#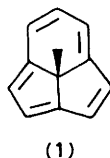 Tricyclic [10]Annulenes. Part 4.[1] The Effect of Benzo-fusion: Synthesis, Properties, and X-Ray Structure of 9c-Methyl-9cH-cyclopenta[jk]fluorene[2]

Raymond McCague, Christopher J. Moody, Charles W. Rees, and David J. Williams
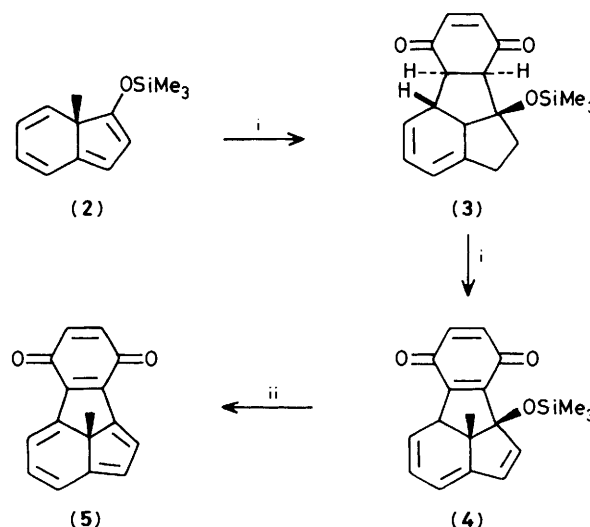*Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY*

The effect of benzo-fusion on the tricyclic [10]annulene (1) has been investigated. The benzo-fused annulene (7) was synthesised from the dialdehyde (6) by a bis-Wittig reaction, and has been shown to retain about two-thirds of the ring current of (1). Accurate bond lengths in (7) have been determined by X-ray crystallography. Synthesis of the annulenequinone (5) and the annulenopyridazine (8), and the X-ray structure determination of the dialdehyde (6) are also described.

In recent years there has been considerable effort in trying to rationalise the effects of benzo-fusion on aromatic annulenes.[3] Of central importance has been the question of whether benzannelation of a delocalised macrocyclic ring reduced delocalisation in the large ring or stopped it all together. The early results showed clearly that the delocalisation was reduced but not suppressed completely.[3] We have recently described the synthesis and properties of 7b-methyl-7bH-cyclopent[cd]-indene (1) and some of its derivatives.[1,4] In this tricyclic [10]annulene, the effects of substituents are easily monitored by the chemical shift of the central methyl group in the ^1H n.m.r. spectrum, and by measuring the rate of isomerisation to the 2aH-isomer, *via* a [1,5]methyl shift, on heating.[4] Hence using these two probes we have investigated the effect of benzo-fusion on the tricyclic [10]annulene (1).

(1)

Scheme 1. *Reagents:* i, benzoquinone; ii, TsOH, CHCl₃, reflux

Results and Discussion

Preparation of Fused Tricyclic [10]Annulenes.—The initial approach to a benzannelated tricyclic [10]annulene involved the cycloaddition of benzoquinone to a 3aH-indene.[5] Thus addition of benzoquinone to a solution of the trimethylsiloxy-3aH-indene (2), prepared as previously described,[5] gave a deep red solution. This colour was possibly due to a charge-transfer complex and slowly disappeared. Isolation of the product was difficult, but after chromatography the yellow adduct (3) was isolated in low yield (10%). The *exo*-stereochemistry was assigned on the basis of its n.m.r. spectrum supported by nuclear Overhauser effect (n.O.e.) measurements; in particular, pre-irradiation of the central methyl or trimethylsilyl groups did not cause any enhancement of the protons at the 9a-position that would be expected if the stereochemistry was *endo*. The adduct (3) was unstable on silica gel, presumably due to its tautomerisation to a hydroquinone, and the quinone (4) could be isolated (up to 24%). This quinone is probably formed by oxidation of the hydroquinone tautomer of (3) by any excess of benzoquinone present. Elimination of the elements of trimethylsilanol from the quinone (4) by heating with toluene-*p*-sulphonic acid in chloroform gave the purple annulene quinone (5) in 33% yield (Scheme 1). The central methyl group in (5) resonates at δ − 1.01 in the ^1H n.m.r. spectrum, and hence established the annulene structure. However, in view of the poor yields further work on the benzoquinone adducts was not

attempted, and an alternative route to the required benzo-fused annulene was investigated based on a bis-Wittig reaction of the annulenedicarbaldehyde (6).

The dialdehyde (6), which was previously used as an intermediate on one of the routes to the parent annulene (1),[4] is readily prepared. It is a stable orange-red crystalline solid, and in view of the disorder shown in the structure of the corresponding dicarboxylic acid,[6] an X-ray analysis of (6) was also undertaken. The molecule (Figure 1) adopts the characteristic 'reversed umbrella' conformation with the central carbon atom remaining tetrahedral. Table 1 lists the fractional atomic co-ordinates. Tables 2 and 3 give the bond lengths and valence angles respectively. The bond lengths between peripheral atoms in the ordered part of the structure have characteristic aromatic values. The principal departures occur in the disordered region with an apparently long C(5)–C(6)† bond of 1.51 Å and short C(6)–C(7)† bond of 1.30 Å. These deviations may however not be genuine.

Because of the different geometries of the 5- and 6-membered rings, atom overlap of the two diastereoisomers cannot be perfect. The atomic positions of the two overlap components for C(4), C(5), C(8), and C(9)† are too close to each other to permit them to be resolved and refined independently. Consequently the effective smearing out of the combined positions has been artificially compensated for by the

---

† Numbering of the crystallographic Figures only.

