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# Structures of Geometric Isomers of a Cyclic Dipeptide Derivative: cyclo(-N-Acetyl-L-phenylalanyl-p-chloro-2,3-dehydrophenylalanyl-)

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**Abstract.** (3$S$)-4-Acetyl-3-benzyl-6-[($Z$)-$p$-chlorobenzylidene]-2,5-piperazinedione ($Z$), $C_{20}H_{17}ClN_2O_3$, $M_r$ = 368·8, orthorhombic, $P2_12_12_1$, $a$ = 7·182 (1), $b$ = 9·813 (1), $c$ = 25·501 (3) Å, $V$ = 1797·2 (4) Å$^3$, $Z$ = 4, $D_m$ = 1·36, $D_x$ = 1·363 Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu$(Cu $K\alpha$) = 1·960 mm$^{-1}$, $F(000)$ = 768, $T$ = 298 K, $R$ = 0·062 for 1730 independent observed reflexions. (3$S$)-4-Acetyl-3-benzyl-6-[($E$)-$p$-chlorobenzylidene]-2,5-piperazinedione ($E$), $C_{20}H_{17}ClN_2O_3$, $M_r$ = 368·8, orthorhombic, $P2_12_12_1$, $a$ = 6·295 (1), $b$ = 16·592 (3), $c$ = 16·678 (2) Å, $V$ = 1742·0 (4) Å$^3$, $Z$ = 4, $D_m$ = 1·41, $D_x$ = 1·406 Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu$(Cu $K\alpha$) = 2·022 mm$^{-1}$, $F(000)$ = 768, $T$ = 298 K, $R$ = 0·051 for 1298 independent observed reflexions. Both molecules are in the folded conformation with the aromatic rings of the benzyl groups facing the 2,5-piperazinedione (PDO) ring [$\chi^1$ = 52·8 (5) and 68·9 (8)° for ($Z$) and ($E$), respectively]. The PDO rings are in boat ($Z$) and twist-boat ($E$) conformations with the benzyl side chains in the flagpole positions. The dihedral angles of the two amido groups in the PDO rings are −31·1 (2) ($Z$) and −25·3 (3)° ($E$), respectively. The $p$-chlorophenyl moiety and ethylene bond of the benzylidene group are nearly coplanar in ($Z$), but not coplanar in ($E$). The conformational angles around the C—C single bond connecting these planes are 4·0 (6) ($Z$) and −46·4 (9)° ($E$), respectively.

**Introduction.** It has been shown that a cyclic dipeptide having one or two *cis* substituents at the 3- and/or 6-positions, especially in the case of an aromatic one, favors the flagpole boat conformation in solution (Kopple & Marr, 1967) and in the solid state (Lin & Webb, 1973) because of the direct interaction between the 2,5-piperazinedione (PDO) and aromatic rings on stacking. The conformation is changeable to planar or bowsprit boat due to the interference between bulky substituents, *trans* orientation of substituents (Benedetti, Marsh & Goodman, 1976) or the special nature of the side chain as in a proline dipeptide (Karle, Ottenheym & Witkop, 1974). It has been proposed, from circular dichroism (CD) experiments in the region of 190–250 nm, that both the $\pi$–$\pi^*$ and $n$–$\pi^*$ transitions in the Cotton effect reflect the conformation of the

PDO ring and a pair of enantiomers having *cis* substituents showed symmetrical spectra (Hooker, Bayley, Radding & Schellman, 1974; Tanihara, Hiza, Imanishi & Higashimura, 1983).

We have proved by synthesis that 3-benzyl-6-benzylidene-PDO, isolated from *Streptomyces noursei* (Brown, Kelley & Wiberley, 1965), has a (3*S*, 6*Z*) configuration, and found that not only the enantiomers but also a pair of their *Z* and *E* isomers showed nearly symmetrical CD spectra, in spite of having the same configuration at the 3-positions of the PDO ring (Shin, Kato, Yonezawa, Hayakawa & Yoshimura, 1980). In this paper, we report the structures of newly synthesized (*Z*) and (*E*) which were examined to obtain fundamental knowledge for the interpretation of the above interrelation in the CD spectra.



