

X-Ray Crystal and Molecular Structures of Three 9,10-Dihydroanthracenes

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The crystal and molecular structures have been determined for *cis*- and *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diols and for *cis*-9,10-diethyl-9,10-dihydroanthracene. Both *cis*-isomers have the central ring in a boat conformation with the 9,10-dialkyl substituents in the pseudo-axial positions. The *trans*-9,10-dipropyl compound has a planar ring structure in which the *n*-propyl group is staggered with the hydrogens β to the 9- and 10-positions eclipsing the C–C bonds of the central ring. This conformation is the same as that deduced in solution by n.m.r. spectroscopy.

In the preceding paper,¹ the n.m.r. spectra and conformations of 9,10-dialkyl-9,10-dihydroanthracenes were discussed. It was concluded that the *trans*-isomers which were substituted in the 9,10, or *peri*-positions, adopted a planar conformation of the central ring with the alkyl substituents, placed over this ring. This paper describes a complementary study of the solid state geometry of the *cis* and *trans*-isomers of 9,10-dihydro-9,10-dipropylanthracene-9,10-diols (1) and (2). In addition an X-ray crystal structure of 9,10-diethyl-9,10-dihydroanthracene (3) is presented which unambiguously defines the *cis*-geometry for the isomer obtained by reductive ethylation of anthracene.

The isomers of 9,10-dihydro-9,10-dipropylanthracene-9,10-diols (1) and (2) were selected for X-ray diffraction studies because the ¹H n.m.r. spectra showed¹ that the methylene protons of the propyl groups formed an AA'BB'-spin-spin system indicating a staggered conformation in solution. This unique conformation offered a means of correlating the conformations in the solid state and in solution.

Structure of *trans*-9,10-Dihydro-9,10-dipropylanthracene-9,10-diol (I).—The molecular symmetry of the *trans* isomer (I; Figure 1) closely approximates to $C_{2h}(2/m)$ although for each of the two crystallographically independent molecules in the unit cell, the required symmetry is $C_i(1)$. Molecules A and B lie across the crystallographic centres of symmetry at (0,0,0) and $(\frac{1}{2}, 0, \frac{1}{2})$ and have approximately identical molecular parameters (Tables 1 and 2). All intermolecular contact distances are larger than the sum of the van der Waals radii of the relevant atoms. There is some evidence, however, for hydrogen bonding between hydroxy groups, since the intermolecular O–O distance of 2.814 Å is only slightly greater than twice the Van der Waals radius for oxygen.

The crystallographic numbering scheme for molecule A is shown in Figure 1. That used for molecule B is the same except

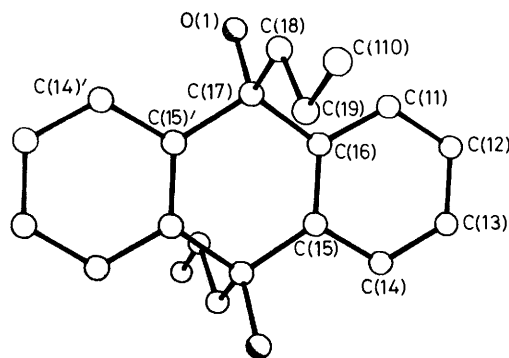


Figure 1.

Table 1. Atomic positional (fractional) coordinates for (I), with estimated standard deviations in parentheses.

