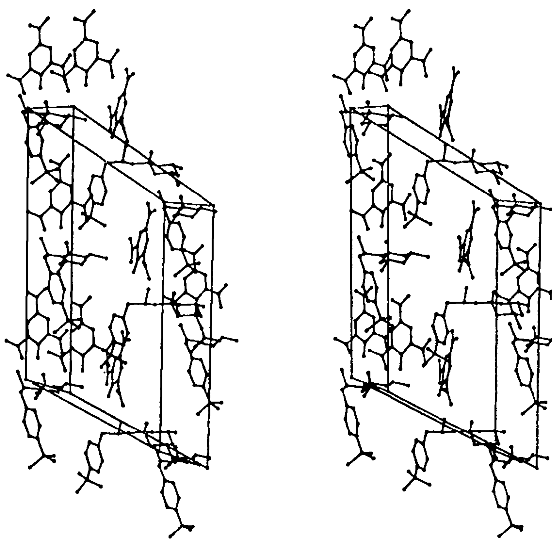

Fig. 2. Stereoview of the crystal packing. The H atoms except H4 have been omitted. The *a* axis points upward, the *b* axis out of the paper and the *c* axis from left to right.

The fenpropimorph ion forms a hydrogen bond N4—H4···O41 to one picrate ion. The distance N4···O41 is 2·687 (6) Å. A stereoview of the crystal packing is shown in Fig. 2. The shape of the fenpropimorph ion in the present structure is roughly that of the letter L. It has been mentioned (Himmele & Pommer, 1980) that the crystal structure of *S*-(−)-fenpropimorph hydrochloride has been examined, but the results have not been made available. Molecular mechanics calculations performed on the fenpropimorph molecule (Jensen, Pettersson, Jørgensen, Klemmensen & Hacksell, 1990) find a low energy conformation similar to that found in fenpropimorph picrate.

The authors thank Mr Flemming Hansen for collecting the X-ray data. The diffractometer and an X-ray generator were acquired by means of Grants 11-1837, 11-2360 and 11-3531 from the Danish Natural Science Research Council.

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*Acta Cryst.* (1990). C**46**, 781–784

# Structure of a Synthetic Taxol Precursor: *N*-*tert*-Butoxycarbonyl-10-deacetyl-*N*-debenzoyltaxol

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(*Received* 15 *March* 1989; *accepted* 14 *August* 1989)

**Abstract.** 4-Acetoxy-2-benzoyloxy-1,7,10-trihydroxy-9-oxo-5,20-epoxy-11-taxen-13-yl *β*-*tert*-butoxycarbonylamino-*α*-hydroxybenzenepropionate–methanol–water (1/1/1), $C_{43}H_{53}NO_{14}.CH_3OH.H_2O$, $M_r = 857\cdot9$, monoclinic, $P2_1$, $a = 20\cdot816\,(10)$, $b = 8\cdot758\,(5)$, $c = 12\cdot726\,(8)$ Å, $\beta = 101\cdot06\,(5)^\circ$, $V = 2277$ Å$^3$, $Z = 2$, $D_x = 1\cdot25$ g cm$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu = 7\cdot07$ cm$^{-1}$, $F(000) = 916$, room temperature, final $R = 0\cdot073$, $wR = 0\cdot084$, for 3438 observed reflexions. X-ray analysis of an intermediate in the hemisynthesis of taxol was performed; this is the first example of X-ray analysis of a taxane diterpenoid containing an oxetan ring and the taxol-type side chain, both of which are essential for biological activity.