(3*S*)-(6*Z*)          (3*S*)-(6*E*)
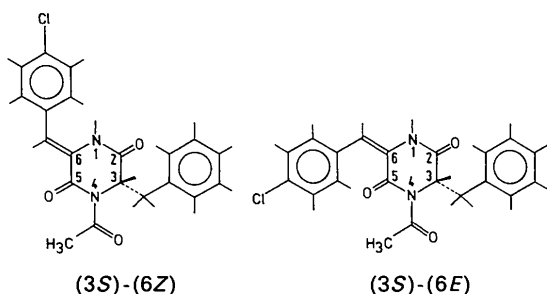
**Experimental.** (*Z*) was synthesized by condensation of (3*S*)-1,4-diacetyl-3-benzyl-PDO and *p*-chlorobenzaldehyde, m.p. 473–475 K; $[\alpha]_D^{25°C}$ −627·9° (*c* 0·2, methanol); $\delta_H$ (CDCl$_3$) 2·59 (*s*, 3H, Ac), 3·23 (*d*, *J* = 4·2 Hz, 2H, —CH$_2$—), 5·30 (*t*, *J* = 4·2 Hz, 1H, H-3), 6·52 (*s*, 1H, —CH=), 7·38–7·02 (*m*, 9H, 2 × Ph), 7·87 (*bs*, 1H, NH). (*E*) was obtained by photoisomerization of (*Z*) (Shin *et al.*, 1980), m.p. 430–434 K; $[\alpha]_D^{25°C}$ + 357·4° (*c* 0·2, methanol); $\delta_H$ (CDCl$_3$) 3·48–3·13 (*m*, 2H, —CH$_2$—), 5·32 (*dd*, *J* = 4·0 and 5·5 Hz, 1H, H-3), 6·10 (*s*, 1H, —CH=),7·28–7·08 (*m*, 9H, 2 × Ph), 9·90 (*s*, 1H, NH). Prismatic colorless crystals of (*Z*) and (*E*) from ethanol solutions, crystal sizes 0·22 × 0·20 × 0·06 mm (*Z*) and 0·22 × 0·08 × 0·08 mm (*E*), $D_m$ by flotation in benzene/carbon tetrachloride solutions. Nicolet *P3/F* four-circle diffractometer, graphite monochromated Cu *Kα* radiation, lattice parameters from least-squares fit of 24 $2\theta$ values [$16 < 2\theta < 38°$ for (*Z*) and $15 < 2\theta < 38°$ for (*E*)]. Intensity data $3 < 2\theta < 153°$ [*h* 0–8, *k* 0–12, *l* 0–32 for (*Z*); *h* 0–6, *k* 0–20, *l* 0–20 for (*E*)], $\omega/2\theta$ scan mode, scan rates 0·5 to 4° min$^{-1}$ in $\omega$. No significant intensity variations for three standard reflexions. 2043 (*Z*) and 1642 (*E*) independent reflexions measured, of which 1730 (*Z*) and 1298 (*E*) had $I_o > 2\sigma(I_o)$. No absorption correction. Structures solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-

matrix least-squares refinement (*SHELX*76; Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms, H atoms geometrically positioned and not refined; $\Sigma w(|F_o| - k|F_c|)^2$ was minimized, where $w = 1·0/[\sigma^2(F_o) + c(F_o)^2]$, *c* values were 0·0197 (*Z*) and 0·0004 (*E*). Final $R = 0·062$, $wR = 0·073$, $S = 1·36$, $(\Delta/\sigma)_{max} = 0·12$, $(\Delta\rho)_{min} = -0·35$, $(\Delta\rho)_{max} = 0·24$ e Å$^{-3}$ in (*Z*), final $R = 0·051$, $wR = 0·049$, $S = 1·12$, $(\Delta/\sigma)_{max} = 0·10$, $(\Delta\rho)_{min} = -0·20$, $(\Delta\rho)_{max} = 0·25$ e Å$^{-3}$ in (*E*). Atomic scattering factors were those incorporated in *SHELX*.

