Table 3. *Torsion angles* (°), *with estimated standard deviations in parentheses*

The convention of Klyne & Prelog (1960) is adopted.

C(1)–N(1)–N(2)–C(1')	59·5 (4)
N(1)–N(2)–C(1')–N(1')	−62·4 (3)
N(2)–C(1')–N(1')–N(2')	58·4 (3)
C(2)–N(1)–N(2)–C(1')	−63·6 (4)
C(2)–N(1)–N(2)–C(9)	66·3 (4)
C(1)–N(1)–N(2)–C(9)	−170·5 (3)
C(1)–N(1)–C(2)–C(3)	76·7 (3)
N(2)–N(1)–C(2)–C(3)	−163·3 (3)
N(1)–C(2)–C(3)–C(4)	−109·7 (5)
N(1)–C(2)–C(3)–C(8)	68·9 (5)
N(1)–N(2)–C(9)–C(10)	159·0 (3)
C(1')–N(2)–C(9)–C(10)	−72·2 (4)
N(2)–C(9)–C(10)–C(11)	−70·1 (4)
N(2)–C(9)–C(10)–C(15)	108·1 (4)

In the tetrazine ring, the angle at C(1) [110·3 (3)°] is very near to the tetrahedral value (109·47°), whilst the angles at the N atoms are considerably different: 105·7 (3)° for N(1) where the benzyl group is axial and 112·3 (3)° for N(2) where the benzyl group is equatorial.

Relevant torsion angles are reported in Table 3. Those in the tetrazine ring are in good agreement with the ideal values for a chair conformation. The non-bonded interactions involving the substituents increase the value of the torsion angle C(2)–N(1)–N(2)–C(9) [66·3 (4)°] and lower that of the torsion angle C(1)–N(1)–N(2)–C(9) [−170·5 (3)°]. Such interactions could help to explain the flattening observed at the N

atoms, which, however, is more pronounced at N(2), where the benzyl group is equatorial. In fact, the angle of the N(2)–C(9) bond with respect to the N(1)–N(2)–C(1') plane is 45·6°, 9·1° lower than the tetrahedral value (54·7°), and the angle of the N(1)–C(2) bond with respect to the C(1)–N(1)–N(2) plane is 49·6°.

No short contacts between adjacent molecules are observed.

References

ANSELL, G. B. & ERICKSON, J. L. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 270–271.
BAKER, V. J., KATRITZKY, A. R., MAJORAL, J., MARTIN, A. R. & SULLIVAN, J. M. (1976). *J. Am. Chem. Soc.* 98, 5748–5759.
CERRINI, S. & SPAGNA, R. (1977). 4th Eur. Crystallogr. Meet., Oxford, England. Abstr. pp. 7–8.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71, 148. Birmingham: Kynoch Press.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.
MORINO, Y., IIJIMA, T. & MURATA, Y. (1960). *Bull. Chem. Soc. Jpn*, 33, 46–48.
YAMAGUCHI, A., ICHISHIMA, I., SHIMANOUCHI, T. & MIZUSHIMA, S. (1959). *J. Chem. Phys.* 31, 843.

1,2β-Dimethoxycarbonyl-3aα-hydroxy-2α,3,3,8,8aα-pentahydropyrrolo[2,3-b]indole

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Abstract. $C_{14}H_{16}N_2O_5$, $P2_1/c$, $a = 10·331$ (6), $b = 11·898$ (6), $c = 15·148$ (8) Å, $\beta = 131·7$ (2)°, $Z = 4$, $d_c = 1·4$ g cm⁻³. The compound is a photo-oxidation production of a derivative of DL-tryptophan. There is a *cis* junction between the two five-membered rings and the hydroxyl group is *exo* to the ring system.

Introduction. The title compound is a photo-oxidation product of a DL-tryptophan derivative (Nakagawa *et al.*, 1977). The X-ray analysis was performed to determine unambiguously the stereoconfiguration of the molecule at C(9). The numbering system used throughout this paper was chosen arbitrarily. The chemical
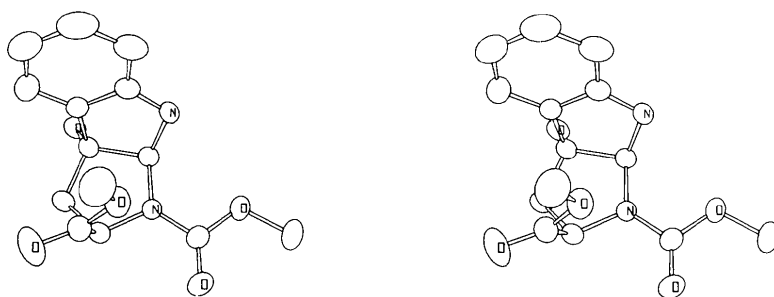
Fig. 1. Results of the structure analysis. The atoms are shown at their final refined positions.