Table 1. Atom co-ordinates (× 10^4) and temperature factors (Å^2 × 10^3)

Atom	x	y	z	U
C(1)	2 321(2)	1 046(2)	3 563(1)	62(1)*
C(2)	1 749(2)	2 519(2)	3 670(1)	63(1)*
C(3)	313(2)	2 418(2)	3 465(1)	72(1)*
C(4)	−856(2)	3 105(2)	3 749(2)	88(1)*
C(5)	−1 956(2)	2 162(2)	3 766(2)	92(1)*
C(6)	−2 113(3)	481(4)	3 674(3)	93(1)*
C(6a)	−1 604(4)	−658(4)	3 611(4)	83(1)
C(7)	−1 030(3)	−162(3)	3 402(2)	76(1)*
C(7a)	−1 391(4)	901(4)	3 468(3)	68(1)
C(8)	−481(2)	−1 663(2)	3 518(2)	94(1)*
C(9)	912(2)	−1 475(2)	3 442(2)	85(1)*
C(10)	1 251(2)	30(2)	3 289(1)	70(1)*
C(11)	−24(2)	916(2)	3 001(1)	71(1)*
C(12)	−423(2)	1 029(2)	1 724(1)	77(1)*
C(13)	2 531(2)	3 860(2)	4 064(1)	81(1)*
C(14)	3 771(2)	607(2)	3 824(2)	85(1)*
O(2)	4 724(1)	1 438(2)	4 121(2)	119(1)*
O(1)	2 008(2)	5 047(1)	4 192(1)	119(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 2. Bond lengths (Å)

C(1)–C(2)	1.446(2)	C(1)–C(10)	1.386(2)
C(1)–C(14)	1.458(2)	C(2)–C(3)	1.392(2)
C(2)–C(13)	1.460(2)	C(3)–C(4)	1.397(3)
C(3)–C(11)	1.474(3)	C(4)–C(5)	1.373(3)
C(5)–C(6)	1.513(4)	C(5)–C(7a)	1.334(4)
C(6)–C(7)	1.301(4)	C(6a)–C(7a)	1.424(5)
C(6a)–C(8)	1.441(5)	C(7)–C(8)	1.443(4)
C(7)–C(11)	1.519(3)	C(7a)–C(11)	1.546(5)
C(8)–C(9)	1.396(3)	C(9)–C(10)	1.406(2)
C(10)–C(11)	1.472(2)	C(11)–C(12)	1.549(2)
C(13)–O(1)	1.200(2)	C(14)–O(2)	1.201(2)

Table 3. Bond angles (°)

C(2)–C(1)–C(10)	109.2(1)	C(2)–C(1)–C(14)	127.2(1)
C(10)–C(1)–C(14)	123.2(2)	C(1)–C(2)–C(3)	108.7(1)
C(1)–C(2)–C(13)	125.9(2)	C(3)–C(2)–C(13)	124.9(2)
C(2)–C(3)–C(4)	140.9(2)	C(2)–C(3)–C(11)	106.4(1)
C(4)–C(3)–C(11)	111.0(2)	C(3)–C(4)–C(5)	114.5(2)
C(4)–C(5)–C(6)	132.8(2)	C(4)–C(5)–C(7a)	98.7(2)
C(5)–C(6)–C(7)	112.4(3)	C(7a)–C(6a)–C(8)	118.0(3)
C(6)–C(7)–C(8)	133.8(3)	C(6)–C(7)–C(11)	114.0(3)
C(8)–C(7)–C(11)	111.7(2)	C(5)–C(7a)–C(6a)	135.7(4)
C(5)–C(7a)–C(11)	121.4(3)	C(6a)–C(7a)–C(11)	102.1(3)
C(6a)–C(8)–C(9)	134.5(2)	C(7)–C(8)–C(9)	103.5(2)
C(8)–C(9)–C(10)	112.4(2)	C(1)–C(10)–C(9)	141.5(2)
C(1)–C(10)–C(11)	106.4(1)	C(9)–C(10)–C(11)	109.6(2)
C(3)–C(11)–C(7)	124.6(2)	C(3)–C(11)–C(7a)	90.9(2)
C(3)–C(11)–C(10)	105.8(1)	C(7)–C(11)–C(10)	98.8(2)
C(7a)–C(11)–C(10)	131.5(2)	C(3)–C(11)–C(12)	109.4(1)
C(7)–C(11)–C(12)	107.5(2)	C(7a)–C(11)–C(12)	106.8(2)
C(10)–C(11)–C(12)	109.6(1)	C(2)–C(13)–O(1)	123.8(2)
C(1)–C(14)–O(2)	125.5(2)		

anisotropic thermal parameters. This can clearly be seen in Figure 2 which shows the diastereoisomeric overlap and the thermal vibrational ellipsoids. Despite apparently good estimated standard deviations for the bond lengths in this region, the bond lengths should be viewed with caution and not too much reliance placed upon them. The internal consistency of the torsion angles for the two diastereoisomers is good (Figure 1) showing a maximum distortion from a planar geometry of 34° about the C(9)–C(10)† bond. The two aldehyde groups are essentially coplanar with a consequent fairly short intramolecular C–H ⋯ O distance of 2.42 Å.

Reaction of the dialdehyde (6) with thiodimethylenebis-(triphenylphosphonium bromide) in the presence of lithium methoxide in dimethylformamide (DMF) at room temperature gave the required hydrocarbon (7) in 14% yield after chromatography (Scheme 2). The process involves a bis-Wittig reaction followed by extrusion of sulphur and has previously been used by Vogel and co-workers for the preparation of a bridged [14]annulene from a dialdehyde.[7] The low yield, like those of other bis-Wittig reactions, probably results from the formation of an intermediate with a *trans*-double bond which therefore cannot cyclise. Treatment of the dialdehyde (6) with hydrazine hydrate in ethanol at 0 °C gave the pyridazino-fused [10]annulene (8) as an unstable semisolid (90%). Thus, as well as being a precursor to the parent annulene (1),[4] the dialdehyde (6) is a useful intermediate in the synthesis of fused annulenes.

