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## Structures of *O*-Palmitoyl Benzophenone Oxime (I) and (*E*)-*O*-Palmitoyl Phenyl 2-Pyridyl Ketone Oxime (II)

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**Abstract.** (I): diphenylmethyleamino palmitate,  $C_{29}H_{41}NO_2$ ,  $M_r = 435.7$ , triclinic,  $P\bar{1}$ ,  $a = 5.764$  (4),  $b = 8.997$  (3),  $c = 25.576$  (7) Å,  $\alpha = 81.79$  (2),  $\beta = 84.62$  (3),  $\gamma = 86.78$  (4)°,  $V = 1305.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.100$ ,  $D_x = 1.108$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.0735$  mm<sup>-1</sup>,  $F(000) = 476$ ,  $T = 296$  K,  $R = 0.058$  for 4545 observed reflections. (II): phenyl-(2-pyridyl)methyleamino palmitate,  $C_{28}H_{40}N_2O_2$ ,  $M_r = 436.6$ , monoclinic,  $P2_1/n$ ,  $a = 8.195$  (2),  $b = 54.46$  (1),  $c = 5.800$  (1) Å,  $\beta = 96.78$  (2)°,  $V = 2570.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.125$ ,  $D_x = 1.128$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 0.554$  mm<sup>-1</sup>,  $F(000) = 952$ ,  $T = 296$  K,  $R = 0.060$  for 2731 observed reflections. The C=N part of the molecule is nearly coplanar with the *trans*-zigzag palmitoyl plane for both (I) and (II). (II) has an unusual eclipsed form about the N–O–C(=O)–C bond in contrast to the *anti* form of (I). The C=N distances are 1.280 (3) Å for (I) and 1.273 (5) Å for (II), and the N–O distances are 1.435 (2) Å for (I) and 1.439 (2) Å for (II). The palmitoyl chains of (I) are packed in a  $T''$  subcell, while those of (II) are packed in a new type of subcell hybridizing the  $T''$  and  $M''$  packings.

**Introduction.** (*E*)-Phenyl 2-pyridyl ketone *O*-acyl oximes and their related compounds were synthesized to study their selective reactions for different classes of amines. The selective reactions for primary and *N*-methyl secondary amines are of special interest in relation to their molecular recognition by epinephrine derivatives at their receptor sites (Miyasaka, Noguchi, Taga, Kajiwara & Fuji, 1986). Molecular dimensions of oxime groups in crystalline states have been discussed

in connection with their intermolecular hydrogen bonds formed by the oxime OH group (Bertolasi, Gilli & Veronese, 1982; Jerslev, 1983), but structures of *O*-substituted oximes have been determined for only a few crystals, e.g. 4,4'-dibromobenzophenone oxime *O*-picryl ether (McCullough, Paul & Curtin, 1972) and *O*-(4-bromobenzoyl) 1,2-benzisoxazol-3-yl phenyl ketone oxime (Sax, Pletcher, Scholtz, Gerkin & Pinkus, 1971). This paper describes two structures of the title *O*-palmitoyl oximes, X-ray studies of which were undertaken in order to elucidate the structural properties of the *O*-substituted oxime moieties. The pyridine group in (II) is changed to a phenyl group in (I), and the effects of this change of aromatic groups on the molecular structure and on the molecular packing are discussed.

**Experimental.** Colourless crystals, (I) 0.2 × 0.2 × 0.3 mm and (II) 0.2 × 0.2 × 0.2 mm, on a Rigaku AFC-5RU; lattice parameters (I) from 20 reflections ( $21.7 < 2\theta < 31.0^\circ$ ) with Mo  $K\alpha$  and (II) from 25 reflections ( $46.6 < 2\theta < 56.6^\circ$ ) with Cu  $K\alpha$ ; densities by flotation method. Intensities collected in an  $\omega$ -2 $\theta$  scanning mode; (I) 7197 measured reflections ( $h$  0→8,  $k$  -12→12,  $l$  -34→34) within  $2\theta = 60^\circ$  using Mo  $K\alpha$ , and (II) 4068 measured reflections ( $h$  -9→9,  $k$  0→39,  $l$  0→6) within  $2\theta = 120^\circ$  using Cu  $K\alpha$ ; three standard reflections recorded every 56 reflections, no change greater than 2% in intensity; Lorentz-polarization corrections applied, no absorption correction. Both structures solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-matrix least-squares refinement minimizing  $\sum w(|F_o| -$