	Atom	x	y	z
Molecule (A)	C(11)	0.0875(4)	0.1643(2)	−0.0317(3)
	C(12)	0.2383(5)	0.1830(2)	−0.0398(3)
	C(13)	0.3474(4)	0.1222(2)	−0.0332(3)
	C(14)	0.3054(4)	0.0426(2)	−0.0209(3)
	C(15)	0.1543(3)	0.0217(2)	−0.0117(2)
	C(16)	0.0447(3)	0.0836(2)	−0.0160(2)
	C(17)	−0.1184(3)	0.0684(2)	0.0030(2)
	C(18)	−0.1337(4)	0.1133(2)	0.1090(3)
	C(19)	−0.0192(4)	0.0854(3)	0.2163(3)
	C(110)	−0.0389(6)	0.1290(4)	0.3165(4)
	O(1)	−0.2380(2)	0.1055(1)	−0.0853(2)
Molecule (B)	C(21)	0.5990(4)	0.1652(2)	0.4896(3)
	C(22)	0.5820(5)	0.2040(2)	0.3879(4)
	C(23)	0.5118(5)	0.1642(2)	0.2904(3)
	C(24)	0.4642(4)	0.0846(2)	0.2935(3)
	C(25)	0.4840(4)	0.0431(2)	0.3951(3)
	C(26)	0.5482(4)	0.0843(2)	0.4946(3)
	C(27)	0.5551(4)	0.0474(2)	0.6081(3)
	C(28)	0.4426(4)	0.0937(2)	0.6642(3)
	C(29)	0.2707(4)	0.0888(3)	0.6012(3)
	C(210)	0.1604(5)	0.1360(3)	0.6541(4)
	O(1)	0.7122(3)	0.0605(2)	0.6814(2)

that the first digit is replaced by 2. As expected, the rings C(11)–C(16) and C(21)–C(26) are planar with mean C–C distances of 1.390(4) Å. Since the molecules lie on centres of symmetry, the aromatic rings in each molecule are coplanar. The bridging carbon atoms, C(17) and C(27) and their centrosymmetric equivalents, are constrained by the aromatic rings in an almost planar cyclohexa-1,3-diene ring; their deviation slightly out of the mean plane of the aromatic rings is 0.135 and 0.168 Å respectively, for molecules A and B. In both molecules, the situation of the bridging atoms places each of the hydroxy oxygen atoms in 'equatorial' positions relative to a pseudo-chair conformation for the central ring. The tricyclic framework of the molecules is thus essentially planar.

The angles at the central ring carbon atoms C(17) and C(27) are distorted away from tetrahedral, with those to the other ring carbon atoms being greater than those subtended by the hydroxy oxygen and the α -C of the propyl groups, namely 113°; *cf.* 104°.

The propyl groups adopt a staggered conformation with a mean C–C distance 1.508(5) Å and a mean C–C–C angle of 114.2(3)°. The principal planes of these groups are almost perpendicular to the mean plane of the ring system, yet not

Table 2. Bond distances (Å) and inter-bond angles (°) for the *trans* isomer (I) with estimated standard deviations in parentheses.