**Discussion.** Final atomic parameters are given in Table 1.* Bond lengths, angles and selected torsion angles are in Table 2. *ORTEP*II (Johnson, 1976) drawings of the molecules with the atomic numbering are shown in Figs. 1 and 2. The benzyl side chains are folded above the PDO rings in both molecules. This feature is commonly observed in the structures of cyclic dipeptides containing phenylalanine residues, such as *cyclo*(-*N*-hydroxyglycyl-L-phenylalanyl-) (Yokomori, Katoh & Akiyama, 1990), *cyclo*(-L-phenylalanyl-*N*-methyl-L-α-aminobutyryl-) (Gdaniec, 1988) and *cyclo*(-*N*-methyl-L-phenylalanyl-L-phenylalanyl-) (Gdaniec & Liberek, 1987). It seems that the unsaturation of a $C^\alpha$—$C^\beta$ bond in a cyclic dipeptide containing phenylalanine residues causes little effect on the overall conformation. Some distortions, however, are observed in the conformation of the PDO rings, which were nearly planar in these molecules, whereas in the present work the PDO rings deviate markedly from planar towards boat (*Z*) and twist boat (*E*) with the benzyl side chains in the flagpole positions. The C(3) atoms deviate from the mean planes calculated from the remaining five atoms in the PDO rings by 0·509 (4) (*Z*) and 0·462 (6) Å (*E*), respectively. The torsion angles N(4)—C(3)—C(8)—C(9) and C(3)—C(8)—C(9)—C(10) [$\chi^1$ and $\chi^2$, respectively, according to IUPAC–IUB Commission on Biochemical Nomenclature (1970)] are 52·8 (5) and −89·4 (5) in (*Z*) and 68·9 (8) and 88·8 (9)° in (*E*), respectively. These values together with the flagpole conformation at the C(3) positions give rise to compact stackings of aromatic rings and PDO rings. The dihedral angles between the average planes of the PDO rings and the benzyl groups are as small as 34·7 (2)° (*Z*) and 38·7 (3)° (*E*). A boat conformation of the PDO ring with folded aromatic ring is also observed in *cyclo*-bis(*N*-methyl-L-phenylalanyl-), although the dihedral angle between these rings is not as small (55°;