Table 1. Atomic parameters for non-hydrogen atoms in *O*-palmitoyl benzophenone oxime
$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

|       | x           | y           | z           | $B_{eq}(\text{\AA}^2)$ |
|-------|-------------|-------------|-------------|------------------------|
| N(1)  | 1.5510 (2)  | 0.2740 (2)  | 0.1435 (1)  | 3.97 (5)               |
| C(2)  | 1.6687 (3)  | 0.1777 (2)  | 0.1183 (1)  | 3.42 (6)               |
| C(3)  | 1.8638 (3)  | 0.2395 (2)  | 0.0805 (1)  | 3.33 (6)               |
| C(4)  | 1.9854 (3)  | 0.3593 (2)  | 0.0907 (1)  | 4.16 (6)               |
| C(5)  | 2.1716 (3)  | 0.4115 (2)  | 0.0564 (1)  | 5.06 (7)               |
| C(6)  | 2.2341 (3)  | 0.3481 (2)  | 0.0110 (1)  | 5.31 (7)               |
| C(7)  | 2.1118 (4)  | 0.2322 (2)  | -0.0003 (1) | 5.21 (8)               |
| C(8)  | 1.9277 (3)  | 0.1762 (2)  | 0.0346 (1)  | 4.36 (6)               |
| C(9)  | 1.6304 (3)  | 0.0133 (2)  | 0.1239 (1)  | 3.53 (6)               |
| C(10) | 1.7969 (3)  | -0.0877 (2) | 0.1459 (1)  | 4.28 (6)               |
| C(11) | 1.7657 (4)  | -0.2413 (2) | 0.1513 (1)  | 5.11 (8)               |
| C(12) | 1.5729 (4)  | -0.2941 (2) | 0.1337 (1)  | 5.52 (8)               |
| C(13) | 1.4105 (3)  | -0.1948 (2) | 0.1109 (1)  | 5.77 (16)              |
| C(14) | 1.4367 (3)  | -0.0407 (2) | 0.1062 (1)  | 4.89 (7)               |
| O(15) | 1.3737 (2)  | 0.2001 (1)  | 0.1795 (0)  | 4.33 (4)               |
| C(16) | 1.2303 (3)  | 0.2987 (2)  | 0.2049 (1)  | 3.85 (6)               |
| O(17) | 1.2504 (2)  | 0.4305 (1)  | 0.1989 (1)  | 5.68 (6)               |
| C(18) | 1.0471 (3)  | 0.2122 (2)  | 0.2400 (1)  | 4.26 (6)               |
| C(19) | 0.8634 (3)  | 0.3095 (2)  | 0.2669 (1)  | 4.13 (6)               |
| C(20) | 0.6967 (3)  | 0.2158 (2)  | 0.3062 (1)  | 4.10 (6)               |
| C(21) | 0.5132 (3)  | 0.3084 (2)  | 0.3355 (1)  | 4.08 (6)               |
| C(22) | 0.3565 (3)  | 0.2131 (2)  | 0.3769 (1)  | 4.17 (6)               |
| C(23) | 0.1719 (3)  | 0.3032 (2)  | 0.4070 (1)  | 4.17 (6)               |
| C(24) | 0.0183 (3)  | 0.2074 (2)  | 0.4484 (1)  | 4.19 (6)               |
| C(25) | -0.1679 (3) | 0.2972 (2)  | 0.4783 (1)  | 4.23 (6)               |
| C(26) | -0.3215 (3) | 0.2023 (2)  | 0.5198 (1)  | 4.33 (6)               |
| C(27) | -0.5060 (3) | 0.2928 (2)  | 0.5497 (1)  | 4.38 (6)               |
| C(28) | -0.6597 (3) | 0.1985 (2)  | 0.5917 (1)  | 4.56 (6)               |
| C(29) | -0.8405 (3) | 0.2899 (2)  | 0.6219 (1)  | 4.94 (7)               |
| C(30) | -0.9965 (3) | 0.1992 (2)  | 0.6637 (1)  | 4.93 (8)               |
| C(31) | -1.1793 (4) | 0.2925 (2)  | 0.6924 (1)  | 6.35 (9)               |
| C(32) | -1.3424 (5) | 0.2037 (3)  | 0.7328 (1)  | 7.86 (21)              |