(a) Distances.				(b) Bond angles			
(i) Molecule (A)		(ii) Molecule (B)		(i) Molecule (A)		(ii) Molecule (B)	
C(11)–C(16)	1.404(4)	C(21)–C(26)	1.409(4)	C(16)–C(11)–C(12)	120.8(3)	C(26)–C(21)–C(22)	120.8(3)
C(11)–C(12)	1.386(6)	C(21)–C(22)	1.386(6)	C(11)–C(12)–C(13)	120.0(3)	C(21)–C(22)–C(23)	120.1(3)
C(12)–C(13)	1.370(5)	C(22)–C(23)	1.376(6)	C(12)–C(13)–C(14)	119.6(3)	C(22)–C(23)–C(24)	120.0(4)
C(13)–C(14)	1.376(5)	C(23)–C(24)	1.374(5)	C(13)–C(14)–C(15)	121.8(3)	C(23)–C(24)–C(25)	121.1(3)
C(14)–C(15)	1.401(5)	C(24)–C(25)	1.405(5)	C(14)–C(15)–C(16)	118.5(3)	C(24)–C(25)–C(26)	119.3(3)
C(15)–C(16)	1.391(4)	C(25)–C(26)	1.395(4)	C(14)–C(15)–C(17) ^{I*}	117.5(3)	C(24)–C(25)–C(27) ^{II*}	118.3(3)
C(16)–C(17)	1.528(4)	C(26)–C(27)	1.519(5)	C(16)–C(15)–C(17) ^{I*}	124.0(3)	C(26)–C(25)–C(27) ^{II*}	122.3(3)
C(17)–C(15) ^{I*}	1.522(4)	C(27)–C(25) ^{II*}	1.522(4)	C(11)–C(16)–C(15)	119.2(3)	C(21)–C(26)–C(25)	118.7(3)
O(1)–C(17)	1.445(3)	O(2)–C(27)	1.463(3)	C(11)–C(16)–C(17)	118.0(3)	C(21)–C(26)–C(27)	118.6(3)
C(17)–C(18)	1.541(5)	C(27)–C(28)	1.543(5)	C(15)–C(16)–C(17)	122.7(3)	C(25)–C(26)–C(27)	122.6(3)
C(18)–C(19)	1.521(4)	C(28)–C(29)	1.516(5)	C(16)–C(17)–O(1)	110.1(2)	C(26)–C(27)–O(2)	109.2(3)
C(19)–C(110)	1.482(7)	C(29)–C(210)	1.512(7)	C(16)–C(17)–C(18)	109.8(2)	C(26)–C(27)–C(28)	109.9(2)
				C(16)–C(17)–C(15) ^{I*}	112.8(2)	C(26)–C(27)–C(25) ^{II*}	114.1(2)
				O(1)–C(17)–C(18)	104.0(2)	O(2)–C(27)–C(28)	104.9(2)
				O(1)–C(17)–C(15) ^{I*}	109.8(2)	O(2)–C(27)–C(25) ^{II*}	109.4(2)
				C(18)–C(17)–C(15) ^{I*}	109.9(3)	C(28)–C(27)–C(25) ^{II*}	109.1(3)
				C(17)–C(18)–C(19)	114.9(3)	C(27)–C(28)–C(29)	114.1(3)
				C(18)–C(19)–C(110)	113.4(4)	C(28)–C(29)–C(210)	114.3(3)

(c) Selected intermolecular contact distances:

O(1) ... H(2) ^I	2.056
O(2) ... H(1) ^{II}	1.931
O(1) ... O(2) ^I	2.814(3)

* Superscripts refer to the following positions relative to the reference atom at x, y, z : I, $-x, -y, -z$; II, $1-x, -y, 1-z$
 Roman superscripts refer to the following symmetry operations: I, $-1+x, y, -1+z$; II, $1+x, +y, 1+z$.

Table 3. Atomic positional fractional co-ordinates for the *cis*-isomer (II) with estimated standard deviations in parenthesis.

Atom	x	y	z
C(1)	0.476 0(8)	0.097 8(3)	0.250 0(7)
C(2)	0.491 3(11)	0.101 0(3)	0.112 4(6)
C(3)	0.651 5(11)	0.109 8(3)	0.080 9(7)
C(4)	0.797 2(9)	0.116 1(3)	0.184 9(6)
C(5)	1.079 4(8)	0.065 0(3)	0.657 6(8)
C(6)	1.066 2(10)	0.035 1(3)	0.777 5(8)
C(7)	0.905 0(10)	0.026 9(3)	0.809 3(7)
C(8)	0.758 2(8)	0.047 0(3)	0.721 3(6)
C(9)	0.602 9(7)	0.100 5(2)	0.507 0(5)
C(91)	0.551 1(9)	0.163 7(3)	0.550 3(6)
C(92)	0.536 4(10)	0.169 9(3)	0.701 0(6)
C(93)	0.477 7(14)	0.232 5(4)	0.735 4(11)
O(9)	0.462 9(6)	0.060 7(2)	0.519 8(4)
C(10)	0.948 4(7)	0.119 8(2)	0.435 6(5)
C(101)	0.995 0(10)	0.186 4(3)	0.473 5(7)
C(102)	1.013 1(12)	0.229 0(3)	0.356 9(8)
C(103)	1.056 1(16)	0.292 2(4)	0.408 5(10)
O(10)	1.097 2(7)	0.098 4(3)	0.385 0(6)
C(11)	0.622 0(7)	0.103 9(2)	0.356 0(5)
C(12)	0.785 0(7)	0.113 2(2)	0.324 0(5)
C(13)	0.930 7(7)	0.085 9(2)	0.566 3(5)
C(14)	0.768 0(7)	0.077 7(2)	0.598 9(6)

