

Fig. 3. View of the hydrogen bonding in the title compound (*R* represents the phenyl group).

group through C(4) and C(3). The C(6)—C(7) distance of 1.49 Å is close to a C(*sp*²)—C(*sp*²) distance; this, together with the value of 17.1° for the dihedral angle between the phenyl and imidazole planes, is consistent with some reduction of delocalization between the two ring systems.

The crystal packing, which is presented in Fig. 2, is determined by hydrogen bonding and van der Waals interactions; in fact, while N(2) and O(1) are involved in hydrogen bonding the phenyl ring is involved in the conventional packing of planar aromatic rings. The molecules form chains (Fig. 3) in one dimension by N—H...O hydrogen bonds [N(2)—H...O(1): N(2)...O(1) 2.87, N(2)—H 0.81, H...O(1) 2.06 Å, ∠N(2)—H...O(1) 176.5°].

These data are in the range frequently observed (Donohue, 1968, and references therein). None of the remaining intermolecular contact distances are shorter than the sum of the van der Waals radii.

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8-Amino-5,7-dimethoxy-6-methylpyrrolo[1,2-*a*]indol-9-one

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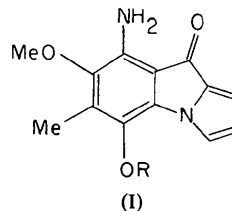
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Abstract. C₁₄H₁₄N₂O₃, orthorhombic, *P*2₁2₁2₁, *a* = 8.955 (2), *b* = 16.250 (3), *c* = 8.794 (2) Å, *V* = 1274.7 (3) Å³, *Z* = 4, *D*_x = 1.33, *D*_m = 1.29 g cm⁻³ (floatation in bromobenzene-*p*-xylene at 25°C). The structure was solved by direct methods using 1448 diffractometer-measured independent observed reflections, and block-diagonal least-squares refinement led to *R* = 0.034 (observed reflections only) and *R*_w = 0.036. The molecules are linked by hydrogen bonding in chains parallel to *a*.

Introduction. Compound (I), with *R* = H, was prepared as a result of a metaphoto-Fries rearrangement of an amino lactone (Siuta, Franck & Ozorio, 1974). Since this product has potential application in mitomycin

synthesis, it was decided to confirm the structure by X-ray crystallographic analysis of the methyl ether (*R* = CH₃). A preliminary report of the results of this work has been published along with a more detailed account of this metaphoto-Fries reaction (Crump *et al.*, 1977).



The crystals were red-gold, somewhat opaque, and had the form of slightly flattened prisms. X-ray data were collected with Cu *K*α radiation (Ni-filtered) on an

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Enraf-Nonius CAD-4 four-circle automated diffractometer using the ω - 2θ mode, a scan width of 1.5° , and a varying scan speed dependent on the intensity of the reflection. Data were collected up to $2\theta = 150^\circ$. Of the 1530 intensities measured, 1448 were found to be significantly above background, *i.e.* $I_{hkl} > 1.5\sigma_I$. Lorentz and polarization corrections were applied and a set of structure amplitudes derived. Absorption corrections were not made and it was calculated from the crystal dimensions ($0.36 \times 0.33 \times 0.22$ mm) that maximum absorption errors would be $\pm 3\%$ in F_o [$\mu(\text{Cu } K\alpha) = 7.96 \text{ cm}^{-1}$].

The structure was solved by direct methods (Karle & Karle, 1966) using the program NRC-5 (Huber & Brisse, 1970). Refinement of the positional and anisotropic thermal parameters of the 19 non-hydrogen atoms by block-diagonal least-squares methods

(Ahmed, 1968) resulted in $R = 0.061$. The 14 H atoms were then located from a difference electron density map. Subsequent refinement of all positional parameters, isotropic thermal parameters for the H atoms and anisotropic thermal parameters for the other atoms resulted in $R = 0.034$ for observed reflections only and $R = 0.037$ ($R_w = 0.036$) for all reflections. The function minimized was $\sum w(|F_o| - k|F_c|)^2$, where w for the observed reflections = $4|I_p|/(\sigma_I^2 + 0.02I^2)$. After refinement a plot of $w|\Delta F|^2$ vs F_o showed no systematic variation. During the final stages the unobserved reflections were included in the refinement with a constant weight such that the mean $w|\Delta F|^2$ was equal to that for the observed reflections. In the final cycle the mean and maximum shift/e.s.d. = 0.027 and 0.126 , and $[\sum w|\Delta F|^2/(m-n)]^{1/2} = 1.62$. The scattering factors were taken from *International Tables for X-ray Crystallography* (1968). The refined positional parameters for the non-hydrogen atoms are given in Table 1,* and the H atom parameters in Table 2.