† Numbering of the crystallographic Figures only.

Properties of 9c-Methyl-9cH-cyclopenta[jk]fluorene (7).— The annulene (7) is a stable bright yellow solid which is obtained analytically pure after recrystallisation from light petroleum, m.p. 74—76 °C. In the n.m.r. spectrum the central methyl group resonates at $\delta(CDCl_3)$ −0.79, and the peripheral protons in the range δ 7.30—7.58 for the protons of the macrocyclic ring and δ 7.67—8.40 for those of the benzo ring. Thus the effect of benzo fusion is to shift the central methyl group signal downfield, and the peripheral protons upfield relative to the annulene (1), implying a reduction in ring current as expected. A calculation [equation (1)] based on the upfield

$$\text{Residual ring current} = \frac{1.01 - (-0.79)}{1.01 - (-1.67)} = 0.67 \quad (1)$$

shifts of the methyl group in (7) (δ − 0.79) and (1) (δ − 1.67) relative to a model compound, 2a-methoxy-7b-methyl-4a,7b-dihydro-2aH-cyclopent[cd]indene (δ + 1.01),[4] in which there can be no ring current suggests that the benzo-fused annulene (7) retains two thirds (67%) of the ring current in (1). Further information on the electron delocalisation in (7) was gained from the coupling constants of the peripheral protons. These were obtained to within ±0.04 Hz from the resolution enhanced 400 MHz n.m.r. spectrum and are shown in Figure 3, together with the complete chemical-shift assignments which were made on the basis of n.O.e. measurements which showed enhancements from 5-H to 6-H and from 1-H to 9-H.

The coupling constants around the benzo-ring are of particular interest since calculations by Günther have established a relationship in which these coupling constants reflect the resonance energy of the macrocyclic annulene ring.[8] The measured coupling constants give a value, Q, of 1.166 as given by equation (2). Günther's calculations predict a value of

$$Q = (0.104 \, J_{6.7} - 0.12)/(0.104 \, J_{7.8} - 0.12) = 1.17 \quad (2)$$

Q of 1.21 for a benzo-fused [10]annulene, and 1.15 for a benzo-fused [14]annulene.

The coupling constants observed for (7) are comparable to those observed for the benzo-fused [14]annulenes (9) and (10) suggesting a similar degree of imposed bond fixation. However, both (9) and (10) only retain about 50% of the ring current of the 'parent' [14]annulene.[3] Since the resonance energy is inversely proportional to the size of the annulene,[9] the
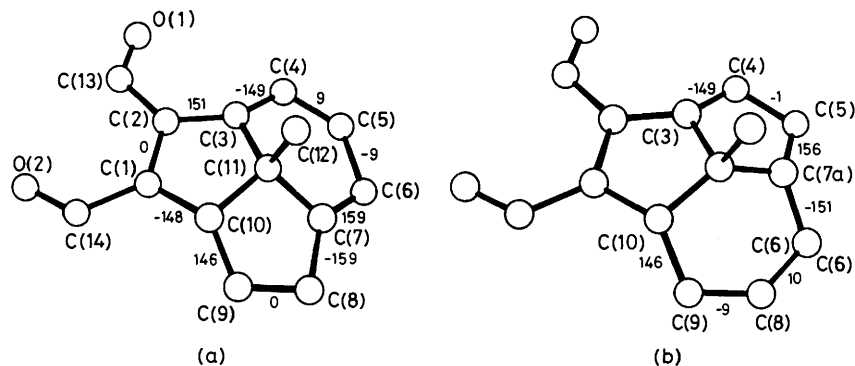
Figure 1 (a, b). Molecular structure of the dialdehyde (**6**) showing the major (a) and minor (b) occupancy diastereoisomers and the crystallographic numbering scheme. Peripheral torsion angles (°) are shown
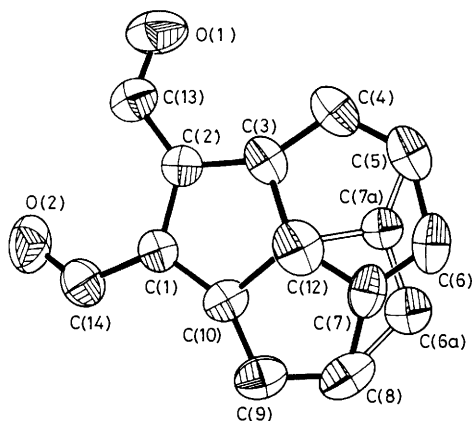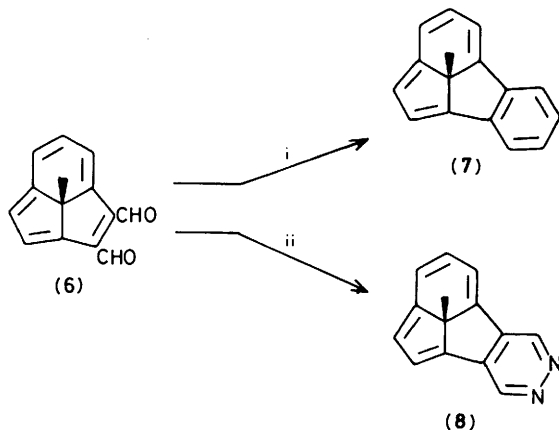

