Dimethyl 7b-Methyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate. A New 10π-Electron Aromatic System [1]

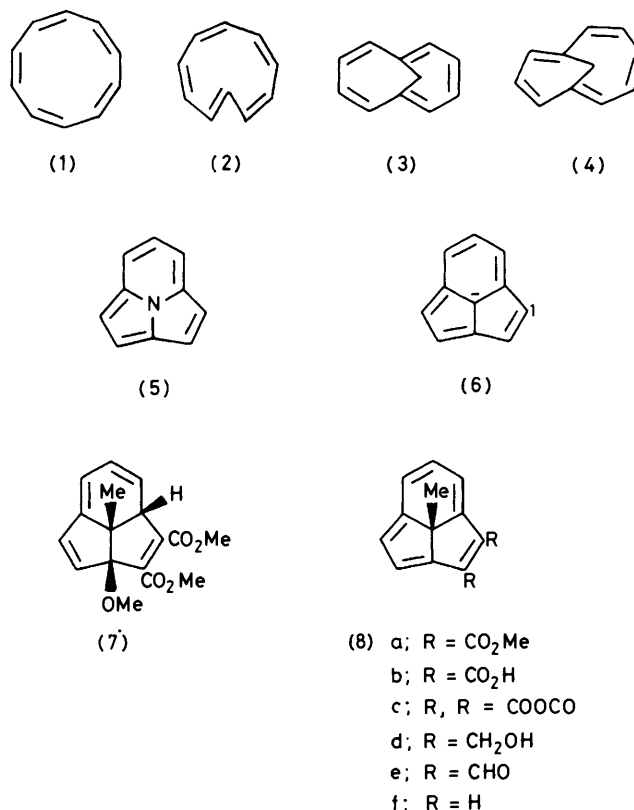**Thomas L. Gilchrist, Charles W. Rees,†and David Tuddenham**
The Robert Robinson Laboratories, University of Liverpool, PO Box 147, Liverpool L69 3BX

The title compound (8a) is formed by the acid-catalysed elimination of methanol from the [8 + 2]-cycloadduct (7) of 3-methoxy-3a-methyl-3aH-indene and dimethyl acetylenedicarboxylate. Its physical and chemical properties are consistent with a 10π-electron aromatic periphery which sustains a diamagnetic ring current. It is photochemically and thermally stable, but rearranges slowly in boiling xylene to the isomer (11) by a [1,5]methyl shift. With copper(ii) nitrate and acetic anhydride, it gives a mixture of mononitro-substitution products. Preliminary experiments show that decarbonylation of the dialdehyde (8e) with tris(triphenylphosphine)rhodium(i) chloride provides a route to the unsubstituted tricyclic [10]annulene (8f).

Investigations of the preparation and properties of [10]annulenes have been important in defining the scope and limitations of the concept of aromaticity. Although [10]annulenes are potentially aromatic according to the Hückel rule, planar or near-planar geometry imposes either severe bond-angle strain or severe steric interactions on the systems. Of the various possible isomers of [10]annulene, only the all-*cis* compound (1) and the compound (2) containing one *trans* double bond have so far been isolated.[2] Both are unstable polyenes which show none of the characteristics expected for aromatic compounds; they are evidently too distorted from planarity to allow overlap of π-bonds. Isomers which contain more than one peripheral *trans*-fused carbon atom suffer a severe interaction between the *endo*-hydrogen atoms in planar or near-planar structures. This problem was overcome by Vogel and his co-workers who replaced the *endo*-hydrogen atoms by bridging groups;[3] 1,6-methano[10]annulene (3) and related compounds show many of the physical and chemical properties associated with aromatic systems. 1,5-Methano[10]annulene [4] (4) and some of its derivatives [5] have been prepared more recently, and also show some evidence of aromatic character. The derivatives of 1,6-methano[10]annulene which have been examined by *X*-ray crystallography are of a ' flattened saucer ' shape, in which the periphery deviates appreciably from planarity,[6] but they still show evidence of delocalisation in terms of bond lengths. No *X*-ray data are available on 1,5-methano[10]annulenes. Both the isomers (3) and (4) also support a diamagnetic ring current, so that signals for the methylene bridge hydrogen atoms appear at high field in the ¹H n.m.r. spectra, and for those on the periphery at low field.