* Lists of observed and calculated structure factors, anisotropic thermal parameters, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53736 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| **(Z)** | | | | |
| N(1) | 0·4282 (5) | −0·2075 (3) | 0·06198 (11) | 3·21 (9) |
| C(2) | 0·2877 (5) | −0·2922 (4) | 0·04963 (13) | 3·28 (10) |
| C(3) | 0·1922 (5) | −0·3609 (4) | 0·09493 (14) | 3·17 (10) |
| N(4) | 0·3194 (5) | −0·3903 (3) | 0·13863 (12) | 3·26 (10) |
| C(5) | 0·4619 (6) | −0·2982 (4) | 0·15147 (13) | 3·46 (10) |
| C(6) | 0·4906 (5) | −0·1856 (4) | 0·11325 (13) | 3·12 (10) |
| O(7) | 0·2382 (4) | −0·3107 (3) | 0·00468 (9) | 4·01 (9) |
| C(8) | 0·0144 (6) | −0·2817 (5) | 0·11229 (18) | 3·95 (12) |
| C(9) | 0·0557 (6) | −0·1538 (4) | 0·14298 (15) | 3·57 (11) |
| C(10) | 0·0721 (7) | −0·1589 (6) | 0·19668 (20) | 5·29 (13) |
| C(11) | 0·1226 (8) | −0·0407 (8) | 0·22476 (22) | 6·79 (13) |
| C(12) | 0·1585 (9) | 0·0789 (8) | 0·19811 (34) | 7·81 (15) |
| C(13) | 0·1364 (8) | 0·0820 (5) | 0·14483 (31) | 6·52 (14) |
| C(14) | 0·0905 (8) | −0·0314 (5) | 0·11713 (23) | 5·13 (13) |
| C(15) | 0·2748 (6) | −0·5057 (5) | 0·16865 (17) | 4·05 (11) |
| C(16) | 0·3887 (9) | −0·5458 (7) | 0·21398 (25) | 6·64 (14) |
| O(17) | 0·1403 (6) | −0·5714 (4) | 0·15627 (16) | 6·04 (12) |
| O(18) | 0·5557 (6) | −0·3061 (4) | 0·19110 (14) | 5·69 (11) |
| C(19) | 0·5759 (6) | −0·0715 (4) | 0·13066 (14) | 3·63 (11) |
| C(20) | 0·6036 (6) | 0·0595 (4) | 0·10529 (14) | 3·61 (11) |
| C(21) | 0·5354 (9) | 0·0972 (5) | 0·05677 (20) | 5·41 (13) |
| C(22) | 0·5518 (8) | 0·2287 (5) | 0·03700 (19) | 5·39 (13) |
| C(23) | 0·6467 (7) | 0·3240 (5) | 0·06707 (20) | 4·36 (12) |
| C(24) | 0·7177 (8) | 0·2929 (5) | 0·11485 (22) | 5·53 (13) |
| C(25) | 0·6961 (8) | 0·1595 (5) | 0·13345 (19) | 4·99 (13) |
| Cl(26) | 0·6727 (2) | 0·49041 (11) | 0·04317 (6) | 5·60 (5) |
| | | | | |
| **(E)** | | | | |
| N(1) | 0·2683 (7) | 0·3906 (2) | 0·2746 (3) | 3·31 (19) |
| C(2) | 0·2721 (9) | 0·4507 (3) | 0·2202 (3) | 3·19 (22) |
| C(3) | 0·4879 (9) | 0·4873 (3) | 0·2017 (3) | 3·14 (22) |
| N(4) | 0·6383 (7) | 0·4738 (3) | 0·2684 (3) | 2·89 (18) |
| C(5) | 0·6505 (9) | 0·3983 (3) | 0·3044 (3) | 2·66 (21) |
| C(6) | 0·4515 (9) | 0·3511 (3) | 0·3060 (3) | 2·48 (19) |
| O(7) | 0·1106 (6) | 0·4759 (2) | 0·1886 (2) | 4·24 (19) |
| C(8) | 0·5718 (10) | 0·4572 (3) | 0·1211 (3) | 4·00 (24) |
| C(9) | 0·5896 (11) | 0·3678 (4) | 0·1132 (3) | 3·67 (23) |
| C(10) | 0·4219 (12) | 0·3220 (4) | 0·0859 (4) | 5·03 (28) |
| C(11) | 0·4300 (14) | 0·2393 (5) | 0·0829 (4) | 6·70 (33) |
| C(12) | 0·6166 (15) | 0·2004 (4) | 0·1064 (4) | 6·49 (31) |
| C(13) | 0·7835 (13) | 0·2440 (4) | 0·1325 (4) | 5·91 (31) |
| C(14) | 0·7747 (11) | 0·3266 (4) | 0·1348 (3) | 4·25 (26) |
| C(15) | 0·7697 (9) | 0·5408 (3) | 0·2876 (3) | 3·43 (22) |
| C(16) | 0·8991 (9) | 0·5370 (3) | 0·3639 (3) | 4·05 (24) |
| O(17) | 0·7621 (7) | 0·6004 (2) | 0·2465 (2) | 4·72 (19) |
| O(18) | 0·8143 (6) | 0·3740 (2) | 0·3366 (2) | 3·03 (16) |
| C(19) | 0·4204 (9) | 0·2809 (3) | 0·3425 (3) | 3·08 (21) |
| C(20) | 0·5674 (9) | 0·2260 (3) | 0·3848 (3) | 2·80 (20) |
| C(21) | 0·7620 (9) | 0·2025 (3) | 0·3564 (3) | 3·30 (23) |
| C(22) | 0·8846 (9) | 0·1446 (3) | 0·3954 (3) | 3·01 (21) |
| C(23) | 0·8074 (9) | 0·1114 (3) | 0·4659 (3) | 3·15 (22) |
| C(24) | 0·6153 (10) | 0·1351 (3) | 0·4970 (3) | 3·48 (23) |
| C(25) | 0·4923 (9) | 0·1904 (3) | 0·4551 (3) | 3·12 (22) |
| Cl(26) | 0·9498 (3) | 0·03643 (9) | 0·51493 (9) | 4·83 (7) |