The bond distances were corrected for rigid-body libration (Schomaker & Trueblood, 1968) and the corrected values are shown in Fig. 1. These corrections were from 0.003 to 0.005 Å. The uncorrected distances have been previously reported (Crump *et al.*, 1977). Corrections to the bond angles were negligible and have not been applied. The r.m.s. ΔU_{ij} was 0.011 Å². The C-H bond distances ranged from 0.88 – 1.04 Å with e.s.d.'s of 0.02 – 0.04 Å, except for that of H2C(13) which was 0.08 Å. The N-H distances were 0.91 (2) and 0.87 (2) Å.

Table 1. Fractional coordinates ($\times 10^4$) for the non-hydrogen atoms

	x	y	z
O(1)	3870 (2)	730 (1)	4192 (2)
O(2)	4597 (2)	2692 (1)	8257 (1)
O(3)	-1071 (2)	1457 (1)	8459 (2)
N(1)	817 (2)	487 (1)	5474 (2)
N(2)	1788 (2)	2426 (1)	9309 (2)
C(1)	-1531 (2)	68 (1)	5669 (3)
C(2)	-840 (3)	-353 (1)	4471 (2)
C(3)	615 (2)	-90 (1)	4361 (2)
C(4)	1962 (2)	1008 (1)	6026 (2)
C(5)	3367 (2)	1141 (1)	5469 (2)
C(6)	4279 (2)	1717 (1)	6238 (2)
C(7)	3711 (2)	2128 (1)	7491 (2)
C(8)	2263 (2)	1998 (1)	8077 (2)
C(9)	-189 (2)	1193 (1)	7508 (2)
C(10)	1386 (2)	1425 (1)	7297 (2)
C(11)	-483 (2)	586 (1)	6293 (2)
C(12)	5858 (2)	1873 (1)	5719 (3)
C(13)	3793 (3)	1224 (2)	2839 (3)
C(14)	4384 (3)	3516 (1)	7718 (3)

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters for the hydrogen atoms

The temperature factors used were of the form $\exp(-B \sin^2 \theta/\lambda^2)$.

	x	y	z	$B(\text{Å}^2)$
HC(1)	-255 (3)	3 (2)	608 (2)	2.5 (5)
HC(2)	-128 (3)	-74 (1)	382 (3)	2.9 (5)
HC(3)	146 (2)	-24 (1)	369 (3)	2.0 (4)
H1C(12)	587 (3)	237 (2)	504 (3)	4.1 (6)
H2C(12)	650 (3)	199 (2)	662 (3)	4.8 (7)
H3C(12)	621 (3)	142 (2)	513 (3)	3.7 (6)
H1C(13)	455 (4)	104 (2)	208 (4)	6.0 (8)
H2C(13)	279 (8)	115 (4)	239 (7)	14.1 (20)
H3C(13)	414 (4)	178 (2)	302 (4)	5.4 (7)
H1C(14)	447 (3)	356 (2)	673 (3)	3.5 (6)
H2C(14)	490 (3)	388 (2)	839 (3)	3.9 (6)
H3C(14)	325 (3)	367 (2)	777 (3)	4.3 (6)
H1N(2)	247 (3)	275 (1)	977 (3)	2.2 (5)
H2N(2)	91 (3)	232 (1)	968 (3)	2.5 (5)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33402 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

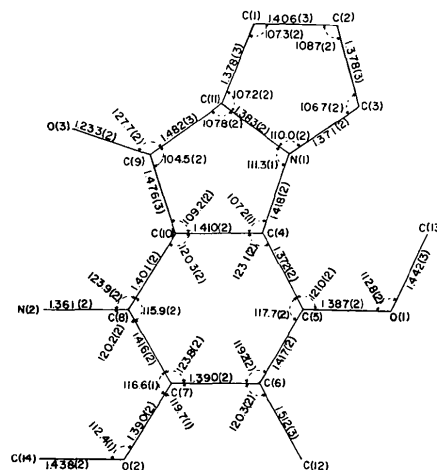


Fig. 1. Bond distances (Å) and angles ($^\circ$). Distances have been corrected for librational motion, angles have not.