**Introduction.** In 1971, antitumoral taxol (1) (see Fig. 1) was isolated from the stem bark of the yew *Taxus brevifolia* Nutt, and its structure and configuration were confirmed by the X-ray analysis of the bis-

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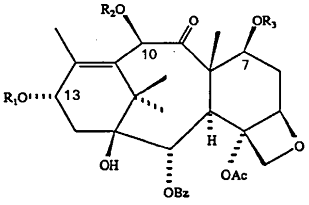
(iodoacetate) (2) and the *p*-bromobenzoate (3) (Wani, Taylor, Wall, Coggon & McPhail, 1971). The absolute configurations of (2) and (3) were established using the anomalous scattering of the halogen atoms, but full details of the X-ray analysis were never published. X-ray crystallographic data of taxane-type diterpenes are available for baccatin V (Della Casa de Marcano, Hallsall, Castellano & Hodder, 1970), bromotaxinol (Shiro & Koyama, 1971), taxagifine (Chauvière, Guénard, Pascard, Picot, Potier & Prangé, 1982), *o*-cinnamoyltaxicin-I triacetate (Begley, Frecknall & Pattenden, 1984), taxin A (Graf, Kirfel, Wolff & Breitmaier, 1982), taxusin (Ho, Lee, Peng, Yeh & Chen, 1987) and taiwanxan (Ho, Lin, Lee, Peng, Yeh & Chen, 1987). However, no X-ray diffraction study has yet been carried out on a taxane diterpene possessing an oxetane ring and the bulky $\alpha$-hydroxy-$\beta$-amino side chain which seems necessary for significant antitumor activity. During the course of our chemical studies on taxol hemisynthesis, we prepared the title compound (5*a*) which contains both structural groups and leads to 10-deacetyltaxol (4) without modification of stereochemistry (Colin, Guénard, Gueritte-Voegelein & Potier, 1986). The X-ray diffraction study was carried out to find the stereochemistry at C2′ and C3′, connected with the biological activity.

**Experimental.** Crystal 0·4 × 0·3 × 0·15 mm. Graphite-monochromated Cu $K\alpha$ radiation, four-circle Philips PW1100 diffractometer, $\theta$-$2\theta$ scan technique. Unit-cell dimensions refined from setting angles of 18 reflections. Three standard reflections measured every 3 h to monitor instrument and crystal stability. 4674 reflections collected up to $2\theta = 120°$ ($-24 \le h \le 24$, $0 \le k \le 10$, $0 \le l \le 15$). 4480 unique, 3438 considered as observed with $I > 3\sigma(I)$; $\sigma(I)$ derived from counting statistics; Lp corrections, absorption ignored. Structure solved by direct methods with a local program (Riche, 1982).



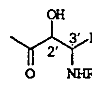
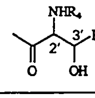
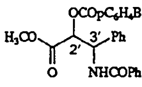
| Compound | $R_1$ | | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|---|
| (2) | H | | $COCH_2I$ | $COCH_2I$ | |
| (1) |  | 2′R,3′S | Ac | H | COPh |
| (4) | | 2′R,3′S | H | H | COPh |
| (5*a*) | | 2′R,3′S | H | H | COOtBu |
| (5*b*) | | 2′S,3′R | H | H | COOtBu |
| (6*a*) |  | 2′R,3′S | H | H | COOtBu |
| (6*b*) | | 2′S,3′R | H | H | COOtBu |
| (3) |  | 2′R,3′S | | | |

Fig. 1. Details of structures related to the title compound [(5*a*)] which have been previously studied.