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

| | (Z) | (E) | | (Z) | (E) |
|---|---|---|---|---|---|
| N(1)—C(2) | 1·344 (5) | 1·347 (8) | C(10)—C(11) | 1·411 (8) | 1·374 (13) |
| N(1)—C(6) | 1·399 (5) | 1·426 (8) | C(11)—C(12) | 1·380 (10) | 1·397 (14) |
| C(2)—C(3) | 1·503 (5) | 1·520 (9) | C(12)—C(13) | 1·368 (10) | 1·348 (13) |
| C(2)—O(7) | 1·214 (5) | 1·219 (8) | C(13)—C(14) | 1·359 (8) | 1·371 (12) |
| C(3)—N(4) | 1·470 (5) | 1·477 (8) | C(15)—C(16) | 1·470 (8) | 1·512 (10) |
| C(3)—C(8) | 1·559 (6) | 1·529 (9) | C(15)—O(17) | 1·203 (6) | 1·204 (8) |
| N(4)—C(5) | 1·405 (5) | 1·391 (8) | C(19)—C(20) | 1·452 (6) | 1·477 (9) |
| N(4)—C(15) | 1·404 (5) | 1·422 (8) | C(20)—C(21) | 1·381 (7) | 1·370 (9) |
| C(5)—C(6) | 1·487 (5) | 1·477 (9) | C(20)—C(25) | 1·386 (6) | 1·395 (9) |
| C(6)—C(19) | 1·352 (5) | 1·329 (9) | C(21)—C(22) | 1·390 (8) | 1·393 (9) |
| C(8)—C(9) | 1·508 (6) | 1·494 (10) | C(22)—C(23) | 1·388 (7) | 1·387 (9) |
| C(9)—C(10) | 1·375 (7) | 1·377 (11) | C(23)—C(24) | 1·356 (7) | 1·373 (9) |
| C(9)—C(14) | 1·393 (7) | 1·398 (10) | C(23)—Cl(26) | 1·753 (5) | 1·738 (7) |
| | | | C(24)—C(25) | 1·400 (8) | 1·389 (9) |