$|F_c|^2$  where  $w = [\sigma^2(F) + (0.023F)^2]^{-1}$  with anisotropic C, N and O, and isotropic H; H atoms located in difference Fourier maps; scattering factors from *International Tables for X-ray Crystallography* (1974); (I)  $R = 0.058$ ,  $wR = 0.070$ ,  $S = 1.56$  for 4545 reflections with  $F_o > 3\sigma(F_o)$ ,  $(\Delta/\sigma)_{\max} = 0.8$ ,  $\Delta\rho = \pm 0.23 \text{ e \AA}^{-3}$ ; (II)  $R = 0.060$ ,  $wR = 0.077$ ,  $S = 1.8$  for 2731 reflections with  $F_o > 3\sigma(F_o)$ ,  $(\Delta/\sigma)_{\max} = 0.7$ ,  $\Delta\rho = \pm 0.25 \text{ e \AA}^{-3}$ . All computations performed on a FACOM M382 in the Data Processing Center of Kyoto University, using *KPPXRAY* programs (Taga, Higashi & Iizuka, 1985).

**Discussion.** The final atomic parameters with their standard deviations are listed in Tables 1 and 2.\* The palmitoyl moieties of both molecules have the same extended conformation, and the C=N oxime part is nearly coplanar with the palmitoyl zigzag plane (Figs. 1 and 2); C(2)–N(1)–O(15)–C(16) torsion angles are  $-175.5 (2)^\circ$  for (I) and  $-172.1 (2)^\circ$  for (II). With respect to a rotation about the O(15)–C(16) bond, (I) has an *anti* form with N(1)–O(15)–C(16)–C(18)

\* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and structure factors for (I) and (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43589 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

=  $178.1 (2)^\circ$ , while (II) has an eclipsed form with the corresponding angle of  $1.0 (4)^\circ$ . The two aromatic rings of (I) tilt towards the C=N plane with N(1)–C(2)–C(9)–C(10) =  $-112.3 (4)^\circ$  and N(1)–C(2)–C(3)–C(4) =  $32.5 (3)^\circ$ , while the corresponding angles of (II) are  $-112.8 (4)$  and  $-14.2 (4)^\circ$ , respectively. The conformation about the aromatic groups of (I) resembles those of other acyl oxime derivatives (Miyasaka, Noguchi, Taga, Kajiwara & Fuji, 1986),

Table 2. Atomic parameters for non-hydrogen atoms in (E)-*O*-palmitoyl phenyl 2-pyridyl ketone oxime
$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