In order to construct a molecule having a periphery containing three *trans*-fused carbon atoms, it is necessary to remove the interactions resulting from the presence of three *endo*-substituents. Boekelheide and his co-workers achieved this by constructing a tricyclic system, cycl[3.2.2]azine (5), with a central nitrogen atom.[7] This ring system is virtually planar,[8] the nitrogen atom is very weakly basic, and the compound supports a diamagnetic ring current; its chemistry is dominated by electron release from the central nitrogen to the periphery. The all-carbon equivalent of the cyclazine (5), the carbanion (6), has also been prepared as its lithium salt;[9] it is protonated and alkylated exclusively at C-1.

As part of our study of the chemistry of 3-methoxy-3a-methyl-3aH-indene we prepared its [8 + 2] cycloadduct (7) with dimethyl acetylenedicarboxylate.[10] The adduct (7)

(1)   (2)   (3)   (4)

(5)   (6)

(7)

(8) a; R = CO₂Me
    b; R = CO₂H
    c; R, R = COOCO
    d; R = CH₂OH
    e; R = CHO
    f; R = H

requires only the elimination of methanol to convert it into the fully conjugated diester (8a). This compound, although having the same carbon skeleton as the carbanion (6), is different in that the central carbon atom is tetra-substituted and so most unlikely to be planar; the CMe group is thus the equivalent of the CH₂ group in the methano[10]annulenes (3) and (4). We therefore undertook a study of the preparation and properties of the diester (8a).

The conversion of the diester (7) into (8a) was achieved by treating the compound with sulphuric acid in methanol at 0 °C, or by heating it with a catalytic amount of toluene-4-sulphonic acid in benzene. The ester (8a) is a stable yellow oil, the electronic spectrum of which shows a long-wavelength absorption at 471 nm (log ε 3.25) (Figure 1). The C-methyl group appears in the ¹H n.m.r. spectrum upfield of tetramethylsilane, at δ − 1.34 whereas the hydrogen atoms on the periphery are in the range δ 7.68—8.22 (Figure 2). The methyl
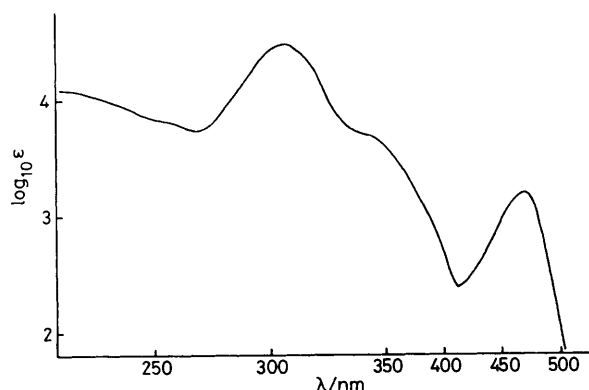
Figure 1. Electronic spectrum of dimethyl 7b-methyl-7bH-cyclo-pent[cd]indene-1,2-dicarboxylate (8a) in ethanol

When it was heated in xylene (138 °C) for 24 h, it was converted in good yield into a colourless, isomeric diester, which was assigned the structure (11). The ^{1}H n.m.r. spectrum showed signals for a C-methyl group at δ 1.68, for the ester methyl groups at δ 3.85 and 3.92, and for two olefinic hydrogen atoms at δ 6.62 and 6.81 as an AB system (J 4.7 Hz); there was also a multiplet centred at δ 7.2 for three hydrogen atoms. These data point to structures (11) and (12) as reasonable alternatives for the rearrangement product. The u.v. spectrum showed the longest wavelength absorption at 311 nm (log ε 3.84) whereas for 1H-cyclopent[c,d]indene [the parent hydrocarbon for structure (12)] the longest wavelength absorption is at 330 nm (log ε 3.60).[9] For this reason, and on mechanistic grounds, we favour structure (11), which can be derived from the diester (8a) by one thermally allowed [1,5]methyl shift. It is evident that the bridged annulene (8a) is less stable than its ' benzenoid ' isomer (11). The diester (8a) was, however, recovered unchanged after irradiation (at 300 nm) for 24 h.
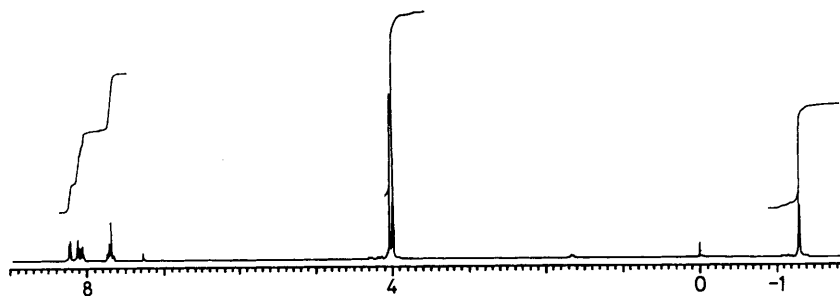

