soc.* **96**, 5604 (1974); H. N. C. Wong and F. Sondheimer, *Tetrahedron* **37(S1)**, 99 (1981).
[5] R. A. G. de Graff, S. Gorter, C. Romers, H. N. C. Wong and F. Sondheimer, *J. Chem. Soc. Perkin Trans 2* 478 (1981).
[6] A. Krebs and J. Wilke, *Top. Curr. Chem.* **109**, 189 (1983).
[7] H. Günther, H. Skyoukh, D. Cremer and K. H. Frisch, *Tetrahedron Lett.* 781 (1974); D. Cremer and H. Günther, *Justus Liebigs Annln Chem.* **763**, 87 (1972).
[8] H. Günther, M.-E. Günther, D. Mondeshka and H. Schmickler, *Ibid.* 165 (1978).
[9] N. Z. Huang, T. C. W. Mak and W.-K. Li, *Tetrahedron Lett.* **22**, 3765 (1981).
[10] R. Destro, T. Pilati and M. Simonetta, *J. Am. Chem. Soc.* **97**, 658 (1975); *Acta Crystallogr. Sect. B* **B33**, 447 (1977).
[11] M.-K. Au, T.-W. Siu, T. C. W. Mak and T.-L. Chan, *Tetrahedron Lett.* 4269 (1978).
[12] C. Romers, private communication (1981).
[13] M. S. Newman and B. T. Lord, *J. Am. Chem. Soc.* **66**, 733 (1944).
[14] M. L. Caspar, J. B. Stothers and N. K. Wilson, *Can. J. Chem.* **53**, 1958 (1975).
[15] W. Carruthers, *J. Chem. Soc.* 5551 (1963).
[16] W. Carruthers, H. N. M. Stewart, P. G. Hansell and K. M. Kelly, *J. Chem. Soc.* (*C*) 2607 (1967).
[17] O. Diels and K. Alder, *Justus Liebigs Annln Chem.* **486**, 191 (1931).
[18] H. P. Figeys and A. Dralants, *Tetrahedron* **28**, 3031 (1972).
[19] P. W. Rabideau, J. B. Hamilton and L. Friedman, *J. Am. Chem. Soc.* **90**, 4465 (1968).
[20] H. Irngartinger and W. R. K. Reibel, *Acta Crystallogr. Sect. B* **B37**, 1724 (1981).
[21] W.-K. Li, S.-W. Chiu, T. C. W. Mak and N. Z. Huang, *J. Mol. Structure* (*Theochem*) **94**, 285 (1983).
[22] O. Diels and K. Alder, *Ber.* **62**, 544 (1929).
[23] R. L. Shriner and F. W. Neumann, *Org. Synth. Coll. Vol.* **3**, 73 (1955).
[24] R. A. Sparks, *Crystallographic Computing Techniques* (Edited by F. R. Ahmed), p. 452. Munksgaard, Copenhagen (1976).
[25] R. Diamond, *Acta Crystallogr. Sect. A* **A25**, 43 (1969).
[26] G. T. DeTitta, J. W. Edmonds, D. A. Langs and H. Hauptman, *Acta Crystallogr. Sect. A* **A31**, 472 (1975).
[27] G. M. Sheldrick, *Computational Crystallography* (Edited by D. Sayre), p. 506. Oxford University Press, New York (1982).
[28] *International Tables for X-Ray Crystallography*, Vol. IV, pp. 99, 149. Kynoch Press, Birmingham (1973).
[29] J. W. Schilling, *Crystallographic Computing* (Edited by F. R. Ahmed), p. 201. Munksgaard, Copenhagen (1970).