Figure 2. View showing the diastereoisomeric overlap in the structure of the dialdehyde (**6**); the major component is shown with filled bonds and the minor component with open bonds

Figure 3. Chemical shifts and coupling constants for 9c-methyl-9c*H*-cyclopenta[*jk*]fluorene (**7**) obtained from the 400 MHz n.m.r. spectrum in deuteriochloroform

(**9**)   (**10**)

Scheme 2. *Reagents:* i, Ph₃P̂CH₂SCH₂P̂Ph₃ 2 Br⁻, LiOMe, DMF; ii, NH₂NH₂, EtOH, 0 °C

[10]annulene should have greater resonance energy than the [14]annulene and therefore be less perturbed by benzo-fusion. However, it is likely that the resonance energy is somewhat more reduced by torsional strain in the periphery of the tricyclic [10]annulenes, than of the tetracyclic [14]annulenes.

In order to obtain further insight into the bonding in (**7**), and in particular the bond lengths, a single crystal *X*-ray analysis was undertaken. Table 4 lists the fractional atomic co-ordinates.
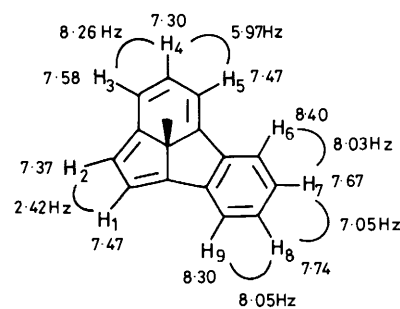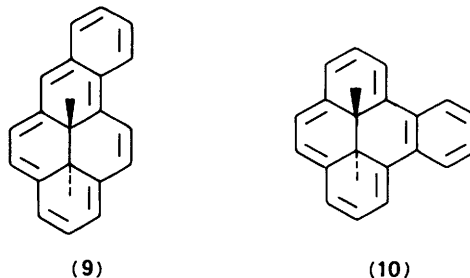
Table 5 gives the angles. The bond lengths are shown in Figure 4. The molecule adopts the same conformation (Figure 4) as (**6**) with the central carbon atom remaining tetrahedral. The problem of diastereoisomers does not arise for this molecule, there being only enantiomers. It is interesting, however, that the molecule has crystallised in a space group that can only contain molecules of the same chirality. It thus exhibits spontaneous resolution on crystallisation and any crystal chosen will contain molecules either all of one chirality or all of the other.

Inspection of the peripheral torsion angles shows departures from planar geometry similar to those observed for (**6**). The maximum deviation is 39° about the C(9a)–C(9b) bond. A librational analysis of rigid body motion was carried out.[10] The consistency index for the agreement between the observed and calculated orthogonalised U_{ij}'s was 0.056. The analysis indicated that the bond lengths should be increased by between 0.005 and 0.007 Å. This correction is small, and at most only slightly greater than two standard deviations. It does not effect the overall alternating periodicity of the peripheral bond lengths.

The results show that benzo-fusion causes a distinct alternation in bond length around the periphery of the tricyclic [10]annulene portion, with variations of between 1.356(3) Å for
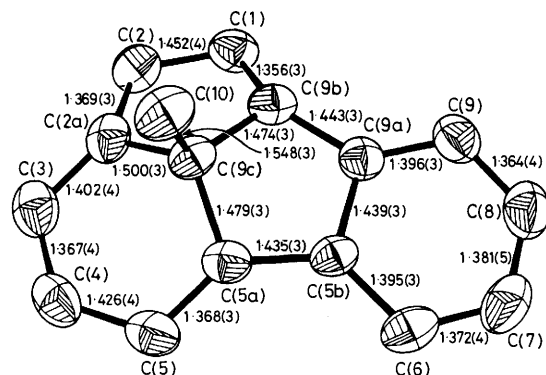
Figure 4. Crystal structure of the benzoannulene (7) showing the bond lengths (Å) with e.s.d.'s in parentheses. Torsion angles about the peripheral bonds: C(1)–C(2) −3.0(3); C(2)–C(2a) −156.4(3); C(2a)–C(3) 146.1(3); C(3)–C(4) −4.7(4); C(4)–C(5) 11.9(4); C(5)–C(5a) −162.0(3); C(5a)–C(5b) −19.9(5); C(5b)–C(6) 175.2(3); C(6)–C(7) −1.1(4); C(7)–C(8) 1.6(5); C(8)–C(9) −0.6(4); C(9)–C(9a) −174.9(2); C(9a)–C(9b) 39.1(5); C(9b)–C(1) 143.4(3)°

Table 4. Atom co-ordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$)

Atom	x	y	z	U
C(1)	−1 243(3)	4 670(3)	1 164(1)	67(1)*
C(2)	−1 010(3)	3 520(3)	1 712(1)	70(1)*
C(2a)	912(4)	3 149(3)	1 747(1)	64(1)•
C(3)	2 058(4)	1 965(3)	1 953(2)	78(1)•
C(4)	3 738(4)	1 731(3)	1 560(1)	74(1)*
C(5)	4 386(4)	2 526(3)	917(1)	69(1)*
C(5a)	3 444(3)	3 781(2)	747(1)	54(1)*
C(5b)	3 222(3)	4 740(2)	117(1)	54(1)*
C(6)	4 345(4)	4 940(3)	−532(1)	73(1)*
C(7)	3 715(5)	5 874(3)	−1 081(1)	84(1)•
C(8)	1 975(5)	6 598(3)	−1 005(2)	83(1)*
C(9)	832(4)	6 449(3)	−380(1)	71(1)*
C(9a)	1 434(3)	5 526(2)	197(1)	54(1)*
C(9b)	518(3)	5 059(2)	889(1)	55(1)*
C(9c)	2 018(3)	4 272(2)	1 317(1)	52(1)*
C(10)	3 076(4)	5 276(3)	1 880(1)	67(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

