Crystal Structure and Nuclear Magnetic Resonance Spectra of a 1 : 1 Complex of Benz[*a*]anthracene and Pyromellitic Dianhydride (Benzene-1,2,4,5-tetracarboxylic Dianhydride)

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The crystal structure of a 1 : 1 complex of benz[*a*]anthracene(BA) and pyromellitic dianhydride(PMDA) has been determined by direct methods from diffractometer data and refined to *R* 0.0825 for 1 354 reflections. Crystals are orthorhombic with a = 11.63(1), b = 20.84(2), c = 7.089(6) Å, Z = 4, space group $Pna2_1$. C–C Bond lengths in BA vary from 1.321(11) to 1.482(11) Å, but are as expected in PMDA. An n.m.r. study of the complex in solution in 1,2-dichloroethane at 33.5 °C gave an association constant (K) of 3.4 mol kg^{-1}, but gave no evidence of the presence of complexes with stoicheiometries other than 1 : 1.

No accurate structure determination has been carried out of benz[*a*]anthracene, although the unit cell and space group were first reported in 1938.[1] The reason is that good crystals have been impossible to obtain. Friedlander and Sayre [2] determined the structure but were able to measure only 518 reflections out of a possible 1 658 with Cu-K_α radiation, and bond lengths and angles were only approximate. In order to obtain better values, and also to study the way benz[*a*]anthracene forms charge-transfer complexes, a 1 : 1 complex of this compound (BA) with pyromellitic (benzene-1,2,4,5-tetracarboxylic) dianhydride (PMDA) was prepared by mixing saturated solutions of both compounds in ethyl acetate in a 1 : 1 molar ratio. Violet crystals, which were recrystallised twice from the same solvent, were needles varying in thickness from 0.1 to 1.0 mm. They tended to shatter when attempts were made to cut them, but specimens suitable for *X*-ray analysis were obtained.

Benz[*a*]anthracene is the parent compound of a large series of aromatic carcinogens but is not regarded as being an active compound itself. All theories regarding relationships between carcinogenic potency and structure (or electronic distribution) have failed to deal satisfactorily with the fact that some monomethyl-substituted benzanthracenes are carcinogenic while others are inactive. It therefore seems important to study complexes of BA (an electron donor) with various electron acceptors. Complexing with for example DNA (or RNA) or with a protein could play an important role in the mechanism of carcinogenesis. The present study, by *X*-ray analysis and by n.m.r. methods is the first of a series of complexes involving BA.

EXPERIMENTAL AND RESULTS

Crystal Data.—$C_{18}H_{12} : C_{10}H_2O_6$, $M = 228.29 + 218.12 = 446.41$, orthohombic, $a = 13.63 \pm 0.01$, $b = 20.84 \pm 0.02$, $c = 7.089 \pm 0.006$ Å, $U = 2073$ Å^3, $D_m = 1.145$, $Z = 4$, $D_c = 1.471$, $F(000) = 920$. Systematic absences, $h0l$ when h odd, $0kl$ when $(k + l)$ odd, $00l$ when l odd. Space group $Pna2_1$ or *Pnam*. *Pnam* Would require BA to be at a special

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[1] J. Iball, *Z. Krist.*, 1938, **99**, 230.

[2] P. H. Friedlander and D. Sayre, *Nature*, 1956, **178**, 999.

position: thus $Pna2_1$ is the probable space group and this was confirmed by the subsequent structure determination. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; Mo-K_α radiation, $\lambda = 0.710\,69$ Å.