Table 1. *Atomic coordinates* (× $10^4$) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| C1 | 7866 (3) | 3480 (6) | −1818 (4) | 46 (4) |
| C2 | 7641 (2) | 4107 (6) | −2989 (4) | 45 (4) |
| C3 | 7896 (2) | 5715 (6) | −3240 (4) | 40 (4) |
| C4 | 7328 (2) | 6744 (6) | −3811 (4) | 43 (4) |
| C5 | 7474 (3) | 8076 (7) | −4529 (4) | 51 (5) |
| C6 | 8177 (3) | 8416 (8) | −4609 (5) | 57 (5) |
| C7 | 8677 (2) | 7475 (6) | −3859 (4) | 48 (4) |
| C8 | 8474 (2) | 5745 (7) | −3855 (4) | 46 (4) |
| C9 | 9122 (3) | 4944 (7) | −3286 (4) | 52 (5) |
| C10 | 9413 (2) | 5144 (8) | −2104 (4) | 55 (5) |
| C11 | 8950 (3) | 4691 (7) | −1396 (4) | 48 (4) |
| C12 | 8789 (3) | 5712 (7) | −694 (4) | 51 (4) |
| C13 | 8222 (3) | 5247 (7) | −180 (4) | 51 (4) |
| C14 | 7652 (3) | 4608 (7) | −1014 (4) | 50 (4) |
| C15 | 8612 (3) | 3129 (7) | −1527 (4) | 53 (5) |
| C16 | 8811 (3) | 2113 (8) | −2382 (5) | 63 (5) |
| C17 | 8803 (3) | 2186 (9) | −464 (5) | 69 (6) |
| C18 | 9093 (3) | 7257 (9) | −416 (6) | 72 (6) |
| C19 | 8298 (3) | 5093 (8) | −4988 (4) | 54 (5) |
| C20 | 6874 (3) | 6167 (7) | −4844 (4) | 50 (4) |
| O1 | 7495 (2) | 2130 (4) | −1752 (3) | 56 (3) |
| O2 | 6934 (2) | 4224 (5) | −3141 (3) | 51 (3) |
| O4 | 6926 (2) | 7237 (5) | −3086 (3) | 49 (3) |
| O5 | 7095 (2) | 7344 (6) | −5495 (3) | 60 (4) |
| O7 | 9307 (2) | 7672 (5) | −4085 (4) | 63 (4) |
| O9 | 9440 (2) | 4270 (6) | −3832 (4) | 66 (4) |
| O10 | 10013 (2) | 4344 (7) | −1810 (4) | 77 (5) |
| O13 | 7972 (2) | 6578 (5) | 282 (3) | 57 (3) |
| C1′ | 8162 (3) | 6742 (7) | 1356 (4) | 56 (5) |
| O1′ | 8465 (3) | 5794 (7) | 1907 (3) | 86 (5) |
| C2′ | 8001 (3) | 8287 (7) | 1730 (4) | 54 (5) |
| O2′ | 8254 (2) | 8363 (6) | 2850 (3) | 69 (4) |
| C3′ | 7278 (3) | 8650 (6) | 1486 (4) | 53 (5) |
| C4′ | 7180 (3) | 10245 (7) | 1890 (4) | 54 (5) |
| C5′ | 7071 (4) | 10513 (8) | 2888 (5) | 66 (6) |
| C6′ | 7061 (4) | 11990 (8) | 3275 (6) | 76 (7) |
| C7′ | 7156 (4) | 13217 (9) | 2647 (6) | 77 (7) |
| C8′ | 7243 (4) | 12959 (8) | 1633 (6) | 81 (8) |
| C9′ | 7258 (4) | 11493 (8) | 1247 (5) | 74 (7) |
| N10′ | 6918 (3) | 7468 (6) | 1961 (4) | 59 (4) |
| C11′ | 6335 (3) | 6988 (9) | 1417 (6) | 67 (6) |
| O11′ | 6103 (3) | 7235 (9) | 482 (4) | 101 (7) |
| O12′ | 6073 (2) | 6064 (6) | 2073 (4) | 74 (5) |
| C13′ | 5443 (4) | 5276 (10) | 1684 (8) | 88 (9) |
| C14′ | 5384 (5) | 4416 (15) | 2669 (10) | 127 (14) |
| C15′ | 4906 (4) | 6410 (16) | 1335 (11) | 126 (14) |
| C16′ | 5511 (6) | 4189 (20) | 792 (13) | 188 (24) |
| C17′ | 6555 (3) | 3126 (9) | −3697 (5) | 64 (6) |
| O17′ | 6776 (3) | 2017 (7) | −4100 (4) | 87 (6) |
| C18′ | 5872 (3) | 3440 (10) | −3786 (6) | 79 (8) |
| C19′ | 5648 (4) | 4461 (14) | −3126 (10) | 110 (12) |
| C20′ | 4975 (5) | 4707 (18) | −3270 (12) | 142 (17) |
| C21′ | 4544 (6) | 4104 (27) | −3929 (22) | 236 (43) |
| C22′ | 4737 (5) | 3194 (25) | −4709 (16) | 201 (32) |
| C23′ | 5421 (5) | 2715 (16) | −4625 (9) | 120 (14) |
| C24′ | 7158 (3) | 8421 (7) | −2401 (4) | 54 (5) |
| O24′ | 7681 (2) | 8969 (5) | −2350 (4) | 63 (4) |
| C25′ | 6665 (4) | 8844 (10) | −1775 (6) | 78 (7) |
| OME1 | 9490 (2) | 7341 (7) | 3845 (4) | 77 (5) |
| CME1 | 9845 (5) | 5894 (15) | 3795 (10) | 125 (13) |
| W1/2* | 9230 | 923 | 2984 | 148 |
| W2/2* | 8963 | 2070 | 3358 | 148 |