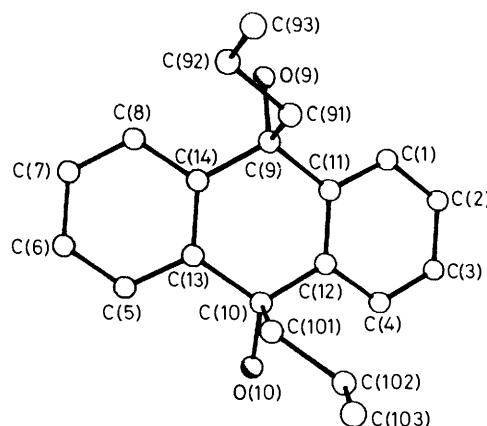
symmetrically related to it, since they show a slight lateral displacement.

It is of particular interest to note that the carbon atoms C(19) and C(29), carrying the methylene hydrogen atoms, which occur at highfield in the n.m.r. spectrum, are folded back over the central ring so that H(191), H(192), H(291) and H(292) eclipse C(16) and C(26) and their centrosymmetric equivalents.

Thus the conformation of *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol (I), in the crystalline state, corresponds precisely to that deduced in the previous paper¹ for the conformation of this isomer in deuteriochloroform solution.

Structure of cis-9,10-Dihydro-9,10-dipropylanthracene-9,10-diol (II).—The space group of the *cis*-isomer (II; Figure 2) is the same as that of the *trans* isomer (I), but in this case there are no crystallographic constraints and only one molecule per asymmetric unit. The molecular parameters are given in Tables 3 and 4. All intermolecular contacts are greater than the sum of the Van der Waals radii for the atoms concerned.

Using the numbering scheme shown in Figure 2, the aromatic

**Figure 2.**

rings C(1), C(2), C(3), C(4), C(12), C(11) (plane 1) and C(5), C(6), C(7), C(8), C(14), C(13) (plane 2) show mean C–C distances of 1.389(9) Å and a maximum deviation from planarity of 0.005 Å. These rings are not coplanar, but are inclined at an angle of 29.8° in a butterfly conformation. Since the plane C(9), C(11), C(12), C(10) (plane 3) is at an angle of 31° to the plane C(9), C(14), C(13), C(10) (plane 4) the molecule consists of two separate planar halves, planes 1 and 3 and planes 2 and 4, which are hinged about the line C(9)–C(10) (dihedral

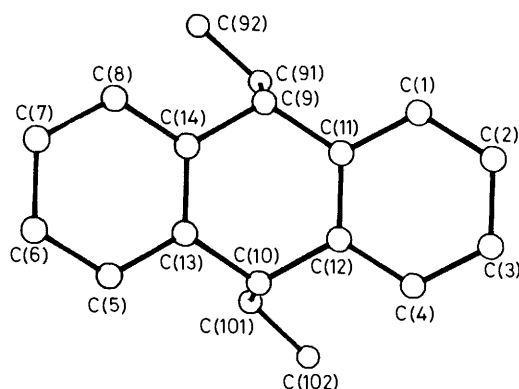
Table 4. Interatomic distances (Å) and bond angles (°) for the *cis*-isomer (II) with estimated standard deviations in parentheses.