TABLE 1

1 : 1 Benz[*a*]anthracene–pyromellitic dianhydride complex. Atomic co-ordinates (× 10^4) and thermal parameters * (× 10^5), with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
(*a*) Pyromellitic dianhydride									
O(1′)	3 777(4)	136(2)	5 747(10)	584(38)	−77(38)	225(162)	162(12)	96(92)	2 220(140)
O(2′)	4 329(4)	−2 860(2)	8 965(9)	633(40)	39(39)	854(152)	174(13)	456(92)	2 389(145)
O(3′)	4 672(5)	−2 334(3)	11 667(9)	608(40)	38(46)	−63(146)	260(15)	396(90)	1 826(136)
O(4′)	4 259(4)	373(3)	8 686(10)	694(42)	−79(44)	−23(193)	197(14)	−277(105)	2 947(179)
O(5′)	3 407(5)	−401(3)	3 063(9)	834(45)	62(53)	−530(165)	253(15)	306(95)	2 068(151)
O(6′)	3 961(5)	−3 110(3)	5 982(10)	723(42)	−181(41)	70(181)	174(13)	−383(92)	2 832(169)
C(1′)	4 097(6)	−741(4)	7 679(12)	392(47)	−98(50)	130(193)	147(17)	−356(112)	1 976(211)
C(2′)	3 854(6)	−976(4)	5 920(13)	370(43)	−108(50)	439(186)	182(18)	−107(118)	1 490(181)
C(3′)	3 822(6)	−1 618(4)	5 556(14)	439(50)	−69(53)	107(208)	189(19)	−310(118)	1 639(181)
C(4′)	4 030(5)	−2 007(3)	7 055(12)	210(36)	−32(42)	20(167)	115(16)	−218(105)	1 886(190)
C(5′)	4 278(6)	−1 762(3)	8 762(12)	363(45)	35(46)	124(187)	144(16)	431(106)	1 605(184)
C(6′)	4 319(6)	−1 116(4)	9 215(12)	430(48)	75(51)	−216(186)	197(19)	167(108)	1 232(174)
C(7′)	4 059(6)	−17(4)	7 605(13)	462(54)	97(54)	−103(202)	195(20)	−73(118)	1 836(217)
C(8′)	3 662(7)	−420(4)	4 654(13)	570(59)	−111(66)	−74(219)	234(22)	−92(135)	2 053(225)
C(9′)	4 098(6)	−2 732(4)	7 135(13)	399(46)	−187(51)	454(194)	188(20)	94(122)	2 159(206)
C(10′)	4 471(7)	−2 324(4)	10 051(15)	428(52)	90(62)	436(225)	219(22)	−54(146)	3 272(293)
(*b*) Benz[*a*]anthracene									
C(1)	3 684(6)	2 437(4)	636(14)	533(55)	−28(55)	−328(226)	173(19)	83(136)	2 063(184)
C(2)	3 629(7)	1 770(4)	429(15)	654(64)	−98(62)	−338(250)	191(20)	4(132)	2 297(233)
C(3)	3 355(7)	1 412(4)	2 000(15)	417(52)	−144(59)	−682(241)	209(21)	−137(153)	3 392(286)
C(4)	3 124(6)	1 685(4)	3 738(14)	527(58)	121(54)	−296(225)	198(19)	954(120)	2 423(216)
C(5)	2 945(6)	2 671(4)	5 623(13)	330(41)	157(52)	335(176)	231(20)	221(123)	135(157)
C(6)	2 947(6)	3 301(4)	5 839(14)	454(51)	46(56)	153(210)	224(21)	169(141)	1 734(199)
C(7)	3 213(6)	4 369(4)	4 603(13)	452(53)	−16(56)	−32(199)	216(21)	−152(123)	1 854(210)
C(8)	3 526(7)	5 476(4)	3 348(14)	695(63)	−54(71)	615(255)	239(23)	−450(141)	2 334(252)
C(9)	3 819(7)	5 853(4)	1 957(16)	615(62)	35(64)	−433(289)	175(22)	46(164)	3 857(329)
C(10)	4 058(8)	5 591(5)	128(15)	729(71)	−133(70)	−282(274)	252(24)	632(145)	3 208(306)
C(11)	4 064(7)	4 946(4)	−166(13)	497(55)	123(60)	−781(215)	246(23)	395(137)	2 450(246)
C(12)	3 780(6)	3 852(4)	1 089(12)	484(53)	6(56)	−664(194)	215(20)	86(118)	1 512(199)
C(13)	3 464(6)	2 746(4)	2 339(12)	254(38)	128(47)	−430(159)	179(18)	−179(109)	1 612(170)
C(14)	3 179(6)	2 361(4)	3 937(15)	358(47)	−37(55)	23(216)	211(21)	208(147)	2 692(229)
C(15)	3 233(6)	3 712(3)	4 322(11)	433(48)	−55(48)	−56(165)	114(16)	−22(100)	1 246(171)
C(16)	3 496(6)	4 780(4)	3 081(14)	491(53)	47(59)	−270(226)	183(20)	138(128)	2 427(236)
C(17)	3 783(6)	4 529(4)	1 339(13)	357(46)	−34(54)	−374(190)	180(18)	−64(123)	2 316(237)
C(18)	3 481(6)	3 455(4)	2 507(13)	312(43)	−64(51)	−267(179)	202(19)	−252(119)	1 899(193)