C(1)–C(9b) to 1.452(4) Å for C(1)–C(2) occurring. There is only a small alternation of bond lengths around the benzo-ring. On this basis alone it is surprising that (7) should retain as much as two-thirds of the ring current of (1). However, the bond common to the macrocyclic and benzo-rings [C(5b)–C(9a)] is slightly longer than expected, 1.44 Å compared with 1.41 Å for the corresponding bond in naphthalene.[11] The lengthening of this bond is probably favoured since it relieves strain in the five-membered ring. The result of this increased single bond character in an internal bond is that the benzo-fused annulene (7) has significant [14]annulene character involving the entire periphery, and hence a higher ring current than might be expected since ring current is proportional to the size of the annulene.[9]

The benzo-fused annulene (7) rearranges when heated in solution to the known[12] 9bH-isomer (11) by a [1,5]methyl shift. The 9bH-isomer (11) is a colourless solid best purified by sublimation. The rearrangement, which has first-order kinetics with $t_{\frac{1}{2}}$ (138 °C, decalin) = 8.3 min, is considerably faster than the corresponding rearrangement of (1) to its 2aH-isomer which has $t_{\frac{1}{2}}$ = 12 h under similar conditions.[4] Rate measurements at different temperatures in the range 110—138 °C give a value of the activation energy for the rearrangement of (7) of 30 kcal mol⁻¹. The corresponding value for the rearrangement of (1) is 33 kcal mol⁻¹ and this difference again reflects the reduction of resonance energy on benzo-fusion. Apart from the thermal

(7)   heat   (11)
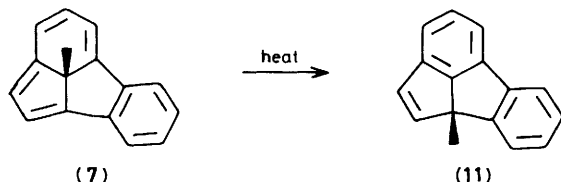
rearrangement, the chemistry of (7) contrasts with that of (1).[1] The annulene (7) reacted with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) at 0 °C but gave complex mixtures, whereas (1) did not react at room temperature but cleanly gave a 1:2 adduct with PTAD in boiling 1,2-dimethoxyethane. Nitration of (7) with copper(ii) nitrate in acetic anhydride was unsuccessful. The annulene was rapidly consumed to give unidentified products.

The pyridazino-fused annulene (8) has properties intermediate between those of (1) and (7). Thus the central methyl

Table 5. Bond angles (°)

C(2)–C(1)–C(9b)	109.7(2)	C(1)–C(2)–C(2a)	108.8(2)
C(2)–C(2a)–C(3)	138.9(3)	C(2)–C(2a)–C(9c)	107.0(2)
C(3)–C(2a)–C(9c)	113.1(2)	C(2a)–C(3)–C(4)	118.0(2)
C(3)–C(4)–C(5)	125.9(2)	C(4)–C(5)–C(5a)	117.9(2)
C(5)–C(5a)–C(5b)	138.7(2)	C(5)–C(5a)–C(9c)	115.4(2)
C(5b)–C(5a)–C(9c)	105.4(2)	C(5a)–C(5b)–C(6)	131.4(2)
C(5a)–C(5b)–C(9a)	109.3(2)	C(6)–C(5b)–C(9a)	119.2(2)
C(5b)–C(6)–C(7)	119.3(3)	C(6)–C(7)–C(8)	121.0(3)
C(7)–C(8)–C(9)	122.0(3)	C(8)–C(9)–C(9a)	118.9(3)
C(5b)–C(9a)–C(9)	119.6(2)	C(5b)–C(9a)–C(9b)	107.7(2)
C(9)–C(9a)–C(9b)	132.4(2)	C(1)–C(9b)–C(9a)	140.8(2)
C(1)–C(9b)–C(9c)	108.1(2)	C(9a)–C(9b)–C(9c)	106.1(2)
C(2a)–C(9c)–C(5a)	117.8(2)	C(2a)–C(9c)–C(9b)	104.5(2)
C(5a)–C(9c)–C(9b)	105.7(2)	C(2a)–C(9c)–C(10)	109.4(2)
C(5a)–C(9c)–C(10)	108.2(2)	C(9b)–C(9c)–C(10)	111.1(2)

group resonates at $\delta(\text{CDCl}_3)$ −1.06, and on heating in solution the compound rearranges by a similar [1,5]methyl shift with $t_{\frac{1}{2}}$ (138 °C) = 38 min.

Conclusion.—The effect of benzannelation on the tricyclic [10]annulene (1) is to give the expected reduction in diatropicity, as evidenced by the chemical shift of the central methyl group in the ¹H n.m.r. spectrum, and by the rate of the [1,5]sigmatropic shift of the methyl group. However, this reduction in diatropicity is less than might be expected. The X-ray crystal structure of (7) reveals a slight lengthening in the (5b)–(9a) bond length, and hence the benzo-fused annulene exhibits significant [14]annulene character. Synthesis of other benzo-fused tricyclic [10]annulenes would obviously be desirable in order to gain a fuller understanding of these novel conjugated systems.

Experimental

For general points, see ref. 1.