Figure 2. 250 MHz ^{1}H N.m.r. spectrum of dimethyl 7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate (8a) in deuteriochloroform

signal is shifted significantly upfield, and those of the hydrogen atoms significantly downfield, compared with those of the precursor (7). The spectrum is consistent with the existence of a diamagnetic ring current: the high-field signal for the central methyl group can be compared with those for the central methylene groups of the methano[10]annulenes (3)[11] and (4)[4] [which appear at δ −0.5 and δ −0.5, −0.95 (AB) respectively] and for the methyl groups of the bridged [14]annulenes (9)[12] and (10)[13] (δ −4.25 and δ −2.06, respectively).

The ester was hydrolysed with potassium hydroxide in aqueous methanol to give the diacid (8b) which crystallised from ether as orange rhombs. An X-ray analysis of a crystal of the diacid showed that the molecule is dish-shaped, with the central carbon atom having tetrahedral geometry.[1] The bond lengths in the periphery were all found to lie in the range 1.35—1.44 Å with the exception of the bond between the atoms bearing the carboxy-groups, which is 1.47 Å. The bonds joining the central carbon atom to the ring periphery are shorter, at 1.47 Å, than the normal carbon–carbon single bond length of 1.54 Å. This shortening of the bonds must be energetically less demanding than either distortion of the central carbon atom away from tetrahedral geometry or further distortion of the periphery from planarity. The bonds joining the central methylene group to the periphery in 1,6-methano[10]annulene-2-carboxylic acid are similarly shortened to 1.47 Å.[6]

The physical properties of the diester (8a) and of the diacid (8b) thus support their formulation as delocalised [10]annulenes. We undertook a preliminary investigation of some reactions of the diester with the objective of determining what influence the presence of the delocalised system has on the properties of the compound.
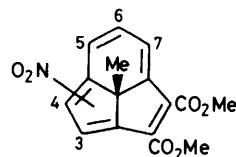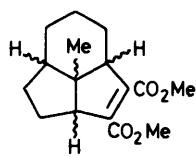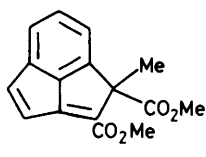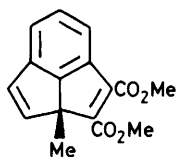
The diester was found to be unstable above about 130 °C.

The ester readily took up 4 mol equivalents of hydrogen when subjected to catalytic reduction with palladium on carbon as catalyst. The ^{1}H n.m.r. spectrum of the product showed no signals for olefinic hydrogen atoms: there was a broad absorption in the range δ 1.0—2.0 with two sharp signals at δ 1.20 and 1.25 and three O-methyl signals were discernible. On this basis, the product is assumed to be a mixture of stereoisomers of the unsaturated diester (13).