(*c*) Hydrogen † atoms of PMDA and BA

	x/*a*	*y*/*b*	*z*/*c*		*x*/*a*	*y*/*b*	*z*/*c*
H(1)C(6′)	4 504	−938	10 555	H(8)C(8)	3 341	5 588	4 777
H(2)C(3′)	3 651	−1 801	4 215	H(9)C(9)	3 863	6 351	2 183
H(3)C(3)	3 334	907	1 861	H(10)C(10)	4 240	5 901	−995
H(4)C(4)	2 903	1 395	4 872	H(11)C(11)	4 263	4 756	−1 493
H(5)C(5)	2 760	2 385	6 797	H(12)C(12)	4 009	3 654	−203
H(6)C(6)	2 736	3 502	7 136	H(13)C(13)	3 908	2 716	−518
H(7)C(7)	2 988	4 560	5 899	H(14)C(14)	3 784	1 552	−869

* In the form $T = -\exp[h^2b_{11} + k^2b_{22} + l^2b_{33} + hlb_{13} + hkb_{12} + klb_{23}]$. † Hydrogen atom co-ordinates (× 10^4). A fixed isotropic B of 5.0 Å^2 was used.

Crystallographic Measurements.—Unit-cell dimensions were determined from calibrated Weissenberg photographs (Cu-K_α) and most of the intensities were measured on a Wooster four-circle diffractometer with Cu-K_α radiation. However, some of the stronger intensities were measured with Mo-K_α radiation on a Hilger linear diffractometer. 1 998 Reflections were considered observed and no absorption corrections were made [μ(Cu-K_α) = 8.75 cm^{-1}]. Three crystals were used, two mounted on the *c* and one on the *b* axis.

N.m.r. Measurements.—The dependence of the chemical shift of the protons in PMDA in dilute solution in 1,2-dichloroethane, as the concentration of added BA was altered gradually (3—58 × 10^{-3} mol kg^{-1} solution), was measured with respect to an internal tetramethylsilane reference by use of a Bruker HX 90 spectrometer operating at 90.00 MHz, 33.5 °C. This particular solvent was chosen because of the low solubilities of the components of the complex in other, less polar, solvents. If Δ is the proton chemical shift for PMDA in solution containing a concentration $[D]_0$ of BA, a plot of $\Delta/[D]_0$ *vs.* Δ from measurements on thirteen such solutions gave a straight line. This corresponds to the so-called Scatchard plot [3] and may be used to evaluate the association constant (K) which is obtained directly from the gradient of the line.[4] A second parameter, (Δ_0), may also be obtained from the Scatchard plot. This is the chemical shift of the measured nucleus in the acceptor complexed to the donor (BA), relative to the shift of the same nucleus in the free acceptor.[4] From a least-squares treatment of the experimental data, the following values were obtained: $K = 3.4$ mol kg^{-1}, and $\Delta_0 = 2.28$ p.p.m.

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[3] G. Scatchard, *Ann. New York. Acad. Sci.*, 1949, **51**, 660.

[4] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626.

The degree of association is relatively high considering the nature of the solvent. Lack of curvature of the Scatchard plot suggests that complexes with stoicheiometries other than 1 : 1 are either absent, or at most, make very little contribution to the overall equilibria.[5] The present technique does not allow for the detection of possible isomeric 1 : 1 complexes. Apart from the fact that the energy barrier between such differing molecular configurations would be low, the rates of formation and dissociation of electron-donor–acceptor complexes under these conditions are sufficiently fast[6] that only one population-averaged signal for the PMDA protons is seen in any case.

Attempts to measure possible changes in the chemical shifts of the various protons in BA in the presence of relatively high concentrations of PMDA have not been possible so far because of solubility limitations. Such experiments might yield information concerning the relative configuration of donor and acceptor as isolated pairs in solution.