Cycloaddition of the 3aH-Indene (2) to Benzoquinone.—(a) A solution of 3a-methyl-3-trimethylsiloxy-3aH-indene (2) [prepared as previously described[5] from 5,7a-dihydro-7a-methyl-1H-inden-1-one (250 mg, 1.7 mmol)] in petroleum (15 ml) was treated with a solution of 1,4-benzoquinone (192 mg, 1.8 mmol) in dry tetrahydrofuran (5 ml). The mixture immediately became

red, but after 3 h at room temperature it was pale yellow. The solvent was evaporated, and the residue heated at 60 °C *in vacuo* (0.05 mmHg) for 1 h, and then chromatographed on silica gel. Elution with petroleum–ether (2:3) gave the exo-*adduct* (3) (53 mg, 10%) as a yellow oil, $\nu_{max.}$(neat) 1 678 cm^{-1}; $\lambda_{max.}$(EtOH) 301 nm (log ε 3.84); δ (250 MHz, CDCl$_3$) 0.05 (9 H, s, SiMe$_3$), 0.89 (3 H, s, 9c-Me), 2.76 (1 H, dd, *J* 4.4, 9.2 Hz, 5b-H), 2.8 (1 H, d, *J* 9.2 Hz, 9a-H), 3.37 (1 H, br t, *J* 5 Hz, 5a-H), 5.85 (1 H, d, *J* 5.0 Hz, 3-H), 5.90 (1 H, dd, *J* 5.7, 9.2 Hz, 5-H), 6.04 (1 H, dd, *J* 5.0, 9.2 Hz, 4-H), 6.29 (1 H, d, *J* 4.8 Hz, 1-H or 2-H), 6.41 (1 H, d, *J* 4.8 Hz, 2-H or 1-H), 6.67 (1 H, d, *J* 11.2 Hz, 7-H or 8-H), and 6.72 (1 H, d, *J* 11.2 Hz, 8-H or 7-H); *m/z* 326 (*M*$^+$), 311, 237, 219, 203, and 167 (base).

(*b*) A solution of 3a-methyl-3-trimethylsiloxy-3a*H*-indene (2) [prepared from 5,7a-dihydro-7a-methyl-1*H*-inden-1-one (300 mg, 2.05 mmol)] in petroleum (20 ml) was treated with a solution of 1,4-benzoquinone (230 mg, 2.13 mmol) in dry tetrahydrofuran (5 ml). After 2 h at room temperature, the solution was evaporated onto silica gel under reduced pressure at 40 °C. The mixture darkened considerably during this pre-adsorption. The residue was chromatographed on silica gel. Elution with petroleum–ether (1:1) gave 9c-*methyl-6,9,9b,9c-tetrahydro-9b-trimethylsiloxy-5aH-cyclopenta*[jk]*fluorene-6,9-dione* (4) (160 mg, 24%) as a deep red oil; $\nu_{max.}$(neat) 1 660 cm^{-1}; $\lambda_{max.}$(EtOH) 247 (log ε 4.19), 3.02 (3.67), and 472 nm (1.90); δ (250 MHz, CDCl$_3$) 0.20 (9 H, s, SiMe$_3$), 0.93 (3 H, s, 9c-Me), 3.60 (1 H, d, *J* 6.7 Hz, 5a-H), 5.85 (1 H, d, *J* 4.7 Hz, 3-H), 6.09 (1 H, dd, *J* 4.7, 9.2 Hz, 4-H), 6.13 (1 H, dd, *J* 6.7, 9.2 Hz, 5-H), 6.41 (1 H, d, *J* 5.3 Hz, 1-H or 2-H), 6.58 (1 H, d, *J* 10.0 Hz, 7-H or 8-H), 6.60 (1 H, d, *J* 5.3 Hz, 2-H or 1-H), and 6.61 (1 H, d, *J* 10.0 Hz, 8-H or 7-H); decoupling at δ 3.60 removes the smaller coupling at δ 6.13; *m/z* 324 (*M*$^+$, base), 309, 296, 294, 281, 236, 235, and 234.

9,9c-*Dihydro-9c-methyl-6H-cyclopenta*[jk]*fluorene-6,9-dione* (5).—A solution of the cyclopentafluorene (4) (68 mg) in chloroform (3 ml) was refluxed under nitrogen with toluene-*p*-sulphonic acid (5 mg) for 45 min. The cooled mixture was diluted with dichloromethane (30 ml) washed with saturated aqueous sodium hydrogencarbonate (10 ml), dried over MgSO$_4$, evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (7:3) gave the *title compound* (5) (14 mg, 33%) as a dark mauve viscous oil (Found: *m/z* 234.0684. C$_{16}$H$_{12}$O$_2$ requires *m/z* 234.0681); $\nu_{max.}$(neat) 1 650 cm^{-1}; $\lambda_{max.}$(EtOH) 275 (log ε 4.25), 295 (4.17), 374 (4.08), and 560 nm (3.67); δ (250 MHz, CDCl$_3$) – 1.01 (3 H, s, 9c-Me), 6.92 (2 H, AB system, *J* 10.8 Hz, 7-H and 8-H), 7.71 (1 H, d, *J* 7.5 Hz, 3-H), 7.81 (1 H, t, *J* 7.5 Hz, 4-H), 8.22 (1 H, d, *J* 3.8 Hz, 2-H), 8.32 (1 H, d, *J* 7.5 Hz, 5-H), and 8.39 (1 H, d, *J* 3.8 Hz, 1-H); *m/z* 234 (*M*$^+$, base), 206, 205, 178, 177, 163, and 152.