|       | x          | y          | z           | $B_{eq}(\text{\AA}^2)$ |
|-------|------------|------------|-------------|------------------------|
| N(1)  | 0.7836 (2) | 0.3348 (0) | 1.3471 (4)  | 4.65 (7)               |
| C(2)  | 0.7748 (3) | 0.3165 (1) | 1.4817 (4)  | 4.05 (7)               |
| C(3)  | 0.9176 (3) | 0.3154 (0) | 1.6694 (4)  | 4.08 (7)               |
| C(4)  | 1.0558 (3) | 0.3295 (1) | 1.6538 (5)  | 5.40 (9)               |
| C(5)  | 1.1842 (3) | 0.3280 (1) | 1.8324 (6)  | 6.21 (10)              |
| C(6)  | 1.1707 (3) | 0.3127 (1) | 2.0142 (5)  | 5.56 (9)               |
| C(7)  | 1.0294 (4) | 0.2993 (1) | 2.0154 (6)  | 6.05 (9)               |
| N(8)  | 0.9024 (3) | 0.3002 (0) | 1.8443 (4)  | 5.17 (7)               |
| C(9)  | 0.6453 (3) | 0.2973 (0) | 1.4579 (5)  | 4.43 (7)               |
| C(10) | 0.5342 (4) | 0.2948 (1) | 1.6158 (5)  | 5.57 (9)               |
| C(11) | 0.4107 (4) | 0.2773 (1) | 1.5843 (6)  | 6.35 (9)               |
| C(12) | 0.4001 (3) | 0.2618 (1) | 1.3995 (6)  | 5.56 (9)               |
| C(13) | 0.5108 (4) | 0.2640 (1) | 1.2407 (6)  | 5.95 (10)              |
| C(14) | 0.6317 (4) | 0.2817 (1) | 1.2687 (5)  | 5.30 (9)               |
| O(15) | 0.6457 (2) | 0.3354 (0) | 1.1688 (3)  | 4.94 (5)               |
| C(16) | 0.6629 (3) | 0.3530 (1) | 1.0048 (5)  | 4.91 (8)               |
| O(17) | 0.5503 (2) | 0.3545 (0) | 0.8525 (4)  | 6.61 (6)               |
| C(18) | 0.8135 (3) | 0.3686 (1) | 1.0215 (5)  | 4.56 (7)               |
| C(19) | 0.8113 (3) | 0.3858 (1) | 0.8179 (5)  | 4.80 (7)               |
| C(20) | 0.9574 (3) | 0.4031 (1) | 0.8312 (5)  | 4.75 (7)               |
| C(21) | 0.9471 (3) | 0.4209 (1) | 0.6287 (5)  | 4.75 (7)               |
| C(22) | 1.0847 (3) | 0.4394 (1) | 0.6386 (5)  | 5.20 (9)               |
| C(23) | 1.0697 (3) | 0.4571 (1) | 0.4356 (5)  | 4.78 (8)               |
| C(24) | 1.2066 (3) | 0.4758 (1) | 0.4411 (5)  | 4.81 (8)               |
| C(25) | 1.1914 (3) | 0.4934 (1) | 0.2385 (5)  | 4.83 (8)               |
| C(26) | 1.3289 (3) | 0.5122 (1) | 0.2448 (5)  | 5.00 (9)               |
| C(27) | 1.3141 (3) | 0.5297 (1) | 0.0417 (5)  | 4.82 (8)               |
| C(28) | 1.4512 (3) | 0.5484 (1) | 0.0483 (5)  | 4.99 (9)               |
| C(29) | 1.4372 (3) | 0.5660 (1) | -0.1539 (5) | 5.24 (9)               |
| C(30) | 1.5735 (3) | 0.5849 (1) | -0.1478 (5) | 5.30 (8)               |
| C(31) | 1.5580 (4) | 0.6023 (1) | -0.3517 (5) | 5.63 (9)               |
| C(32) | 1.6940 (4) | 0.6212 (1) | -0.3461 (7) | 7.27 (12)              |

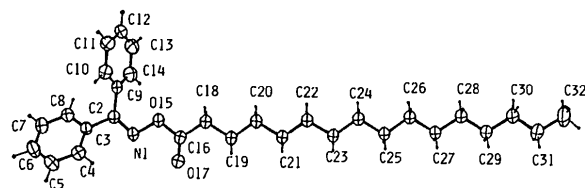


Fig. 1. Molecular structure and numbering scheme of (I).

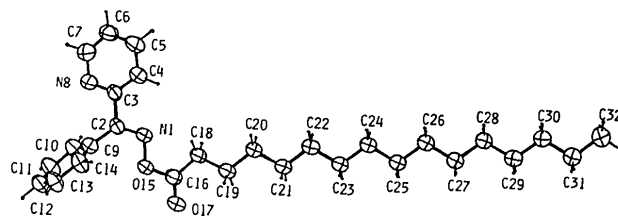


Fig. 2. Molecular structure and numbering scheme of (II).

and the conformation of (II) is exceptional. The bond distances for the corresponding bonds of the two molecules agree well (Table 3); The C(2)=N(1) distances are 1.280 (3) Å for (I) and 1.273 (5) Å for (II), and the N(1)—O(15) distances are 1.435 (2) Å for (I) and 1.439 (2) Å for (II). The C(2)=N(1)—O(15) angle of 109.7 (2)° for (I) is close to 111.2 (2)° for (II). The O(15)—C(16)—C(18) angle, 120.4 (2)°, for (II) is, however, significantly larger than for (I), 108.7 (2)°, possibly due to the nonbonding repulsion between N(1) and H(18) which are in close proximity for the eclipsed form of (II) about O(15)—C(16).