In order to investigate whether the diester (8a) would undergo electrophilic substitution, it was treated with acetic anhydride and copper(II) nitrate, the reagent previously used for the nitration of cycl[3.2.2.]azine (5)[7] and of the dihydropyrene (9).[12] Two new components were detected in the product mixture and were isolated by preparative-layer chromatography. The more polar component, a red oil, was a single substance. It was identified as a mono-nitration product and it was isolated in 17% yield. From the ^{1}H n.m.r. spectrum it was evident that this was either the 5-nitro-derivative (14c) or the 7-nitro-derivative (14e): the AB system for the two hydrogens at C-3 and C-4 was still present and there were two adjacent hydrogen atoms at δ 7.74 and 8.60 (J 7.8 Hz) in the six-membered ring. The less polar component, also a red oil, was a mixture of two mononitro-derivatives (25%); the signals due to the two components could be distinguished in the n.m.r. spectrum. One component was the 6-nitro-derivative (14d); the other was either the 3- or the 4-nitro-derivative (14a) or (14b). Thus the diester undergoes mono-nitration, but the product is a mixture of three major isomers, of which only one (the 6-nitro-compound) could be identified unambiguously.

We also undertook a preliminary study of possible routes to the parent hydrocarbon, 7b-methyl-7bH-cyclopent[c,d]indene, based on the removal of the methoxycarbonyl groups from the diester (8a). Attempts to decarboxylate the diacid (8b)

(9)

(10)

(11)

(12)

(13)

(14) a; NO_2-3
b; NO_2-4
c; NO_2-5
d; NO_2-6
e; NO_2-7

using copper chromite in quinoline (a method previously used in a successful synthesis of cycl[3.2.2]azine[14]) were foiled by the thermal instability of the system. A route to the 1,2-dichloro-derivative based on the decarbonylation of the diacid chloride was not pursued when an attempt to convert the diacid (8b) into the diacid chloride gave only the anhydride (8c). The diester was then converted into the dialdehyde (8e) *via* the diol (8d) in the hope that this could be decarbonylated by the use of tris(triphenylphosphine)rhodium(I) chloride. There was insufficient material available to characterise fully the intermediates (8d) and (8e), but the transformations were followed by i.r. and n.m.r. spectroscopy. The position of the bridgehead methyl signal was useful in this respect: it appeared at δ − 1.62 in the spectrum of the diol (8d) and at δ − 1.15 in that of the dialdehyde (8e).

Decarbonylation of the dialdehyde was carried out using an equimolar amount of tris(triphenylphosphine)rhodium(I) chloride in benzene at 80 °C. This gave, in low yield, an impure sample of the parent hydrocarbon (8f) as indicated by the mass spectrum and by the ^{1}H n.m.r. spectrum which showed a signal for the 7bH-methyl group at δ − 1.67 and a pattern of signals in the aromatic region consistent with the symmetrical structure. A survey of the properties of this interesting new hydrocarbon depends on developing an improved procedure for its preparation: this is currently being explored,[15] and full experimental details for the sequence (8d) ⟶ (8e) ⟶ (8f) will be reported shortly.

Experimental

For general points see ref. 10.

Dimethyl 7b-Methyl-7bH-cyclopent[c,d]*indene-1,2-dicarboxylate* (8a).—(a) The dihydrocyclopent[c,d]indene[10] (7) (0.38 g, 1.26 mmol) was suspended in methanol (2 cm^3) and the suspension was cooled to 0 °C. Concentrated sulphuric acid (2 cm^3) was added with stirring. The solution darkened rapidly. After 10 min the mixture was poured into ice–water (20 cm^3) and the product was extracted with ether (3 × 10 cm^3). The combined extracts were washed with brine, dried, and evaporated. Column chromatography of the residue [silica (10 g); ether–light petroleum, 7 : 3] gave the *ester* (8a) (0.255 g, 75%) as a bright yellow oil, b.p. 80—85 °C at 0.02 mmHg; $\nu_{max.}$ (film) 1 715 and 1 705 cm^{-1}; $\lambda_{max.}$ (EtOH) 217 (log ε 3.99), 262sh (3.82), 305 (4.60), 336sh (3.84), and 471 nm (3.25); δ_H − 1.34 (3 H, 7b-Me), 3.99 (3 H, OMe), 4.04 (3 H, OMe), 7.68(2 H, m, $J_{5,6}$ 6.8 Hz, 5-H and 6-H), 8.06 (1 H, d, $J_{6,7}$ 6.8 Hz, 7-H), 8.08 (1 H, d, $J_{3,4}$ 3.6 Hz, 4-H), and 8.22 (1 H, d, $J_{3,4}$ 3.6 Hz, 3-

H); δ_c 29.31 (q, 7b-Me), 52.12 (q, 2 OMe), 58.87 (s, C-7b), 117.58 (d), 120.62 (d), 128.13 (s), 132.56 (d), 134.45 (d), 135.04, 139.84 (d), 159.55 (s), 160.61 (s), 164.48 (s), 164.78 (s), and 174.80 (s); *m/z* 270 (M^+). Further elution gave a mixture (0.05 g) of partially hydrolysed products.