* Occupancy factor $f = 0·5$.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C1—C2 | 1·573 (7) | O13—C1′ | 1·356 (6) |
| C1—C14 | 1·548 (7) | C1′—O1′ | 1·187 (8) |
| C1—C15 | 1·555 (8) | C1′—C2′ | 1·493 (9) |
| C1—O1 | 1·423 (6) | C2′—O2′ | 1·423 (7) |
| C2—C3 | 1·560 (7) | C2′—C3′ | 1·510 (9) |
| C2—O2 | 1·450 (6) | C3′—C4′ | 1·517 (8) |
| C3—C4 | 1·551 (7) | C3′—N10′ | 1·474 (8) |
| C3—C8 | 1·558 (7) | C4′—C5′ | 1·352 (8) |
| C4—C5 | 1·547 (8) | C4′—C9′ | 1·394 (9) |
| C4—C20 | 1·550 (7) | C5′—C6′ | 1·386 (10) |
| C4—O4 | 1·428 (6) | C6′—C7′ | 1·376 (11) |
| C5—C6 | 1·516 (8) | C7′—C8′ | 1·356 (11) |
| C5—O5 | 1·473 (7) | C8′—C9′ | 1·377 (10) |
| C6—C7 | 1·514 (8) | N10′—C11′ | 1·345 (9) |
| C7—C8 | 1·573 (8) | C11′—O11′ | 1·214 (9) |
| C7—O7 | 1·406 (7) | C11′—O12′ | 1·350 (9) |
| C8—C9 | 1·570 (8) | O12′—C13′ | 1·481 (9) |
| C8—C19 | 1·528 (7) | C13′—C14′ | 1·487 (16) |
| C9—C10 | 1·520 (7) | C13′—C15′ | 1·497 (15) |
| C9—O9 | 1·201 (7) | C13′—C16′ | 1·509 (19) |
| C10—C11 | 1·494 (7) | C17′—O17′ | 1·228 (9) |
| C10—O10 | 1·418 (7) | C17′—C18′ | 1·430 (10) |
| C11—C12 | 1·351 (8) | C18′—C19′ | 1·369 (14) |
| C11—C15 | 1·533 (8) | C18′—C23′ | 1·428 (14) |
| C12—C13 | 1·511 (8) | C19′—C20′ | 1·394 (13) |
| C12—C18 | 1·506 (10) | C20′—C21′ | 1·224 (27) |
| C13—C14 | 1·539 (8) | C21′—C22′ | 1·391 (31) |
| C13—O13 | 1·447 (7) | C22′—C23′ | 1·468 (16) |
| C15—C16 | 1·523 (8) | C24′—O24′ | 1·180 (7) |
| C15—C17 | 1·571 (9) | C24′—C25′ | 1·462 (9) |
| C20—O5 | 1·452 (7) | OME1—CME1 | 1·476 (14) |
| O2—C17′ | 1·355 (8) | | |