(a) Bond distances				(b) Bond angles			
C(1)–C(11)	1.392(8)	C(9)–C(11)	1.535(7)	C(11)–C(1)–C(2)	120.6(6)	C(10)–C(13)–C(14)	120.5(4)
C(1)–C(2)	1.395(10)	C(9)–C(14)	1.511(7)	C(1)–C(2)–C(3)	119.8(6)	C(13)–C(14)–C(9)	122.1(5)
C(2)–C(3)	1.371(12)	C(9)–O(9)	1.439(7)	C(2)–C(3)–C(4)	120.2(7)	C(11)–C(9)–O(9)	110.2(4)
C(3)–C(4)	1.380(9)	C(9)–C(91)	1.549(8)	C(3)–C(4)–C(12)	121.0(7)	C(14)–C(9)–O(9)	108.4(4)
C(4)–C(12)	1.402(8)	C(91)–C(92)	1.527(9)	C(4)–C(12)–C(11)	118.7(5)	C(91)–C(9)–O(9)	106.7(5)
C(11)–C(12)	1.396(8)	C(92)–C(93)	1.527(12)	C(12)–C(11)–C(1)	119.7(5)	C(9)–C(91)–C(92)	115.5(5)
C(5)–C(13)	1.402(8)	C(10)–C(12)	1.519(7)	C(13)–C(5)–C(6)	121.0(7)	C(91)–C(92)–C(93)	112.9(6)
C(5)–C(6)	1.383(11)	C(10)–C(13)	1.529(8)	C(5)–C(6)–C(7)	119.7(6)	C(12)–C(10)–O(10)	109.8(4)
C(6)–C(7)	1.378(12)	C(10)–O(10)	1.444(8)	C(6)–C(7)–C(8)	120.2(7)	C(13)–C(10)–O(10)	110.6(4)
C(7)–C(8)	1.371(9)	C(10)–C(101)	1.556(9)	C(7)–C(8)–C(14)	121.3(6)	C(101)–C(10)–O(10)	103.4(5)
C(8)–C(14)	1.407(8)	C(101)–C(102)	1.524(11)	C(8)–C(14)–C(13)	118.6(5)	C(10)–C(101)–C(102)	117.7(6)
C(13)–C(14)	1.393(8)	C(102)–C(103)	1.513(12)	C(14)–C(13)–C(5)	119.3(5)	C(101)–C(102)–C(103)	111.9(7)
				C(14)–C(9)–C(11)	111.1(5)	C(1)–C(11)–C(9)	120.0(5)
				C(9)–C(11)–C(12)	120.4(4)	C(4)–C(12)–C(10)	119.5(5)
				C(11)–C(12)–C(10)	121.8(5)	C(5)–C(13)–C(10)	120.1(5)
				C(12)–C(10)–C(13)	111.0(4)	C(8)–C(14)–C(9)	119.3(5)

angle 149°). The aromatic rings fold away from the *cis*-propyl groups.

The angles about the central ring carbon atoms C(9) and C(10) are again larger than tetrahedral (111°), but the increase is less than for the *trans* isomer (I). There is a consequent decrease in the O–C–αC angle (105°), as before. The central ring adopts a pseudo-boat conformation with the propyl groups occupying the 'axial' positions. The propyl groups are in a staggered arrangement, with a mean C–C of 1.523(11) Å and a mean C–C–C angle of 114.5(6)°. Unlike the *trans* isomer however, the propyl groups are not bent back over the system such as to eclipse any of the central ring atom vectors. The closest approach between hydrogen atoms on the *cis* propyl groups is 2.28 Å.

Structure of cis-9,10-Diethyl-9,10-dihydroanthracene (III).—The molecular structure (III) shown in Figure 3 comprises one

**Figure 3.**

asymmetric unit in the same space group as the previous two compounds. The molecular parameters are given in Tables 5 and 6.

The central ring of the molecule, C(9), C(11), C(12), C(10), C(13), C(14), adopts the boat conformation, where C(9) and C(10) lie 0.35 Å from the mean plane of C(11), C(12), C(13), C(14), (dihedral angle 24°). The ethyl groups occupy *cis* 'axial' positions. The closest point of approach of any hydrogen atoms on these *cis* substituents is 2.21 Å. The ethyl groups are staggered with respect to one another, and for obvious steric reasons do not eclipse any of the central ring carbon atoms. Taking the vector C(9)–C(10) as the 'hinge' of the molecule as a

Table 5. Atomic positional parameters (fractional co-ordinates) for compound (III) with estimated standard deviations in parentheses.