(b) The dihydrocyclopent[c,d]indene (7) (0.05 g, 0.166 mmol) was heated with toluene-4-sulphonic acid (*ca.* 50 mg) in boiling benzene under nitrogen for 2 h, and gave after flash column chromatography, the ester (8a) (0.04 g, 90%).

7b-Methyl-7bH-cyclopent[c,d]*indene-1,2-dicarboxylic Acid* (8b).—The diester (8a) (0.22 g, 0.81 mmol) was stirred with aqueous methanolic potassium hydroxide (0.14 g KOH in 10 cm^3 50% aqueous methanol) for 20 h at room temperature. The methanol was removed under reduced pressure and the basic solution was acidified with hydrochloric acid. The product was extracted with chloroform (3 × 5 cm^3). After drying and evaporation, this solution gave *the diacid* (8b) (0.15 g, 76%), m.p. 194—196 °C (from ether) as orange rhombs (Found: C, 69.4; H, 4.1. C$_{14}$H$_{10}$O$_4$ requires C, 69.4; H, 4.1%); $\nu_{max.}$ (KBr) 3 100—2 300, 1 670, and 1 605 cm^{-1}; $\lambda_{max.}$ (EtOH) 204 (log ε 3.30), 222 (3.08), 2.58 (3.93), 312.5 (4.58), 347 (3.85), and 480 nm (3.49); δ_H [CDCl$_3$–(CD$_3$)$_2$SO] − 1.25 (3 H, 7b-Me), 7.70 (1 H, d, $J_{5,6}$ 6.7 Hz, 5-H), 7.78 (1 H, dd, $J_{5,6}$ 6.7 Hz, $J_{6,7}$ 7.2 Hz, 6-H), 8.22 (1 H, d, $J_{3,4}$ 3.3 Hz, 4-H), 8.48 (1 H, d, $J_{6,7}$ 7.2 Hz, 7-H), and 8.53 (1 H, d, $J_{3,4}$ 3.3 Hz, 3-H); *m/z* 242 (M^+).

7b-Methyl-7bH-cyclopent[c,d]*indene-1,2-dicarboxylic Acid Anhydride* (8c).—The diacid (8b) (0.13 g, 0.54 mmol) was heated in thionyl chloride (5 cm^3) under reflux for 0.5 h. The excess of thionyl chloride was distilled off; flash chromatography of the residue (silica; diethyl ether–light petroleum, 3 : 7) gave the anhydride (0.065 g, 54%) as an orange solid which sublimes at 100 °C and 0.03 mmHg, m.p. 128—130 °C (Found: M^+, 224.0487. C$_{14}$H$_8$O$_3$ requires M^+, 224.0474); $\nu_{max.}$ (KBr) 1 815 and 1 750 cm^{-1}; δ_H − 1.15 (3 H, 7b-Me) 7.90 (2 H, m, 5-H and 6-H), 8.17 (1 H, d, $J_{6,7}$ 7.2 Hz, 7-H), 8.34 (1 H, d, $J_{3,4}$ 3.2 Hz, 4-H), and 8.36 (1 H, d, $J_{3,4}$ 3.2 Hz, 3-H).