| | | | |
|---|---|---|---|
| C2—C1—C14 | 109·4 (4) | C11—C15—C16 | 114·6 (5) |
| C2—C1—C15 | 113·4 (4) | C11—C15—C17 | 109·9 (5) |
| C2—C1—O1 | 106·2 (4) | C16—C15—C17 | 104·4 (5) |
| C14—C1—C15 | 111·7 (4) | C4—C20—O5 | 92·4 (4) |
| C14—C1—O1 | 105·2 (4) | C2—O2—C17′ | 119·6 (4) |
| C15—C1—O1 | 110·4 (4) | C4—O4—C24′ | 117·2 (4) |
| C1—C2—C3 | 117·2 (4) | C5—O5—C20 | 90·6 (4) |
| C1—C2—O2 | 105·2 (4) | C13—O13—C1′ | 115·9 (4) |
| C3—C2—O2 | 106·6 (4) | O13—C1′—O1′ | 122·7 (6) |
| C2—C3—C4 | 111·3 (4) | O13—C1′—C2′ | 112·2 (5) |
| C2—C3—C8 | 116·4 (4) | O1′—C1′—C2′ | 124·9 (6) |
| C4—C3—C8 | 110·3 (4) | C1′—C2′—O2′ | 107·4 (5) |
| C3—C4—C5 | 119·8 (4) | C1′—C2′—C3′ | 113·6 (5) |
| C3—C4—C20 | 119·6 (4) | O2′—C2′—C3′ | 111·0 (5) |
| C3—C4—O4 | 111·2 (4) | C2′—C3′—C4′ | 108·5 (5) |
| C5—C4—C20 | 84·4 (4) | C2′—C3′—N10′ | 109·4 (5) |
| C5—C4—O4 | 111·1 (4) | C4′—C3′—N10′ | 113·3 (5) |
| C20—C4—O4 | 108·0 (4) | C3′—C4′—C5′ | 122·4 (6) |
| C4—C5—C6 | 119·2 (5) | C3′—C4′—C9′ | 119·0 (5) |
| C4—C5—O5 | 91·8 (4) | C5′—C4′—C9′ | 118·4 (6) |
| C6—C5—O5 | 113·5 (5) | C4′—C5′—C6′ | 120·8 (6) |
| C5—C6—C7 | 114·0 (5) | C5′—C6′—C7′ | 120·5 (7) |
| C6—C7—C8 | 111·9 (4) | C6′—C7′—C8′ | 118·9 (7) |
| C6—C7—O7 | 111·0 (5) | C7′—C8′—C9′ | 120·7 (7) |
| C8—C7—O7 | 112·4 (4) | C4′—C9′—C8′ | 120·6 (7) |
| C3—C8—C7 | 104·6 (4) | C3′—N10′—C11′ | 119·2 (5) |
| C3—C8—C9 | 116·0 (4) | N10′—C11′—O11′ | 126·8 (7) |
| C3—C8—C19 | 113·6 (4) | N10′—C11′—O12′ | 107·5 (6) |
| C7—C8—C9 | 103·0 (4) | O11′—C11′—O12′ | 125·5 (7) |
| C7—C8—C19 | 111·9 (4) | C11′—O12′—C13′ | 120·6 (6) |
| C9—C8—C19 | 107·3 (4) | O12′—C13′—C14′ | 99·5 (7) |
| C8—C9—C10 | 123·3 (5) | O12′—C13′—C15′ | 110·7 (8) |
| C8—C9—O9 | 118·1 (5) | O12′—C13′—C16′ | 109·9 (8) |
| C10—C9—O9 | 118·0 (5) | C14′—C13′—C15′ | 114·1 (9) |
| C9—C10—C11 | 112·6 (5) | C14′—C13′—C16′ | 110·4 (9) |
| C9—C10—O10 | 111·6 (5) | C15′—C13′—C16′ | 111·6 (9) |
| C11—C10—O10 | 110·3 (5) | O2—C17′—O17′ | 123·5 (6) |
| C10—C11—C12 | 119·6 (5) | O2—C17′—C18′ | 112·1 (6) |
| C10—C11—C15 | 120·5 (5) | O17′—C17′—C18′ | 124·4 (7) |
| C12—C11—C15 | 119·7 (5) | C17′—C18′—C19′ | 121·9 (8) |
| C11—C12—C13 | 114·9 (5) | C17′—C18′—C23′ | 118·3 (8) |
| C11—C12—C18 | 127·1 (5) | C19′—C18′—C23′ | 119·7 (9) |
| C13—C12—C18 | 117·9 (5) | C18′—C19′—C20′ | 118·2 (10) |
| C12—C13—C14 | 111·3 (4) | C19′—C20′—C21′ | 127·5 (16) |
| C12—C13—O13 | 109·3 (4) | C20′—C21′—C22′ | 117·5 (20) |
| C14—C13—O13 | 106·4 (4) | C21′—C22′—C23′ | 121·4 (17) |
| C1—C14—C13 | 113·9 (4) | C18′—C23′—C22′ | 114·6 (11) |
| C1—C15—C11 | 105·5 (4) | O4—C24′—O24′ | 123·2 (5) |
| C1—C15—C16 | 110·0 (5) | O4—C24′—C25′ | 109·7 (5) |
| C1—C15—C17 | 112·7 (5) | O24′—C24′—C25′ | 127·1 (6) |