Atom	x	y	z
C(1)	0.499 12(10)	0.543 6(2)	0.210 17(9)
C(2)	0.397 35(11)	0.485 8(2)	0.152 64(10)
C(3)	0.395 30(10)	0.376 1(2)	0.079 18(9)
C(4)	0.495 28(10)	0.325 1(1)	0.063 80(8)
C(5)	0.882 40(11)	0.472 3(2)	0.092 09(9)
C(6)	0.965 71(11)	0.597 8(3)	0.118 95(10)
C(7)	0.966 90(11)	0.709 5(2)	0.190 86(10)
C(8)	0.884 97(10)	0.694 7(2)	0.236 06(9)
C(9)	0.710 91(10)	0.555 6(2)	0.260 31(8)
C(10)	0.706 97(9)	0.320 9(15)	0.104 08(8)
C(11)	0.600 74(9)	0.490 6(1)	0.196 10(8)
C(12)	0.598 73(9)	0.378 7(1)	0.122 68(8)
C(13)	0.798 68(9)	0.456 2(1)	0.136 96(8)
C(14)	0.800 47(9)	0.568 1(1)	0.210 54(8)
C(91)	0.747 57(11)	0.443 0(2)	0.349 22(9)
C(92)	0.847 90(12)	0.513 6(3)	0.424 13(9)
C(101)	0.746 74(10)	0.138 6(2)	0.144 62(8)
C(102)	0.666 21(11)	–0.008 4(2)	0.101 00(10)

whole, the two 'halves' show a dihedral angle of 147°, *cf.* II with 149°.

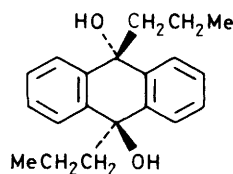
The angle subtended at the bridging carbon atoms C(9) and C(10) show the same trends as in I and II, namely being greater than tetrahedral within the ring, and smaller for the H–C–αC angle. (111° compared with 104°). The mean value for C–C in the aromatic rings is 1.388(2), in the central ring 1.513(2) and for the ethyl substituents it is 1.534(2) Å. This follows the expected trend and this low temperature study gives considerably more accurate parameters for which the differences are significant.

Discussion

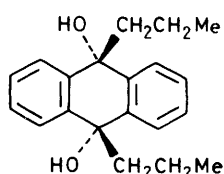
The geometry of cyclohexa-1,4-dienes has been investigated extensively; the evidence, mainly from n.m.r. studies, has now been reviewed by Rabideau.² In the case of 9,10-dihydroanthracenes two previous crystallographic studies have been reported. Firstly the parent compound (IV) has been shown³ to be in a butterfly conformation with an angle of 145° between the plane of the benzene rings. Secondly 9,10-dihydro-9,9,10,10-tetrachloroanthracene (V) has been shown⁴ to have a planar ring structure. These and our results show that, in the crystalline state, the conformations of 9,10-dihydroanthracene depend upon the degree and stereochemistry of substituents at the 9- and 10-positions.

Table 6. Bond lengths (Å) and interbond angles (°) for compound (III) with estimated standard deviations in parentheses.