numbering system (shown in the following formula as the smaller numbers when the two systems differ) was used to derive the name of the substance.
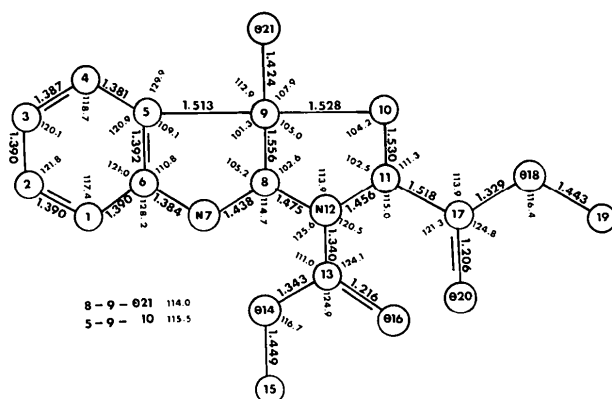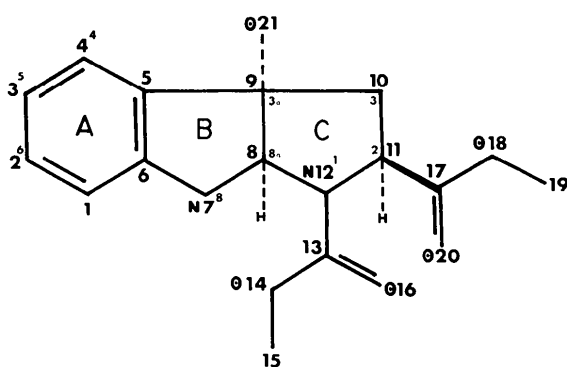

Fig. 2. Bond lengths and angles. Standard deviations are of the order of 0·002 Å for bond lengths and 0·2° for bond angles.

Crystals were provided by M. Nakagawa of Chiba University (Japan) and B. Witkop of NIAMD (Washington, DC). 2243 independent reflections were collected on an automatic diffractometer with the 2θ scan technique, Cu $K\alpha$ radiation, Ni filter, $\lambda = 1·54178$ Å, $2\theta_{max} = 126·5°$. Cell dimensions were determined from a least-squares fit of 12 independently measured reflections.

The structure was solved by routine application of the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966) and the results are displayed in Fig. 1 (Johnson, 1965). The full-matrix least-squares program ORXFLS3 (Busing et al., 1975) was used to refine the structure. Atomic scattering factors used were those listed in International Tables for X-ray Crystallography (1962). A difference map revealed all 16 H atoms; their positional coordinates, as well as a correction for isotropic extinction, were included in the final cycles of refinement. The function minimized by the least squares was $\Sigma w(|F_o| - |F_c|)^2$ where the weights (w) were derived from estimated standard deviations of observed intensity (Gilardi, 1973). When refinement was complete the standard deviation for an observation of unit weight was 3·5. The final R factors were $R = 0·043$ and $R_w = 0·051$. Bond lengths and angles are illustrated in Fig. 2. Table

1 lists the refined positional parameters for the molecule.*

Discussion. The present molecule differs from other tryptophan derivatives (see, for example, Yamane, Andou & Ashida, 1977; Vijayalakshmi & Srinivasan, 1975; Cotrait & Barrans, 1974) in that during the photo-oxidation reaction the peptide nitrogen, N(12), bonds to C(8) and the second heterocyclic five-membered ring is created with elimination of the C(8)—C(9) double bond. The ring closure causes the indole ring to deviate from planarity [C(8) is twisted out of the plane of the other four atoms]. The other five-membered ring shows a larger degree of twist with C(10) being out of the plane formed by C(9), C(8), N(12) and C(11). See Table 2 for a list of torsion angles describing the conformations of these rings. The junction between the two five-membered rings is cis and the hydroxyl oxygen, O(21), is exo to the ring system. C(9) and C(8) are asymmetric and occur in the crystal

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33168 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters* ($\times 10^4$; *for* H $\times 10^3$) *with standard deviations in parentheses*

The standard deviations are based solely on least-squares results.