The molecular packings of (I) and (II) have a bilayer arrangement (Figs. 3 and 4). The long chain axis of (I) is approximately parallel to  $[\bar{5}01]$ , and the conventional unit cell, for which the *c* axis coincides with the chain axis, has cell dimensions  $a' = 5.764$  (4),  $b' = 8.997$  (1),  $c' = 36.695$  (7) Å,  $\alpha' = 86.82$  (2),  $\beta' = 136.06$  (4),  $\gamma' = 86.78$  (4)°. The palmitoyl chains of (I) are packed in a typical triclinic  $T''$  arrangement (Abrahamsson, Dahlén, Löfgren & Pascher, 1978). The reduced subcell dimensions are  $a_s = 2.54$ ,  $b_s = 4.22$ ,  $c_s = 4.70$  Å,  $\alpha_s = 71.2$ ,  $\beta_s = 86.4$ ,  $\gamma_s = 75.8$ °. The palmitoyl chains of (II) are arranged in a new type of triclinic subcell with the unit-cell dimensions  $a_s = 8.38$ ,  $b_s = 5.06$ ,  $c_s = 2.544$  Å,  $\alpha_s = 93.4$ ,  $\beta_s = 97.1$ ,  $\gamma_s = 117.8$ °. This subcell is made by hybridization of  $T''$  and  $M''$  cells. The  $T''$  cell has  $a_s = 4.35$ ,  $b_s = 5.06$ ,  $c_s = 2.544$  Å,  $\alpha_s = 93.4$ ,  $\beta_s = 109.6$ ,  $\gamma_s = 115.2$ °, and the  $M''$  cell has  $a_s = 4.20$ ,  $b_s = 5.06$ ,  $c_s = 2.544$  Å,  $\alpha_s = 93.4$ ,  $\beta_s = 94.9$ ,  $\gamma_s = 120.3$ °;  $b_s$  is shorter than the usual  $b_s$  (5.3–5.55 Å) for  $T''$ , while it is longer than those (4.6–4.8 Å) for  $M''$  (Abrahamsson, Dahlén, Löfgren & Pascher, 1978). These two cells contact each other in the *bc* plane. The head groups of the long chains have close contacts between the molecules packed along the *a* axis for (I) and the *c* axis for (II). When the molecular contacts are viewed along the plane normal of the oxime part, N—O—C—O lies on the aromatic ring of the lower molecule. In (II), N(1)—O(15)—C(16)—O(17) overlaps C(7)—N(8)—C(3)—C(2) with intermolecular distances 3.525 (5) [N(1)⋯C(7)], 3.546 (5) [O(15)⋯N(8)], 3.640 (5) [C(16)⋯C(3)] and 3.605 (5) Å [O(17)⋯C(2)]. On the other hand, in (I), these groups slide in parallel within the plane, and N(1)—O(15) is at the center of one of the phenyl rings with intermolecular distances 3.331 (3) [N(1)⋯C(5)] and 3.447 (3) Å [O(15)⋯C(4)]. The partial charges on the individual atoms were calculated by the CNDO/2 method (Pople & Segal, 1966). The face-to-face contact of the  $\pi$ -conjugated groups in (II) may be more favourable for electrostatic intermolecular interactions compared with that of (I).

The CNDO/2 molecular orbitals were calculated for *anti* and eclipsed conformations of each molecule (I) and (II), the palmitoyl group being changed to an ethyl group, and the atomic coordinates being fixed at the

Table 3. Bond distances (Å) and bond angles (°) in molecules (I) and (II)