| | (Z) | (E) | | (Z) | (E) |
|---|---|---|---|---|---|
| C(2)—N(1)—C(6) | 123·7 (3) | 124·9 (5) | C(9)—C(10)—C(11) | 119·8 (5) | 122·3 (8) |
| N(1)—C(2)—C(3) | 116·1 (3) | 116·6 (6) | C(10)—C(11)—C(12) | 119·8 (6) | 118·9 (9) |
| N(1)—C(2)—O(7) | 122·3 (3) | 122·0 (6) | C(11)—C(12)—C(13) | 119·1 (7) | 119·8 (9) |
| C(3)—C(2)—O(7) | 121·6 (3) | 121·4 (6) | C(12)—C(13)—C(14) | 121·7 (6) | 121·0 (8) |
| C(2)—C(3)—N(4) | 112·8 (3) | 111·1 (5) | C(9)—C(14)—C(13) | 120·3 (5) | 121·0 (7) |
| C(2)—C(3)—C(8) | 111·6 (3) | 110·9 (5) | N(4)—C(15)—C(16) | 121·2 (4) | 118·0 (6) |
| N(4)—C(3)—C(8) | 113·1 (3) | 113·0 (5) | N(4)—C(15)—O(17) | 118·2 (4) | 119·4 (6) |
| C(3)—N(4)—C(5) | 120·2 (3) | 119·8 (5) | C(16)—C(15)—O(17) | 120·6 (5) | 122·3 (6) |
| C(3)—N(4)—C(15) | 115·5 (3) | 115·0 (5) | C(6)—C(19)—C(20) | 130·5 (4) | 131·8 (6) |
| C(5)—N(4)—C(15) | 124·0 (3) | 125·1 (5) | C(19)—C(20)—C(21) | 126·0 (4) | 124·8 (6) |
| N(4)—C(5)—C(6) | 115·2 (3) | 116·0 (5) | C(19)—C(20)—C(25) | 117·5 (4) | 116·7 (6) |
| N(4)—C(5)—O(18) | 123·8 (4) | 121·9 (6) | C(21)—C(20)—C(25) | 116·4 (4) | 118·2 (6) |
| C(6)—C(5)—O(18) | 121·0 (4) | 122·0 (6) | C(20)—C(21)—C(22) | 122·9 (5) | 122·1 (6) |
| N(1)—C(6)—C(5) | 117·0 (3) | 115·8 (5) | C(21)—C(22)—C(23) | 117·8 (5) | 118·4 (6) |
| N(1)—C(6)—C(19) | 125·4 (3) | 116·9 (6) | C(22)—C(23)—C(24) | 121·9 (5) | 121·0 (6) |
| C(5)—C(6)—C(19) | 117·6 (3) | 126·7 (6) | C(22)—C(23)—Cl(26) | 119·2 (4) | 120·2 (5) |
| C(3)—C(8)—C(9) | 113·7 (3) | 115·3 (6) | C(24)—C(23)—Cl(26) | 118·9 (4) | 118·8 (5) |
| C(8)—C(9)—C(10) | 120·2 (4) | 121·3 (7) | C(23)—C(24)—C(25) | 118·3 (5) | 119·4 (6) |
| C(8)—C(9)—C(14) | 120·5 (4) | 121·7 (6) | C(20)—C(25)—C(24) | 122·6 (5) | 120·9 (6) |
| C(10)—C(9)—C(14) | 119·2 (4) | 117·0 (7) | | | |

| | (Z) | (E) |
|---|---|---|
| C(6)—N(1)—C(2)—C(3) | 2·3 (4) | −10·3 (7) |
| N(1)—C(2)—C(3)—N(4) | −33·2 (4) | −23·0 (8) |
| C(2)—C(3)—N(4)—C(5) | 36·9 (4) | 44·6 (7) |
| C(3)—N(4)—C(5)—C(6) | −9·4 (4) | −31·2 (7) |
| N(4)—C(5)—C(6)—N(1) | −22·6 (4) | −3·5 (7) |
| C(5)—C(6)—N(1)—C(2) | 26·9 (5) | 25·1 (7) |
| N(4)—C(3)—C(8)—C(9) | 52·8 (5) | 68·9 (8) |
| C(3)—C(8)—C(9)—C(10) | −89·4 (5) | 88·8 (9) |
| C(6)—C(19)—C(20)—C(21) | 4·0 (5) | −46·4 (8) |



Fig. 2. *ORTEP*II drawing of (E) with atomic numbering.
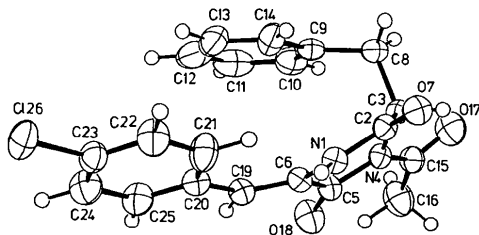


Fig. 1. *ORTEP*II drawing of (Z) with atomic numbering.

Benedetti *et al.*, 1976). As a consequence, the conformations around the 3-positions of the PDO rings, including the orientation of the benzyl groups, which is thought to be responsible for the characteristic Cotton effect (Tanihara *et al.*, 1983), are considered to be almost the same for (Z) and (E).