Discussion. The chemical structural formulation was established to be that shown in (I). In the crystal the molecules were found to contain a nearly planar tricyclic skeleton and to be linked by hydrogen bonding.

The packing diagram (Fig. 2), which is a projection on (100), shows the three shortest intermolecular distances between non-hydrogen atoms. Two of these are between N(2) in the standard molecule and O(3') and O(2'') in two different molecules related by one translation along *a*. The singly- and doubly-primed atoms are in the molecules at $\pm\frac{1}{2} + x$, $\frac{1}{2} - y$, $2 - z$ respectively. Since the N—H distances show the usual shortening in X-ray measurements, the H positions were corrected by moving outward along the N—H bonds to a distance of 1.02 Å. Distances and angles based on these positions as the most probable proton locations are shown in Fig. 3. Hydrogen bonding undoubtedly exists between H2N(2) and O(2'') and between H1N(2) and O(3'). The reverse interactions are not shown but O(2) bonds to N(2') and O(3) to N(2'') so that from each molecule there are four hydrogen bonds, two to each of two different molecules, giving infinite chains along *a*. While the two intramolecular distances H1N(2)—O(2) and H2N(2)—O(3) are shorter than the van der Waals distance the constrained position of the NH₂ group makes these interactions more difficult to interpret. Infrared measurements in solution indicate no hydrogen bonding outside the crystalline state. Apart from the distances between hydrogen-bonded atoms there are no abnormally short intermolecular distances and thus no evidence of charge transfer between molecules.

The equation of the least-squares mean plane for all non-hydrogen atoms, excluding the methoxy C(13) and

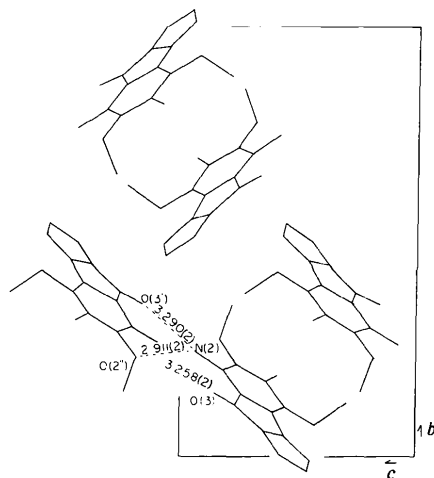


Fig. 2. Packing diagram projected on (100). The three shortest intermolecular contacts between non-hydrogen atoms are shown. Doubly-primed atoms are in the molecule one translation below that containing singly-primed atoms.

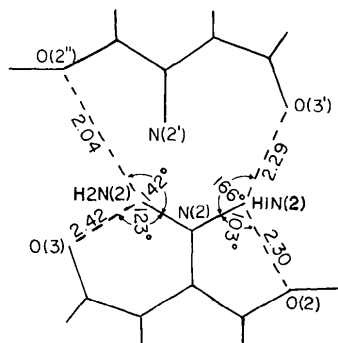


Fig. 3. Interactions involving H atoms. Distances (Å) and angles (°) have been 'corrected' by adjusting the refined H atom positions so that the N—H distances are 1.02 Å. The e.s.d.'s of the angles shown are 2°.