|                   | (I)      | (II)     | (I)               | (II)     |
|-------------------|----------|----------|-------------------|----------|
| N(1)—C(2)         | 1.280(3) | 1.273(5) | O(15)—C(16)       | 1.369(2) |
| N(1)—O(15)        | 1.435(2) | 1.439(2) | C(16)—O(17)       | 1.185(2) |
| C(2)—C(3)         | 1.490(3) | 1.502(3) | C(16)—C(18)       | 1.497(3) |
| C(2)—C(9)         | 1.492(3) | 1.485(5) | C(18)—C(19)       | 1.514(3) |
| C(3)—C(4)         | 1.386(3) | 1.380(4) | C(19)—C(20)       | 1.521(3) |
| C(3)—C(8)         | 1.387(3) | —        | C(20)—C(21)       | 1.518(6) |
| C(3)—N(8)         | —        | 1.327(3) | C(21)—C(22)       | 1.523(3) |
| C(4)—C(5)         | 1.380(3) | 1.389(4) | C(22)—C(23)       | 1.520(3) |
| C(5)—C(6)         | 1.375(3) | 1.359(6) | C(23)—C(24)       | 1.516(3) |
| C(6)—C(7)         | 1.369(3) | 1.369(5) | C(24)—C(25)       | 1.521(3) |
| C(7)—C(8)         | 1.389(3) | —        | C(25)—C(26)       | 1.513(3) |
| C(7)—N(8)         | —        | 1.351(4) | C(26)—C(27)       | 1.519(3) |
| C(9)—C(10)        | 1.386(3) | 1.372(4) | C(27)—C(28)       | 1.518(3) |
| C(9)—C(14)        | 1.381(3) | 1.382(5) | C(28)—C(29)       | 1.514(3) |
| C(10)—C(11)       | 1.389(3) | 1.386(6) | C(29)—C(30)       | 1.507(3) |
| C(11)—C(12)       | 1.370(4) | 1.359(6) | C(30)—C(31)       | 1.512(3) |
| C(12)—C(13)       | 1.369(3) | 1.372(5) | C(31)—C(32)       | 1.502(3) |
| C(13)—C(14)       | 1.390(3) | 1.378(6) |                   |          |
| C(2)—N(1)—O(15)   | 109.7(2) | 111.2(2) | C(11)—C(12)—C(13) | 119.7(2) |
| N(1)—C(2)—C(3)    | 115.1(2) | 112.3(3) | C(12)—C(13)—C(14) | 120.8(2) |
| N(1)—C(2)—C(9)    | 126.4(2) | 125.9(2) | C(9)—C(14)—C(13)  | 119.8(2) |
| C(3)—C(2)—C(9)    | 118.4(2) | 121.8(3) | N(1)—O(15)—C(16)  | 112.6(1) |
| C(2)—C(3)—C(4)    | 120.9(2) | 120.4(2) | O(15)—C(16)—O(17) | 124.4(2) |
| C(2)—C(3)—C(8)    | 120.1(2) | —        | O(15)—C(16)—C(18) | 108.7(1) |
| C(2)—C(3)—N(8)    | —        | 116.3(2) | O(17)—C(16)—C(18) | 126.9(2) |
| C(4)—C(3)—C(8)    | 119.0(2) | —        | C(16)—C(18)—C(19) | 114.1(2) |
| C(4)—C(3)—N(8)    | —        | 123.3(2) | C(18)—C(19)—C(20) | 111.8(2) |
| C(3)—C(4)—C(5)    | 120.3(2) | 118.3(3) | C(19)—C(20)—C(21) | 113.9(2) |
| C(3)—C(4)—C(6)    | 120.4(2) | 119.4(3) | C(20)—C(21)—C(22) | 113.1(2) |
| C(5)—C(6)—C(7)    | 120.0(2) | 118.5(3) | C(21)—C(22)—C(23) | 114.2(2) |
| C(6)—C(7)—C(8)    | 120.1(2) | —        | C(22)—C(23)—C(24) | 113.8(2) |
| C(6)—C(7)—N(8)    | —        | 123.7(4) | C(23)—C(24)—C(25) | 113.9(2) |
| C(3)—C(8)—C(7)    | 120.2(2) | —        | C(24)—C(25)—C(26) | 114.2(2) |
| C(3)—N(8)—C(7)    | —        | 116.8(3) | C(25)—C(26)—C(27) | 113.9(2) |
| C(2)—C(9)—C(10)   | 119.2(2) | 122.1(3) | C(26)—C(27)—C(28) | 114.2(2) |
| C(2)—C(9)—C(14)   | 121.6(2) | 119.8(3) | C(27)—C(28)—C(29) | 113.8(2) |
| C(10)—C(9)—C(14)  | 119.2(2) | 118.1(3) | C(28)—C(29)—C(30) | 115.0(2) |
| C(9)—C(10)—C(11)  | 120.2(2) | 120.8(3) | C(29)—C(30)—C(31) | 114.0(2) |
| C(10)—C(11)—C(12) | 120.2(2) | 120.6(3) | C(30)—C(31)—C(32) | 114.9(2) |