Structure Determination.—All intensities were placed on a common scale and converted to structure factors in the normal manner. Normalized structure factors ($|E|$ values) were computed and the $|E|^2$ distribution indicated a hypercentric structure. Several attempts were made to determine the structure with the programs MULTAN[7] and TANFIZ[8] on the Elliott 4130 computer with 346 $|E|$ values >1.40, but it was impossible to interpret any of the Fourier E maps. The limited store capacity of the computer prevented the use of a greater number of E values, so the ICL 1906A computer at Oxford University was used with a multisolution tangent refinement program XTAN.[9] 578 Reflections with E values >1.20 were used and the following reflections were given phases: 4,0,0 (180°), given by Σ_1; 2,9,0 (0°), 3,1,1 (0°), 1,15,2 (0°). The following had variable phases, 2,10,1 (±90°), 4,1,1 (±45°, ±135°), 8,2,1 (±45, 135°). The best solution gave an E Fourier map which indicated 29 peaks which could be interpreted as corresponding to parts of both molecules. An F_o Fourier based on the phases calculated from the co-ordinates of the 29 peaks from the E map revealed the positions of the missing five atoms. The R value for 1 998 reflections was 0.45 at this stage. Subsequent refinement, first with isotropic temperature parameters, excluding hydrogen atoms and then with anisotropic parameters for carbon atoms and isotropic parameters for hydrogen atoms reduced R to 0.0825 for 1 354 reflections (many of the weaker reflections whose structure factors were regarded as unreliable were omitted from the later stages of the refinement). The weighting scheme in the last part of the refinement was: $\sqrt{w} = 1/\{1 + [(|F_o| - F^*)/G^*]^2\}^{\frac{1}{2}}$, where $F^* = 40.0$, and $G^* = 20.0$. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21644 (10 pp., 1 microfiche).†

Final atomic co-ordinates and temperature parameters are given in Table 1 and bond lengths and angles in Table 2. The molecular mean planes have the equations (where X, Y, Z are parallel to a, b, and c respectively):

$$\text{BA:}\quad 0.9559X - 0.0588Y + 0.2878Z + 4.5976 = 0$$

$$\text{PMDA:}\quad 0.9655X + 0.0184Y - 0.2596Z + 3.9072 = 0$$

Both molecules are essentially planar, the maximum deviations being 0.039 for BA and 0.071 Å for PMDA (see Figure 1).

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Benz[*a*]anthracene			
(i) Distances			
C(1)–C(2)	1.399(11)	C(8)–C(9)	1.322(14)
C(1)–C(13)	1.400(12)	C(9)–C(10)	1.443(15)
C(2)–C(3)	1.391(14)	C(10–C(11)	1.361(13)
C(3)–C(4)	1.392(14)	C(11)–C(17)	1.427(13)
C(4)–C(14)	1.418(11)	C(12)–C(17)	1.422(11)
C(5)–C(14)	1.396(13)	C(12)–C(18)	1.364(12)
C(5)–C(6)	1.321(11)	C(13)–C(14)	1.441(12)
C(6)–C(15)	1.429(12)	C(13)–C(18)	1.482(11)
C(7)–C(15)	1.385(11)	C(15)–C(18)	1.433(12)
C(7)–C(16)	1.430(13)	C(16)–C(17)	1.395(13)
C(8)–C(16)	1.464(12)		
(ii) Angles			
C(13)–C(1)–C(2)	122.4(8)	C(17)–C(16)–C(8)	118.5(8)
C(1)–C(2)–C(3)	117.6(9)	C(16)–C(8)–C(9)	120.1(9)
C(2)–C(3)–C(4)	123.3(8)	C(8)–C(9)–C(10)	120.9(8)
C(3)–C(4)–C(14)	118.8(8)	C(9)–C(10)–C(11)	120.8(9)
C(4)–C(14)–C(13)	119.3(8)	C(10)–C(11)–C(17)	119.0(9)
C(13)–C(14)–C(5)	118.4(7)	C(11)–C(17)–C(16)	118.7(8)
C(14)–C(5)–C(6)	124.0(9)	C(16)–C(17)–C(12)	118.7(8)
C(5)–C(6)–C(15)	120.6(8)	C(17)–C(12)–C(18)	120.8(8)
C(6)–C(15)–C(18)	121.0(7)	C(12)–C(18)–C(15)	120.3(7)
C(18)–C(15)–C(7)	120.2(7)	C(15)–C(18)–C(13)	116.2(7)
C(15)–C(7)–C(16)	118.6(8)	C(18)–C(13)–C(14)	119.7(8)
C(7)–C(16)–C(17)	121.3(7)	C(1)–C(13)–C(14)	118.6(7)
(*b*) Pyromellitic dianhydride			
(i) Distances			
C(1′)–C(2′)	1.379(12)	C(5′)–C(10′)	1.507(12)
C(1′)–C(6′)	1.373(12)	C(7′)–O(1′)	1.408(11)
C(1′)–C(7′)	1.511(11)	C(7′)–O(4′)	1.149(11)
C(2′)–C(3′)	1.364(11)	C(8′)–O(1′)	1.402(11)
C(2′)–C(8′)	1.489(12)	C(8′)–O(5′)	1.180(11)
C(3′)–C(4′)	1.366(12)	C(9′)–O(2′)	1.361(11)
C(4′)–C(5′)	1.355(12)	C(9′)–O(6′)	1.149(11)
C(4′)–C(9′)	1.517(10)	C(10′)–O(2′)	1.371(11)
C(5′)–C(6′)	1.386(10)	C(10′)–O(3′)	1.178(12)
(ii) Angles			
C(1′)–C(2′)–C(3′)	121.8(8)	C(4′)–C(9′)–O(2′)	104.1(7)
C(1′)–C(2′)–C(8′)	108.1(7)	C(5′)–C(10′)–O(2′)	105.6(8)
C(1′)–C(7′)–O(4′)	132.5(9)	C(5′)–C(10′)–O(3′)	130.1(8)
C(1′)–C(7′)–O(1′)	105.6(7)	C(7′)–O(1′)–C(8′)	111.1(6)
C(1′)–C(6′)–C(5′)	111.1(7)	C(9′)–O(2′)–C(10′)	114.1(6)
C(2′)–C(3′)–C(4′)	115.4(8)	O(4′)–C(7′)–O(1′)	121.8(8)
C(2′)–C(8′)–O(1′)	106.9(7)	O(5′)–C(8′)–O(1′)	122.2(8)
C(2′)–C(8′)–O(5′)	130.8(8)	O(2′)–C(9′)–O(6′)	125.5(7)
C(3′)–C(4′)–C(5′)	121.5(7)	O(2′)–C(10′)–O(3′)	124.3(8)
C(4′)–C(5′)–C(6′)	125.7(7)	C(2′)–C(1′)–C(7′)	108.3(7)
C(4′)–C(5′)–C(10′)	106.9(6)	C(2′)–C(1′)–C(6′)	108.3(7)
C(4′)–C(9′)–O(6′)	130.3(7)	C(5′)–C(4′)–C(9′)	109.1(7)