Table 3. *Least-squares mean plane for the tricyclic skeleton and its first substituent atoms, and distances of the atoms from the plane*

Standard deviations of the distances are 0.001–0.002 Å.

$$-0.3227X + 0.7293Y - 0.6033Z = -2.5315$$

O(1)	0.054 Å	C(5)	0.009 Å
O(2)	0.012	C(6)	0.020
O(3)	0.080	C(7)	0.006
N(1)	-0.032	C(8)	-0.040
N(2)	-0.049	C(9)	0.016
C(1)	0.047	C(10)	-0.052
C(2)	-0.016	C(11)	0.027
C(3)	-0.067	C(12)	0.024
C(4)	-0.038		

C(14), and atomic distances from the plane are given in Table 3. The benzene ring and the pyrrole ring are each planar within experimental error, but the dihedral angle between their planes is 4.3°. This, together with the non-planarity of the central ring, where there are displacements of up to 0.017 Å, accounts for the lack of planarity of the tricyclic system. The largest deviation from the 17-atom plane is shown by O(3), which is also 0.04 Å from the central-ring mean plane. This displacement shortens the H1N(2)—O(3') distance, but only by 0.01 Å.

The internal dimensions of the molecule (Fig. 2) are, in general, normal but present some points of interest. The benzene ring, though planar, is quite irregular, with angles varying from 116 to 124°. This is partly due to the fusion at C(10)—C(4) of a five-membered ring, and the interior angles here are close to those found in 3-indolylacetic acid (Karle, Britts & Gum, 1964). The lengthening of the formal double bonds C(1)—C(11) and C(2)—C(3) and the shortening of the other three bonds of the pyrrole ring indicate a considerable delocalization of the double-bond π electrons.

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1-*tert*-Butoxycarbonyl-2,7,12-tris(2-methoxycarbonylethyl)-8,13-bis(methoxycarbonylmethyl)-3,14-dimethyl-5,16-dihydro-15*H*-tripyrrin Hydrobromide

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Abstract. $C_{39}H_{52}N_3O_{12}Br^-$, triclinic $P\bar{1}$, $a = 13.27(1)$, $b = 16.97(2)$, $c = 10.85(1)$ Å, $\alpha = 103.1(1)$, $\beta = 113.0(1)$, $\gamma = 71.0(1)^\circ$, $Z = 2$, $M_r = 834.8$, $D_x = 1.31$ g cm $^{-3}$. The pyrromethene chromophore displays a slightly twisted *syn-Z* conformation (interplanar angle 10.3°) with a wide methine bridge angle of $135.1(4)^\circ$. The Br $^-$ anion is situated 0.077 Å from the best least-squares plane of the pyrromethene system and makes two non-linear N–H \cdots Br hydrogen bonds of length 3.26 and 3.30 Å. The N–H proton of the non-conjugated pyrrole ring is involved in an N–H \cdots O intermolecular bond.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ diffractometer (Cu $K\alpha$, $\lambda = 1.54178$ Å). Intensity measurements were carried out in the θ – 2θ mode ($3.5 \leq 2\theta \leq 135.0^\circ$) with graphite-monochromated Cu $K\alpha$ radiation. No absorption correction

$[\mu(\text{Cu } K\alpha) = 17.1 \text{ cm}^{-1}]$ was applied. After application of the rejection criterion $I < 2.0\sigma(I)$, 4075 unique reflexions were retained for the refinement. The structure was solved by Patterson and difference

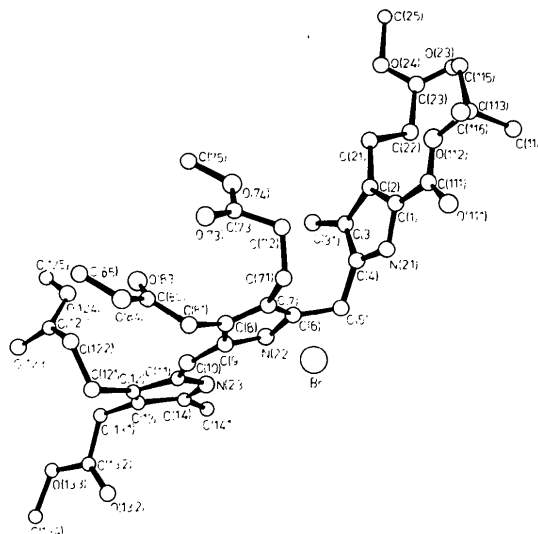


Fig. 1. The molecule of (I) in perspective with atom numbering.

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