The dihedral angle between the two amide planes, which is a direct measure of the folding of the PDO ring itself (Hooker *et al.*, 1974), has values of −31·1 (2) and −25·3 (3)° for (Z) and (E), respectively. Both amido groups in (Z) and the non-acetyl-

ated amido group in (E) are close to planar, whereas the remaining N-acetylated one in (E) is appreciably nonplanar, which causes the conformation of the PDO ring of (E) to be twist boat. The torsion angles of these amido groups ($\omega_1$ and $\omega_2$) are 2·3 (4) and −9·4 (4)° in (Z) and −10·3 (7) and −31·2 (7)° in (E).

The conformations of the benzylidene groups are quite different for (Z) and (E). The p-chlorophenyl group and the ethylene group are close to coplanar in (Z) but not coplanar in (E). The torsion angles around the C—C single bond connecting these planes are 4·0 (5)° (Z) and −46·4 (8)° (E). These differences are probably caused by intramolecular repulsion between the carbonyl O(18) atom and the p-chlorobenzylidene group in (E). A short intra-molecular contact between O(18) and C(21) of 2·884 (8) Å is observed in (E), whereas the shortest intramolecular contact, between N(1) and the p-chlorophenyl group, in (Z) is 3·090 (6) Å.

The symmetrical features observed in the CD spectra around 250–350 nm for (Z) and (E) (Shin et al.,

1980) may be attributed not to the conformation around the C(3) position but to the differences in conformations of the PDO rings and the p-chlorobenzylidene groups, because of the conformational similarity around the C(3) positions and large dissimilarity of the benzylidene groups in (Z) and (E). Snow, Hooker & Schellman (1977) ascribed the Cotton effect around 280 nm to a weak $^1L_b$ transition of the phenolic ring in cyclo-bis(-L-tyrosyl-) and found that its sign is quite sensitive to rotation about the p-hydroxybenzyl chromophore. In the present molecules, however, it is considered that the strong absorption extremum around 300 nm may arise not from $^1L_b$ but from a $\pi-\pi^*$ transition of the conjugated chromophore of the benzylidene and carbonyl groups (Shin et al., 1980). The relative conformation between the chromophore and the PDO ring may then be responsible for the characteristic feature in the CD spectrum, although the relationship between the conformation and sign in the Cotton effect is still obscure.

The molecular packings are shown in Figs. 3 and 4. In both crystals, N—H⋯O hydrogen bonds are formed and connect the molecules related by the $2_1$ axis along a in (Z) [N⋯O(7) 2·807 (4) Å] and an a translation in (E) [N⋯O(18) 3·052 (7) Å].
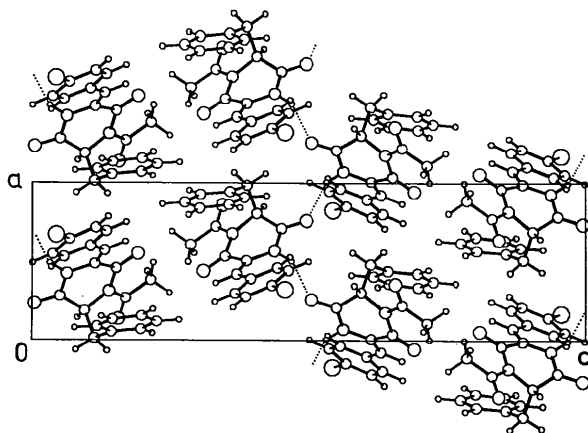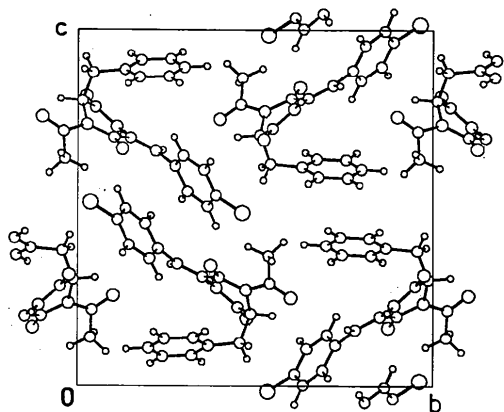


Fig. 3. The crystal packing of (Z) viewed down b.



Fig. 4. The crystal packing of (E) viewed down a.

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