DISCUSSION

The bond lengths in the benz[*a*]anthracene molecule are very different from these given by Friedlander and Sayre,[2] but the degree of accuracy in the latter's work was so low that comparison is not useful. Three bond lengths in the present results are worthy of comment: as expected, the bond C(5)–C(6), which forms the '*K*'

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† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[5] B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gorton, *J. Chem. Soc.* (*B*), 1971, 1283.

[6] E. F. Caldin, J. E. Crooks, D. O'Donnell, D. Smith, and S. Toner, *J.C.S. Faraday I*, 1972, 849.

[7] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[8] A. C. Larson and W. D. S. Motherwell, 1970, personal communication.

[9] G. M. Sheldrick, 1974, personal communication.

region of the phenanthrene nucleus is very short, but so is C(8)–C(9) where there is no theoretical basis for a short bond. However, in two carcinogenic compounds based on benz[*a*]anthracene, short bonds are found in the same two positions. In methylcholanthrene [10] the lengths of the two bonds corresponding to C(5)–C(6) and C(8)–C(9) are 1.348 and 1.362 Å, and in benzo[*c*]pyrene [11] they are 1.342 and 1.374 Å.

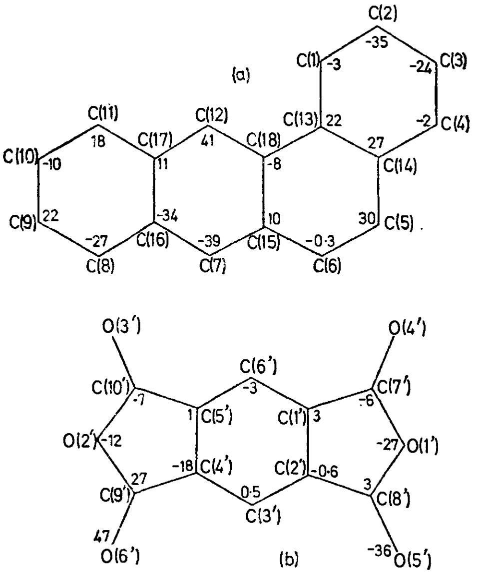

FIGURE 1 (a) Benz[*a*]anthracene and (b) pyromellitic dianhydride, showing the atom numbering system and deviations (Å × 10^3) of atoms from the mean plane through each molecule

The third bond which is unusually long for an aromatic compound, is C(13)–C(18) 1.482 Å. A long bond in this position of a phenanthrene nucleus was first pointed out by Burns and Iball[12] in chrysene, and subsequently several similar long bonds have been observed. There is overcrowding due to the hydrogen atoms attached to C(12) and C(1).