	x	y	z
C(1)	3567 (2)	6563 (1)	3951 (1)
C(2)	4981 (2)	7227 (2)	4366 (1)
C(3)	4874 (2)	8392 (2)	4293 (1)
C(4)	3335 (2)	8927 (1)	3817 (1)
C(5)	1924 (2)	8278 (1)	3412 (1)
C(6)	2030 (2)	7110 (1)	3470 (1)
N(7)	453 (1)	6640 (1)	2985 (1)
C(8)	− 639 (2)	7495 (1)	2864 (1)
C(9)	116 (2)	8629 (1)	2865 (1)
C(10)	21 (2)	9426 (1)	3611 (1)
C(11)	302 (2)	8665 (1)	4540 (1)
N(12)	− 498 (1)	7616 (1)	3895 (1)
C(13)	−1034 (1)	6861 (1)	4249 (1)
O(14)	−1696 (1)	5947 (0)	3551 (0)
C(15)	−2441 (2)	5096 (1)	3783 (1)
O(16)	− 934 (1)	6993 (1)	5089 (0)
C(17)	2212 (2)	8580 (1)	5642 (1)
O(18)	2857 (1)	7555 (0)	5856 (1)
C(19)	4711 (2)	7447 (2)	6800 (2)
O(20)	3033 (1)	9396 (1)	6235 (1)
O(21)	− 850 (1)	9116 (0)	1723 (0)
H(1)	368 (2)	570 (1)	400 (1)
H(2)	604 (2)	687 (1)	468 (1)
H(3)	588 (3)	890 (2)	458 (2)
H(4)	333 (2)	977 (2)	381 (1)
H(N7)	41 (2)	596 (1)	312 (1)
H(8)	−184 (2)	737 (1)	218 (1)
H(10)	97 (2)	1005 (1)	403 (1)
H(10)	−122 (2)	975 (1)	308 (1)
H(11)	− 28 (2)	894 (1)	480 (1)
H(15)	−176 (2)	496 (1)	459 (2)
H(15)	−241 (2)	443 (2)	345 (2)
H(15)	−364 (3)	531 (1)	347 (1)
H(19)	503 (3)	666 (2)	673 (2)
H(19)	506 (3)	748 (2)	756 (2)
H(19)	520 (3)	810 (2)	659 (2)
H(O21)	− 73 (2)	871 (1)	127 (1)

as *RS* and *SR* pairs since both enantiomorphs are present. The two methyl ester groups are *gauche* with respect to one another.

Except for hydrogen bonding there are no intermolecular approaches less than van der Waals distances. The hydroxyl O takes part in two intermolecular hydrogen bonds. It is the donor in an O(21)—H···O(16) bond with the following parameters: O···O = 2·76, H···O = 1·85 Å and O—H···O = 168°. It is the acceptor in a weak N(7)—H···O(21) hydrogen bond where O···O = 3·02, H···O = 2·21 Å and N—H···O = 159°. Both hydrogen bonds are illustrated in the packing diagram (Fig. 3).

Table 2. *Selected torsion angles* (°)

N(7)−C(6)−C(5)−C(9)	1·6
C(6)−C(5)−C(9)−C(8)	10·9
C(5)−C(9)−C(8)−N(7)	−19·0
C(9)−C(8)−N(7)−C(6)	21·3
C(8)−N(7)−C(6)−C(5)	−14·9
C(11)−N(12)−C(8)−C(9)	−2·0
N(12)−C(8)−C(9)−C(10)	−19·2
C(8)−C(9)−C(10)−C(11)	32·7
C(9)−C(10)−C(11)−N(12)	−33·0
C(10)−C(11)−N(12)−C(8)	22·0
C(13)−N(12)−N(11)−C(17)	81·3
H(C8)−C(8)−C(9)−O(21)	−20·1

Fig. 3. Packing diagram showing the two independent hydrogen bonds. The view shown has *c* vertical and *a* approximately horizontal.

References

BUSING, W. R., MARTIN, K. O., LEVY, H. A., BROWN, G. M., ELLISON, R. D., HAMILTON, W. C., IBERS, J. A., JOHNSON, C. K. & THIESSEN, W. E. (1975). *ORXFLS3 Crystallographic Structure-Factor, Least-Squares Program.* Oak Ridge National Laboratory, Tennessee.
COTRAIT, M. & BARRANS, Y. (1974). *Acta Cryst.* B30, 510–513.
GILARDI, R. D. (1973). *Acta Cryst.* B29, 2089–2095.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849–859.
NAKAGAWA, M., WATANABE, H., KODATO, S., OKAJIMA, H., HINO, T., FLIPPEN, J. L. & WITKOP, B. (1977). *Proc. Natl Acad. Sci. USA*, 74, 4730–4733.
VIJAYALAKSHMI, B. K. & SRINIVASAN, R. (1975). *Acta Cryst.* B31, 999–1003.
YAMANE, T., ANDOU, T. & ASHIDA, T. (1977). *Acta Cryst.* B33, 1650–1653.