9c-*Methyl-9cH-cyclopenta*[jk]*fluorene* (7).—A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarbaldehyde (6)[4] (450 mg, 2.14 mmol) in dry dimethylformamide (10 ml) was added to a stirred suspension of thiodimethylenebis(triphenylphosphonium bromide)[13] (1.6 g, 2.15 mmol) in dry dimethylformamide (20 ml), and the resulting mixture was treated with lithium methoxide (170 mg, 4.5 mmol). After 1 h at room temperature a further portion of lithium methoxide (170 mg) was added. After a further 1 h, the mixture was poured into water (200 ml), and the product extracted with ether (3 × 50 ml). The combined ether extracts were washed with water (3 × 200 ml), dried (Na$_2$SO$_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave 9c-*methyl-9cH-cyclopenta*[jk]*fluorene* (7) (62 mg, 14%) as yellow crystals, m.p. 74—76 °C (from cold petroleum) (Found: C, 94.2; H, 5.9. C$_{16}$H$_{12}$ requires C, 94.1, H, 5.9%); $\nu_{max.}$(CCl$_4$) 3 060m, 2 980m, 2 925m, 2 860m, 1 440m, 1 328m, 696m, and 632m cm^{-1}; $\lambda_{max.}$(EtOH) 311 (log ε 4.43) 400br (3.34) and 464sh nm

(2.82); δ (400 MHz, CDCl$_3$) – 0.79 (3 H, s, 7b-Me), 7.30 (1 H, dd, *J*$_{3,4}$ 8.26 Hz, *J*$_{4,5}$ 5.97 Hz, 4-H), 7.37 (1 H, d, *J*$_{1,2}$ 2.42 Hz, 2-H), 7.47 (1 H, d, *J*$_{4,5}$ 5.97 Hz, 5-H, and 1 H, d, *J*$_{1,2}$ 2.42 Hz, 1-H), 7.58 (1 H, d, *J*$_{3,4}$ 8.26 Hz, 3-H), 7.67 (1 H, ddd, *J*$_{6,7}$ 8.03 Hz, *J*$_{7,8}$ 7.05 Hz, *J*$_{7,9}$ 1.19 Hz, 7-H), 7.74 (1 H, ddd, *J*$_{8,9}$ 8.05 Hz, *J*$_{7,8}$ 7.05 Hz, *J*$_{6,8}$ 1.21 Hz, 8-H), 8.30 (1 H, ddd, *J*$_{8,9}$ 8.05 Hz, *J*$_{7,9}$ 1.19 Hz, *J*$_{6,9}$ 0.91 Hz, 9-H), and 8.40 (1 H, ddd, *J*$_{6,7}$ 8.03 Hz, *J*$_{6,8}$ 1.21 Hz, *J*$_{6,9}$ 0.91 Hz, 6-H); ^{13}C δ(CDCl$_3$) 27.4 (9c-Me), 62.0 (9c-C), 113.6, 119.2, 123.9, 124.7, 124.9, 126.4, 128.2, 128.6, 131.1, 139.2, 144.7, 153.0, 159.0, and 171.4 (9c-C); *m/z* 204 (*M*$^+$, base), and 189.

Thermal Rearrangements of 9c-Methyl-9cH-cyclopenta[jk]*fluorene.*—(*a*) *Kinetic measurements.* The following rates were recorded for the rearrangement of (7) in decalin: *t*$_{\frac{1}{2}}$ (138 °C) 8.3 (±0.4) min, *t*$_{\frac{1}{2}}$ (132 °C) 15.2 (±0.5) min, *t*$_{\frac{1}{2}}$ (117 °C) 64 (±2) min, and *t*$_{\frac{1}{2}}$ (109 °C) 132 (±3) min. The rates were measured by the u.v. method described previously.[4]

(*b*) *Preparative run.* A solution of the annulene (7) (13.4 mg) in xylene (3 ml) was refluxed under nitrogen for 3 h. The solvent was evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave 9b-methyl-9b*H*-cyclopenta-[*jk*]fluorene (11) (6.6 mg, 49%) as a colourless solid, m.p. 50—51 °C (after sublimation at 75 °C/0.1 mmHg) (lit.,[11] m.p. 53 °C), δ (90 MHz, CDCl$_3$) 1.56 (3 H, s, 9b-Me), 6.67 (1 H, d, *J* 5 Hz), 6.90 (1 H, d, *J* 5 Hz), 6.94—7.47 (5 H, m), and 7.49—7.62 (2 H, m).

7,8-*Diaza-9c-methyl-9cH-cyclopenta*[jk]*fluorene* (8).—A solution of the dialdehyde (6) (70 mg, 0.33 mmol) in ethanol (2 ml) was treated with hydrazine hydrate (*ca.* 50 mg) at 0 °C. The reaction was instantaneous. The solvent was evaporated and the residue was chromatographed on alumina (basic, Brockmann grade 1). Elution with dichloromethane–ethyl acetate (9:1) gave the *title compound* (8) (62 mg, 90%) as a dark red semisolid (Found: *m/z* 206.0845. C$_{14}$H$_{10}$N$_2$ requires *m/z* 206.0844); $\lambda_{max.}$(EtOH) 248 (log ε 3.91), 321 (4.25), 406 (3.34), and 478sh nm (2.92); δ (250 MHz, CDCl$_3$) – 1.06 (3 H, s, 9c-Me), 7.56 (1 H, dd, *J* 6.2, 8.3 Hz, 4-H), 7.64 (1 H, d, *J* 2.9 Hz, 1-H or 2-H), 7.82 (1 H, d, *J* 8.3 Hz, 3-H), 7.86 (1 H, d, *J* 6.2 Hz, 5-H), 7.89 (1 H, d, *J* 2.9 Hz, 2-H or 1-H), and 10.09 (2 H, AB, 6-H and 9-H); ^{13}C δ(CDCl$_3$) 27.4 (9c-Me), 62.2 (9c-C), 119.5 (3-C), 121.7 (5-C), 130.8 (1-C or 4-C), 131.3 (4-C or 1-C), 132.1 (5b-C or 9a-C), 134.7 (2-C), 138.1 (9a-C or 5b-C), 148.4 (6-C or 9-C), 148.6 (9-C or 6-C), 151.1 (5a-C), 162.9 (2a-C), and 168.4 (9b-C); *m/z* 206 (*M*$^+$, base), 177, 163, and 152.