Refinement by large blocks (Sheldrick, 1976) with anisotropic temperature factors; $\sum w||F_o| - |F_c||^2$ minimized; $w = 1/[\sigma^2(F_o) + 0{\cdot}005F_o^2]$. H atoms introduced in their theoretical positions (C—H = 1·08 Å) and assigned the equivalent isotropic thermal factor of the bonded C atom. H atom fixed on N and OH groups found by difference Fourier synthesis (except those of hydroxyl groups fixed at C1 and C7) and introduced in the calculations with a constant temperature factor. One methanol molecule and one disordered water molecule ($\frac{1}{2},\frac{1}{2}$) were located. In spite of the high value of the thermal factors of C20′, C21′ and C22′, no additional disorder observed on difference Fourier synthesis. Final $R = 0{\cdot}073$, $wR = 0{\cdot}084$ (for the 3438 reflections and 719 variables). $(\Delta/\sigma)_{\max} = 1{\cdot}06$. Minimum and maximum peaks in the $\Delta F$ map were $-0{\cdot}017$ and $0{\cdot}30\ \mathrm{e}\ \mathrm{Å}^{-3}$. Atomic scattering factors from Cromer & Mann (1968).

**Discussion.** Final atomic parameters are given in Table 1,* bond distances and angles are reported in Table 2. Fig. 2 gives a perspective view of the title compound (*5a*) with the numbering scheme, using the absolute configuration of taxol (1). The asymmetric carbons C2′ and C3′ adopt respectively the *R* and *S* configurations. In the course of the hemisynthesis of taxol, four isomers [(*5a*), (*5b*), (*6a*), (*6b*)] have been prepared. It is noteworthy that only the title compound (2′*R*,3′*S*) posseses *in vitro* and *in vivo* activity better than taxol itself. Epimerization of carbons 2′ and 3′ [(*5b*): 2′*S*, 3′*R*] and substitution at