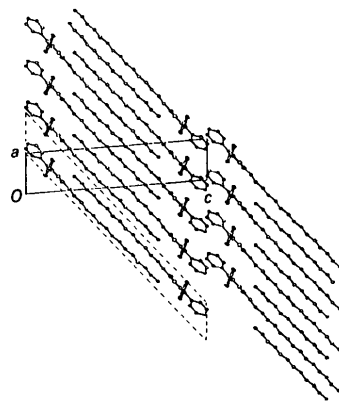


Fig. 3. Packing diagram of (I) projected down *b*. The broken lines indicate the conventional unit cell.

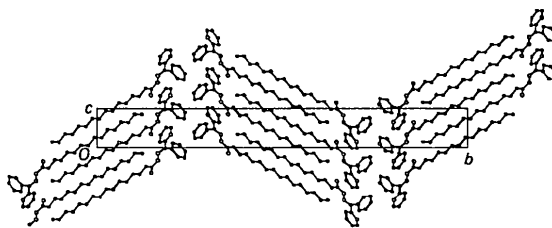


Fig. 4. Packing diagram of (II) projected down *a*.

present X-ray parameters. The *anti* conformer of (I) showed lower bonding energy than the eclipsed conformer of (I) with an energy difference of about 14.2 kJ mol<sup>-1</sup>, while the two conformers of (II) gave approximately the same bonding energy. The eclipsed conformer of (II), however, showed a large dipole moment in comparison with the other conformers. Hence the unique eclipsed conformation observed in (II) is comparatively stable with respect to the molecular structure, and furthermore it must be stabilized by the intermolecular interactions such as the dipole-dipole interactions between the head groups in the bilayer structure.

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## Structure of a New Macrocyclic Antibiotic

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**Abstract.** 16-Allyl-1,14-dihydroxy-12-[2-(4-hydroxy-3-methoxycyclohexyl)-1-methylvinyl]-23,25-dimethoxy-13,19,21,27-tetramethyl-11,28-dioxa-4-azatricyclo-[22.3.1.0<sup>4,9</sup>]octacos-18-ene-2,3,10,16-tetrone-water (1/1), C<sub>44</sub>H<sub>69</sub>NO<sub>12</sub>·H<sub>2</sub>O, *M<sub>r</sub>* = 804.0, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>, *a* = 10.939 (1), *b* = 15.878 (1), *c* = 27.184 (1) Å, *V* = 4721.0 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.131 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ = 0.629 mm<sup>-1</sup>, *F*(000) = 1744, *T* = 295 K, *R*(*F*) = 0.071 for 4249 observed reflections. The molecule has a 21-membered macrolide ring fused to two six-membered rings (piperidine and tetrahydropyran) and linked to another six-membered ring (cyclohexane) through a *trans*-substituted ethylene bond. A piperidinodiketone group is involved in the macrolide ring, and a specific allyl group links to the ring.

**Introduction.** A new antibiotic (FR 900506) isolated from *Streptomyces tsukubaensis* has pharmacological

activities such as immunosuppressive activity and antimicrobial activity. The compound is neutral and rich in O atoms, but the crystal is insoluble in water. The structural characteristics of this compound have been studied by chemical and spectroscopic methods so far, and it was known that the molecule has a macrolide ring. The present X-ray work was undertaken in order to determine the total structure including the relative stereochemistry of the ring and its substitution groups.

**Experimental.** Single crystals obtained from methanol solution; colourless; 0.2 × 0.2 × 0.3 mm; 20 reflections for lattice parameters; intensity data collected on a Rigaku AFC5-RU diffractometer with graphite-monochromated Cu Kα radiation; 4484 observed reflections within range 2θ < 130°; *h* 0-12, *k* 0-18, *l* 0-31; three standard reflections monitored every 60 reflections; corrected for Lorentz and polarization factors; no absorption correction; 4249 reflections with