7b-Methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxylic Acid, a New 10 π-Electron Aromatic System; *X*-Ray Crystal Structure

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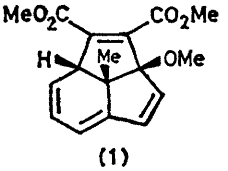
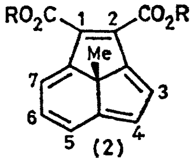
Summary The title compound (**2b**)‡ and its dimethyl ester (**2a**) have been synthesised from the cycloadduct of 3-methoxy-3a-methyl-3a*H*-indene and dimethyl acetylenedicarboxylate; n.m.r. spectra and an *X*-ray crystallographic analysis of (**2b**) show that they are aromatic compounds.

The cycloaddition of dimethyl acetylenedicarboxylate to 3-methoxy-3a-methyl-3a*H*-indene, reported in the preceding Communication,[1] provides an entry into the cyclopent[*cd*]indene ring system. Adduct (**1**) simply requires the removal of the elements of methanol to convert it into a cyclopent[*cd*]indene (**2a**) with a fully conjugated periphery and a methyl group at the central (7b) position. This reaction proved to be straightforward; the adduct (**1**) was converted into (**2a**) (65%), b.p. 80—85 °C at 0·02 mmHg, by dissolving it in 1 : 1 concentrated H_2SO_4–MeOH at 0 °C.



(**1**)

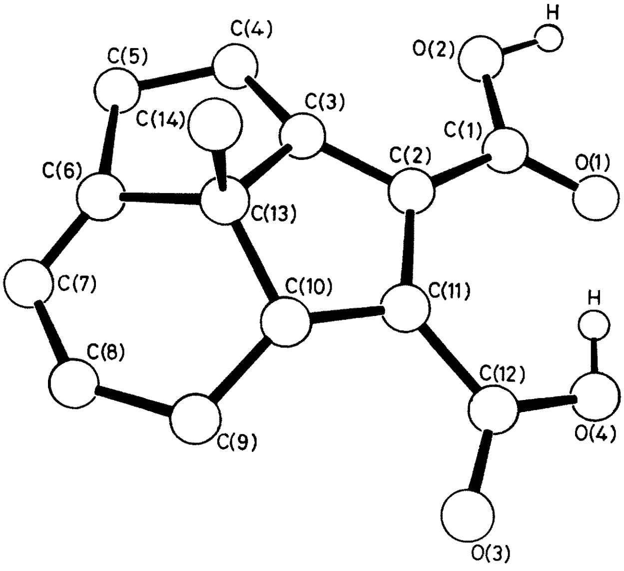


(**2**)
a; R = Me
b; R = H

Compound (**2a**) is a stable yellow oil, λ_{max} (EtOH) 217 (log ε 3·99), 262 (3·82), 305 (4·60), 336 (3·84), and 471 (3·25) nm. The ^{1}H n.m.r. spectrum ($CDCl_3$) shows a signal upfield of tetramethylsilane (at δ −1·34) for the 7b-methyl group. The ester methyl groups are at δ 3·99 and 4·04, and the peripheral hydrogen atoms at δ 7·68 (H-5 and H-6), 8·06 (H-7), 8·08 (H-4), and 8·22 (H-3); $J_{3,4}$ 3·6, $J_{5,6}$ 6·8, and $J_{6,7}$ 6·8 Hz. The n.m.r. spectrum is consistent with the existence of a diagmagnetic ring current, the central methyl group being shifted upfield, and the peripheral hydrogen atoms downfield, compared with the spectrum of the precursor (**1**).[1]

The ester was readily hydrolysed to the dicarboxylic acid (**2b**), m.p. 195—197 °C, which is a stable orange solid with spectral characteristics similar to those of the ester. Thus, it shows a long-wavelength absorption at 480 nm (log ε 3·49), the central methyl group appears in the ^{1}H n.m.r. spectrum at δ −1·25 ($CDCl_3$), and the peripheral hydrogen atoms appear in the range δ 7·7—8·5.

Crystal data: crystals of the dicarboxylic acid (**2b**) are beautiful rhombs. They are monoclinic, $a = 8·543(1)$, $b = 14·068(1)$, $c = 9·901(1)$ Å, $\beta = 107·45(1)°$ space-group $P2_1/n$, $Z = 4$. Intensities of 1931 reflections (1776 classed as observed) were measured ($\theta \leqslant 65°$) on a Siemens off-line four-circle diffractometer with Cu-K_α radiation. The structure was solved by direct methods and refined to give $R = 0·049$.§



Figure

The analysis has shown the molecule (Figure) to be dish-shaped with C(13) having tetrahedral geometry.¶ The peripheral bonds all exhibit partial double-bond character consistent with aromaticity. Bond lengths lie in the range 1·35—1·44 Å except for C(2)–C(11) (1·47 Å) which is dominated by the hydrogen-bonded carboxylic acid groups. There is a strong asymmetric intramolecular hydrogen bond [2·520(3) Å] between O(4) and O(1) and an intermolecular hydrogen bond [2·609(3) Å] between O(2) and O(3) linking screw-related molecules. The structure is

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‡ Alternative names: 11-methyl-1,4,7-metheno[10]annulene-2,3-dicarboxylic acid and 11-methyltricyclo[6.2.1.0^{4,11}]undecapentaene-2,3-dicarboxylic acid.

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

¶ The angles at C(13) are: C(14)–C(13)–C(10) = 109·5(2), C(14)–C(13)–C(3) = 109·1(2), and C(14)–C(13)–C(6) = 108·1(2)°.

disordered with approximately 35% of sites occupied by the configurational isomer of (**2b**) with the carboxyl groups at the 3 and 4, rather than the 1 and 2, positions **

The ring system (**2**) is thus a [10]annulene with three *trans* double bonds where the three inner hydrogens are replaced by a one-carbon bridge, leaving the peripheral ring sufficiently near to planarity for delocalisation of the π-electrons It is structurally related to, and intermediate between, Vogel's bicyclic [10]annulenes[2] and Boekelheide's tetracyclic [14]annulenes[3] Few tricyclic annulenes are known,[4] (**2**) is the smallest one yet reported and is the first tricyclic [10]annulene

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** This diastereoisomer can alternatively be visualised as the enantiomer of (**2b**), with the carboxyl groups at the 1 and 2 positions as shown, but with the pattern of single and double C–O bonds of each group reversed

[1] T L Gilchrist, C W Rees, and D Tuddenham, *J Chem Soc*, *Chem Commun*, preceding communication

[2] E Vogel and H D Roth, *Angew Chem*, *Int Ed Engl*, 1964, **3**, 228 E Vogel W Klug, and A Breuer, *Org Synth*, 1974, **54**, 11

[3] V Boekelheide and J B Phillips, *J Am Chem Soc*, 1967, **89**, 1695, J B Phillips, R J Molyneux, E Sturm, and V Boekelheide, *ibid*, p 1704, R H Mitchell and V Boekelheide, *ibid*, 1970, **92**, 3510

[4] E Vogel, J Sombroek, and W Wagemann, *Angew Chem*, *Int Ed Engl*, 1975, **14**, 564