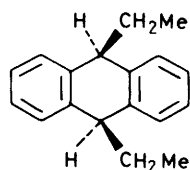
(a) Distances.			
C(1)–C(2)	1.382(2)	C(7)–C(8)	1.381(2)
C(2)–C(3)	1.384(2)	C(8)–C(14)	1.398(2)
C(3)–C(4)	1.382(2)	C(6)–C(7)	1.377(2)
C(4)–C(12)	1.395(1)	C(6)–C(5)	1.384(2)
C(1)–C(11)	1.398(2)	C(5)–C(13)	1.398(2)
C(11)–C(12)	1.394(2)	C(13)–C(14)	1.396(2)
C(11)–C(9)	1.513(1)	C(14)–C(9)	1.512(2)
C(10)–C(12)	1.515(2)	C(13)–C(10)	1.513(2)
C(10)–C(101)	1.547(2)	C(9)–C(91)	1.547(2)
C(101)–C(102)	1.523(2)	C(91)–C(92)	1.519(2)
(b) Bond angles			
C(11)–C(1)–C(2)	120.8(1)	C(13)–C(5)–C(6)	121.1(1)
C(1)–C(2)–C(3)	119.9(1)	C(5)–C(6)–C(7)	120.0(1)
C(2)–C(3)–C(4)	119.7(1)	C(6)–C(7)–C(8)	119.6(1)
C(3)–C(4)–C(12)	121.1(1)	C(7)–C(8)–C(14)	121.4(1)
C(4)–C(12)–C(11)	119.2(1)	C(8)–C(14)–C(13)	118.9(1)
C(12)–C(11)–C(1)	119.2(1)	C(14)–C(13)–C(5)	119.1(1)
C(4)–C(12)–C(10)	119.9(1)	C(8)–C(14)–C(9)	120.5(1)
C(9)–C(11)–C(1)	119.7(6)	C(5)–C(13)–C(10)	119.7(1)
C(12)–C(10)–C(13)	111.2(1)	C(14)–C(9)–C(11)	111.2(1)
C(12)–C(10)–C(101)	112.9(1)	C(14)–C(9)–C(91)	112.9(1)
C(13)–C(10)–C(101)	111.4(1)	C(9)–C(91)–C(92)	114.7(1)
C(10)–C(101)–C(102)	113.7(1)	C(11)–C(9)–C(91)	110.9(1)
C(12)–C(11)–C(9)	121.1(1)	C(13)–C(14)–C(9)	120.6(1)
C(14)–C(13)–C(10)	121.3(1)	C(11)–C(12)–C(10)	120.8(1)



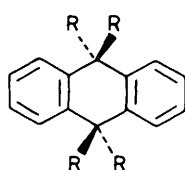
(I)



(II)



(III)



(IV) R = H

(V) R = Cl

For *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol (I), the conformation in the crystalline state is the same as that deduced in the preceding paper¹ for this compound in solution from n.m.r. data. In particular, the planar ring structure, with a staggered conformation of the propyl groups in which the protons β - to the 9- and 10-positions are in the shielding zones of the benzene rings and of the eclipsing C–C bonds of the central ring, support the explanation offered in the previous paper for the highfield signals of these β -protons.

It is also reassuring that the conformation of *cis*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol and *cis*-9,10-diethyl-9,10-dihydroanthracene in the solid state are the same as the conformations deduced for these compounds in solution by n.m.r. studies, *i.e.* a boat conformation of the central ring with pseudo-axial *cis*-substituents (see Rabideau² for leading references).

Experimental

X-Ray diffraction studies: much of the detail is common to the three investigations, therefore only the differences from (I) are reported for (II) and (III). Similarly for the crystal data parameters.

Crystal data.—(I): C₂₀H₂₄O₂, *M* = 296.4. Monoclinic, *a* = 8.774(6), *b* = 16.414(13), *c* = 12.396(5) Å, β = 104.59(4)°, *U* = 1 728(2) Å³, 293 K, *D_m* 1.12 g cm⁻³, *Z* = 4, *D_c* 1.14 g cm⁻³, *F*(000) = 640, space group *P*2₁/*c* (No. 14) Mo-*K_α* X-radiation λ = 0.710 69 Å, μ (Mo-*K_α*) 0.78 cm⁻¹. Nicolet P3/m four-circle automated diffractometer, $2\theta_{\max}$ = 50°.

(II): C₂₀H₂₄O₂, *M* = 296.4. Monoclinic, *a* = 7.854(4), *b* = 22.277(16), *c* = 9.904(11) Å, β = 101.86(7)°, *U* = 1 692(2) Å³, 293 K, *D_m* 1.11 g cm⁻³, *Z* = 4, *D_c* 1.16 g cm⁻³, space group *P*2₁/*c* (No. 14).