Crystal Data.—Crystals of the dialdehyde (6), C$_{14}$H$_{10}$O$_2$, are monoclinic, α = 9.813(2), *b* = 8.940(2), *c* = 12.247(2) Å, β = 99.82(2)°, *U* = 1 059 Å^3, space group *P*2$_1$/*n*, *Z* = 4, *M* = 210.2, *D*$_c$ = 1.32 g cm^{-3}, μ(Cu-*K*$_α$) = 7 cm^{-1}. Refined unit cell parameters were obtained by centring 18 reflections on a Nicolet R3m diffractometer. 1 324 Independent reflections were measured (θ ⩽ 55°) with Cu-*K*$_α$ radiation (graphite monochromator) using the omega-scan measuring routine. Of these 1 290 had |*F*$_o$| > 3σ (|*F*$_o$|) and were considered to be observed. The data were corrected for Lorentz and polarisation factors. No absorption correction was applied.

The structure was solved by direct methods and refined isotropically. The first Δ*F* map revealed two major peaks, indicating the co-existence in the structure of the diastereoisomer with the sequence of 5- and 6-membered rings opposite the dialdehyde groups reversed, though with all other atomic positions superimposed. This situation also occurred in the structure of the dicarboxylic acid.[6] Attempts were made to resolve the two diastereoisomers into discrete independent molecules by reducing the space group constraints. Both space groups *Pn* and *P*2$_1$ were tried, each permitting two independent molecules in the asymmetric unit. However, both resulted in the

same diastereoisomeric overlap occurring. The occupancies of the two diastereoisomers were estimated at 60 and 40%.

The non-hydrogen atoms of the major component were refined anisotropically and those of the minor isotropically. With the exception of the methyl group which was refined as a rigid body, all hydrogen positions were idealised (C–H = 0.96 Å) and assigned isotropic thermal parameters, $U(H) = 1.2$ $U_{eq}(C)$. Refinement was by block-cascade full-matrix least-squares to $R = 0.039$, $R_w = 0.051$, $[w^{-1} = \sigma^2(F) + 0.00035$ $F^2]$. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[14]

The anisotropic thermal parameters, the structure factors, and the hydrogen co-ordinates and temperature factors have been treated as a Supplementary publication [SUP No. 23860 (19 pp.)].*

Crystals of benzoannulene (7), $C_{16}H_{12}$, are orthorhombic, $a = 6.887(1)$, $b = 9.297(2)$, $c = 17.673(3)$ Å, $U = 1\,132$ Å^3, space group $P2_12_12_1$, $Z = 4$, $M = 204.3$, $D_c = 1.20$ g cm^{-3}, μ(Cu-K_α) = 5 cm^{-1}.

To minimise errors due to absorption a small single crystal was ground into a sphere of radius 0.1 mm. Refined unit cell parameters were obtained by centring 16 reflections. Data collection and processing were the same as for (6) resulting in 896 independent observed reflections ($\theta \leqslant 58°$). The structure was solved by direct methods. Surprisingly, in view of the small size of the structure, an initial attempt to solve the structure fully automatically failed. However, incorporation into the starting set of the two principal contributors to the list of negative quartets immediately resulted in a successful phase solution.

The non-hydrogen atoms were refined anisotropically. With the exception of the methyl group which was refined as a rigid body, all hydrogen positions were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, $[U = 1.2\ U_{eq}(C)]$ and allowed to ride on their parent carbon atoms. Refinement was as for (6) to $R = 0.032$, $R_w = 0.039$, $[w^{-1} = \sigma^2\ (F) + 0.000\ 12$ $F^2]$. Maximum residual electron density was 0.14 eÅ^{-3}.

---

* For details of the Supplementary publications scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, issue 1.

The anisotropic thermal parameters, the structure factors, and the hydrogen co-ordinates and temperature factors, have been treated as a Supplementary publication [SUP 23860 (19 pp.)].*

References
1 Part 3, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1984, 175.
2 Preliminary communication, R. McCague, C. J. Moody, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 1063.
3 For example see R. H. Mitchell, *Isr. J. Chem.*, 1980, **20**, 294, and references therein.
4 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1984, 165
5 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2399.
6 T. L. Gilchrist, C. W. Rees, D. Tuddenham, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1980, 691.
7 E. Vogel, J. Sombroek, and W. Wagemann, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 564.
8 D. Cremer and H. Günther, *Liebigs Ann. Chem.*, 1972, **763**, 87.
9 R. C. Haddon, *J. Am. Chem. Soc.*, 1979, **101**, 1722.
10 V. Schomaker and K. N. Trueblood, *Acta Crystallogr.. Ser. B*, 1968, **24**, 63.
11 D. W. J. Cruickshank, *Acta Crystallogr.*, 1957, **10**, 504.
12 P. Luger, C. Tucksherer, M. Grosse, and D. Rewicki, *Chem. Ber.*, 1976, **109**, 2596.
13 K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, 1966, **99**, 642.
14 G. M. Sheldrick, SHELXTL, 'An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data,' University of Göttingen, Federal Republic of Germany (revised version 1983).