Thermal Rearrangement of the Diester (8a).—The diester (0.16 g, 0.59 mmol) was heated in dry degassed xylene (5 cm^3) under reflux (138 °C) for 24 h. The solvent was removed; flash chromatography of the residue (silica; diethyl ether–light petroleum 1 : 9) gave *dimethyl 2a-methyl-2aH-cyclopent*[c,d]-*indene-1,2-dicarboxylate* (11) (0.113 g, 71%), b.p. 110—115 °C at 0.2 mmHg (Found: M^+, 270.088 7. C$_{16}$H$_{14}$O$_2$ requires M^+, 270.087 5); $\nu_{max.}$ (film) 1 730, 1 720, 1 705, and 1 555 cm^{-1}; $\lambda_{max.}$ (EtOH) 205 (log ε 4.42), 252 (3.95), 270 (3.92), 283 (3.88), and 311 nm (3.84); δ_H 1.68 (3 H, 2a-Me), 3.85 (3 H, OMe), 3.92 (3 H, OMe), 6.62 (1 H, d, $J_{3,4}$ 4.7 Hz, 4-H), 6.81 (1 H, d, $J_{3,4}$ 4.7 Hz, 3-H), and 7.2 (3 H, m, ArH).

Hydrogenation of the Diester (8a).—A solution of the diester (0.049 g, 0.18 mmol) in ethanol (1 cm^3) was added rapidly to a suspension of 5% palladium on carbon (0.1 g) in ethanol (2 cm^3) under hydrogen. The diester absorbed 4 equivalents of

hydrogen in 0.5 h, then the absorption ceased. The catalyst and solvent were removed to leave *dimethyl 7b-methyl-3,4,5,5a,6,7,7a,7b-octahydro-7aH-cyclopent*[c,d]*indene-1,2-dicarboxylate* (13) (0.050 g, 99%) as a colourless oil, b.p. 95—100 °C at 0.3 mmHg (Kugelrohr) (Found: C, 68.9; H, 7.8. $C_{16}H_{22}O_4$ requires C, 69.1; H, 7.9%); $\nu_{max.}$ 1 730, 1 715, and 1 705 cm^{-1}; δ_H 0.8—2.0 (13 H, m), 2.92—3.05 (1 H, d), and 3.7 (6 H, OMe); m/z 278 (M^+).

Nitration of the Diester (8a).—Powdered cupric nitrate trihydrate (0.05 g, 0.2 mmol) was added to a solution of the diester (0.054 g, 0.2 mmol) in acetic anhydride (2 cm^3) and the mixture was stirred at room temperature for 6 h. It was then poured into ice–water (20 g). The product was extracted with ether (3 × 5 cm^3). The ethereal solution was washed with saturated aqueous sodium hydrogencarbonate, dried, and evaporated to leave an orange oil (0.08 g). Layer chromatography was carried out on silica, the plate being developed first with diethyl ether–light petroleum (2 : 5) and again with diethyl ether–light petroleum (3 : 5). This gave (i) the starting ester (0.013 g, 24%); (ii) at R_F 0.6, a mixture of the 6-nitro-(14 d) and the 3- or 4-nitro-derivatives (14a) or (14b) (0.012 g, 25%) as a red oil; m/z 315 (M^+). The ^1H n.m.r. spectrum of this oil contains signals which can be assigned to each of the two components: $\delta - 1.08$ (3 H, two s, 7b-Me); then for (14d): 8.30 (d, $J_{3,4}$ 3.9 Hz, 4-H), 8.38 (d, $J_{3,4}$ 3.9 Hz, 3-H), 8.56 (s, 5-H), and 8.90 (s, 7-H); for (14a) or (14b): 7.90 (t, $J_{5,6}$ 7.8, $J_{6,7}$ 7.8 Hz, 6-H), 8.08 (d, $J_{6,7}$ 7.8 Hz, 7-H), 8.32 (d, $J_{5,6}$ 7.8 Hz, 5-H) and 8.42 (s, 3-H or 4-H). Fraction (iii) from the plate contained as a single component at R_F 0.2, the 5- or 7-nitro-derivative (14c) or (14e) (0.008 g, 17%) as a red oil; δ_H −1.10 (3 H, 7b-Me), 4.05 (6 H, OMe), 7.74 (1 H, d, $J_{6,7}$ 7.8 Hz, 6-H or 7-H), 8.25 (1 H, d, $J_{3,4}$ 3.8 Hz, 3-H or 4-H), 8.50 (1 H, d, $J_{3,4}$ 3.8 Hz, 4-H or 3-H), and 8.60 (1 H, d, $J_{6,7}$ 7.8 Hz, 7-H or 6-H); m/z 315 (M^+).

Acknowledgement

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