(III): C₁₈H₂₀, *M* = 236.4, *a* = 12.405(4), *b* = 7.658(1), *c* = 15.046(5) Å, β = 106.73(2)°, *U* = 1 370(6) Å³, 200 K, *D_c* 1.15 g cm⁻³, *Z* = 4, space group *P*2₁/*c*, *F*(000) = 512, μ (Mo-*K_α*) 0.6 cm⁻¹.

(I) Diffracted intensities were recorded from a well formed prism of (I) grown from an ethyl acetate solution. Dimensions approximately 0.63 × 0.10 × 0.15 mm. The total 3 145 data gave 1 779 as independent and satisfying the criterion $I \geq 2.5 \sigma(I)$ where $\sigma(I)$ is the estimated standard deviation of the intensity recorded, based on counting statistics alone. Three standard reflections, monitored throughout the data collection to measure the stability of the crystal, showed only random fluctuations and no appreciable crystal decay in the X-ray beam. No corrections were made for the effects of X-ray absorption and the structure was solved from the complete data set by direct methods.⁵ It was subsequently refined to convergence at $R(R')$ 0.061 (0.068).⁶ A weighting scheme of the form $[w^{-1} = a + bF_0 + c|F|^2]$ gave a satisfactory weight analysis for *a* = 1.085, *b* = 0.085, *c* = 0.0029. All non-hydrogen atoms were refined using anisotropic thermal parameters.

All the hydrogen atoms were included at their calculated positions, (C–H 0.96 Å) except the hydroxy H atoms which were located from difference density syntheses and their contribution fixed in the refinement. The final difference synthesis showed no peaks $> \pm 0.2 e \text{ \AA}^{-3}$. Final atomic positional parameters are given in Table 1.*

(II) Diffracted intensities were measured from a flat needle grown from ethyl acetate solution, dimensions approximately 0.28 × 0.10 × 0.33 mm. The data were not corrected for the effects of X-ray absorption, and the full data set (3 245) was used initially to solve the structure by direct methods.⁵ In the final stages of refinement only 1 188 unique reflections with $I \geq 2.5 \sigma(I)$ were used. Convergence occurred at $R(R')$ 0.054 (0.055) using a weighting scheme⁶ of the form $w^{-1} = [\sigma(F) + g|F|]$, with *g* = 0.06. Final difference density syntheses showed no peaks ≥ 0.4 or $\leq -0.8 e \text{ \AA}^{-3}$. Atomic positional parameters are given in Table 4.*

(III) The data collection for (III) was carried out at reduced temperature, (200 K), using a stream of cold, dry N₂ gas colinear with the diffractometer Φ axis. The standard reflections used to monitor the stability of the experiment showed no appreciable decay nor gross fluctuations throughout the period of data collection. From a total of 3 081 data recorded, 2 332 were deemed unique with $I \geq 2.5 \sigma(I)$. No corrections were made for X-ray absorption effects and the full data set was used to solve

* Tables of atomic co-ordinates for all hydrogen atoms, all thermal parameters, and tables of selected least squares planes, are available as a Supplementary publication [SUP no. 56273 (12 pp.); for details of the Supplementary publications scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. I*, 1985, Issue 1. Copies of the structure factors are available on request from the Editorial office.

the structure,⁷ which was subsequently refined to $R(R')$ 0.042 (0.044). All hydrogen atoms were located from the Fourier maps and refined satisfactorily with isotropic thermal parameters. All C atoms were refined with anisotropic temperature factors.* A weighting scheme of the form $w^{-1} = [\sigma(F) + g(F)^2]$ with $g = 0.00035$, gave a sensible analysis. No peaks were observed $\geq \pm 0.1 \text{ e } \text{Å}^{-3}$, in the final difference density syntheses. The final atomic positional parameters are given in Table 5.

* See footnote on preceding page.

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