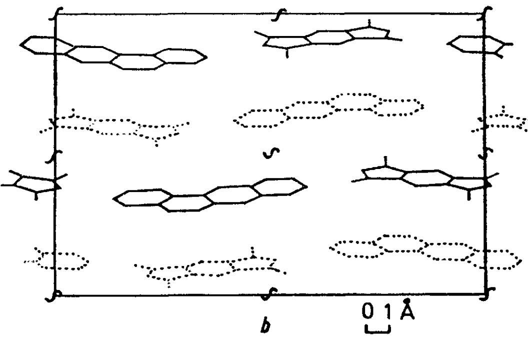

FIGURE 2 The stacking of the molecules in the *ab* plane

In the PMDA molecule the bond lengths and angles are as expected and in agreement with those found previously.[13]

The stacking of the molecules in the crystal is rather unusual, quite different from that normally found in 1 : 1 $\pi\rightarrow\pi^*$ EDA complexes. In the first place most of these complexes are in centrosymmetric space groups with the two molecules alternating A–D–A–D so that the overlap between A (electron acceptor) and D (electron donor) is the same as between D and A. In the present complex the overlap is as shown in Figure 2. There are two different environments for each donor and for each acceptor molecule. The projection of the PMDA molecule above the BA molecule on to the mean plane of the BA molecule is shown in Figure 3 [overlap (I)] while the projection of the PMDA molecule below the BA molecule on the same mean plane is shown in Figure (4) [overlap (II)]. The angle between the mean planes of the donor and acceptor molecules in overlap (I) is 4.7° and the mean separation, in the region of the overlap, is 3.37 Å. The corresponding values in overlap (II) are 2.8° and 3.39 Å.

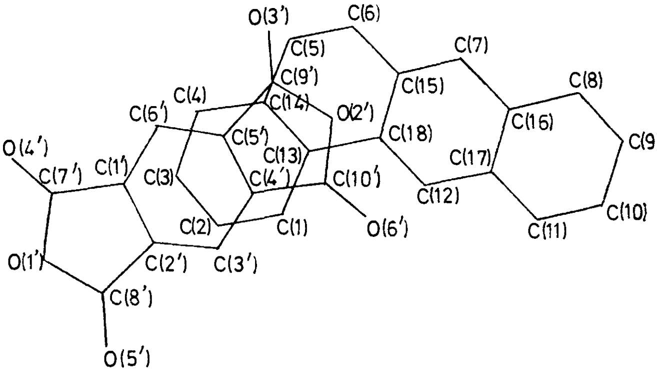

FIGURE 3 Projection of PMDA molecule at $1 - x, -y, \frac{1}{2} - z$ on the least-squares mean plane of BA at x, y, z

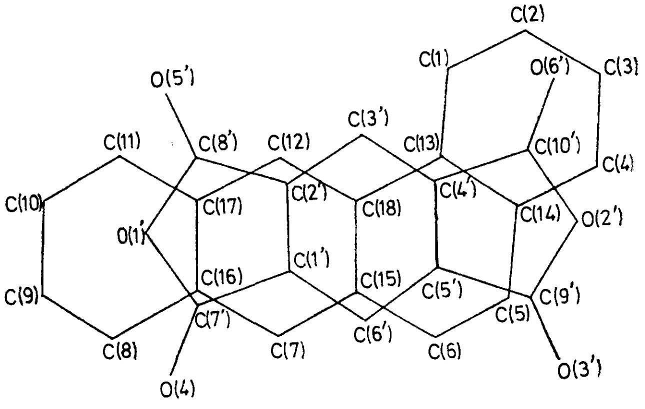

FIGURE 4 Projection of PMDA molecule at $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$ on the least-squares mean plane of BA at x, y, z

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