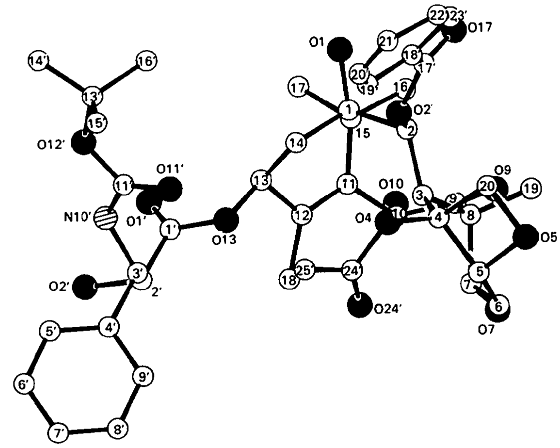


Fig. 2. Perspective view of the molecule showing the atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52489 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C2′ and C3′ in (*6a*) and (*6b*) strongly reduced the biological activity. So it seems that this X-ray analysis provides a structural description of the taxol-like active molecule.

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# The Structure of Hexaphenylbenzene Anisole Clathrate, $2C_6(C_6H_5)_6.C_6H_5OCH_3$

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(*Received* 28 *November* 1988; *accepted* 20 *June* 1989)

**Abstract.** Hexaphenylbenzene–anisole (2/1), $2C_{42}H_{30}.C_7H_8O$, $M_r \simeq 1177.44$, monoclinic, *Aa*, $a =$ 11·648 (6), $b =$ 45·99 (2), $c =$ 12·428 (4) Å, $\beta =$ 99·82 (4)°, $V =$ 6560·1 Å$^3$, $Z = 4$, $D_m =$ 1·182, $D_x =$ 1·192 g cm$^{-3}$, $\lambda$(Cu $K\alpha_1$) = 1·54051 Å, $\mu =$ 4·87 cm$^{-1}$, $F(000) = 2488$, $T = 298$ K, $R =$ 9·2 and $wR =$ 3·8% for 3616 unique observed reflections having $I_o > \sigma(I_o)$. The asymmetric unit consists of two hexaphenylbenzene molecules and one anisole molecule. The hexaphenylbenzene molecules adopt a propeller conformation with the phenyl rings twisted by an average of 75° from the molecular plane. The hexaphenylbenzene forms an unusual array, where the molecules are arranged in layers which alternate between body-centered and hexagonal packing. The anisole occupies one set of the pseudo-octahedral holes in this array.

**Introduction.** The study of clathrated and intercalated molecules forms a broad discipline which has been reviewed extensively (Davies, 1981; MacNicol, McKendrick & Wilson, 1978). The available structural data obtained from X-ray diffraction have also been reviewed (Andreetti, 1981). One common feature of these complexes is the formation of six-membered rings *via* hydrogen bonding between adjacent molecules. The six-membered rings serve as the ceiling and floor of the cavity, which encloses the guest molecule. This feature is important because the geometry and overall dimensions of the aforementioned rings closely resemble those of a substituted benzene. Therefore, hexasubstituted benzenes were proposed as host compounds in an effort to understand better the structures of clathrates (MacNicol *et al.*, 1978). Several of these complexes have been synthesized and their structures reported (Burns, Gilmore, Mallinson, MacNicol & Swanson, 1981; Freer, Gall & MacNicol, 1982; Freer, Gilmore, MacNicol & Swanson, 1980; Gilmore, MacNicol, Murphy & Russell, 1983). We now report the structure of one of these non hydrogen bonded clathrates, hexaphenyl–anisole, recently synthesized in our laboratory.

**Experimental.** Hexaphenylbenzene was prepared using a modification of the published procedure (Fieser & Williams, 1975). It was sublimed under vacuum as a last purification step, and a saturated solution was prepared by dissolving 3 g in 100 ml of boiling anisole which had been distilled three times. After cooling to room temperature, the solution was filtered into Petri dishes containing 5–10 drops of anisole. After four weeks of slow evaporation, small colorless crystals formed. A crystal having dimensions 0·1 × 0·5 × 0·1 mm, after being cut, was chosen

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0108-2701/90/050784-05$03.00