

**Related literature.** The pyridine nucleus is a structural unit in many natural products having simple or very complex structures, like co-enzymes, alkaloids and others (Yates, 1984). Because of the importance of this ring system and the pharmacological properties of functionalized pyridines, a number of methods of pyridine synthesis have been developed (Jones, 1984; Barluenga, Fustero & Gotor, 1975; Barluenga, Joglar, González, Gotor & Fustero, 1988; Guzmán, Romero, Maddox & Muchowski, 1990).

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## 4-Methoxyindan-1-one Oxime

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**Abstract.**  $C_{10}H_{11}NO_2$ ,  $M_r = 177.19$ , monoclinic,  $P2_1/n$ ,  $a = 14.422$  (3),  $b = 7.468$  (8),  $c = 8.270$  (2) Å,  $\beta = 97.47$  (1)°,  $V = 883.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.338$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.087$  mm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 291$  K,  $R = 0.0385$  for 1770 unique reflections with  $F > 6\sigma(F)$ . The bond lengths and angles are all close to their expected values and the molecule is essentially planar with the nine atoms of the ring system having an r.m.s. deviation of 0.011 Å and methoxy O and C atoms being 0.002 (1) and 0.094 (2) Å, respectively, away from this plane. The oxime N and O atoms are respectively 0.104 (1) and 0.118 (1) Å above the ring

plane with molecules related by a centre of symmetry forming hydrogen-bonded dimers through the oxime atoms. The crystal is made up of extended sheets of molecules stacked perpendicular to the  $b$  axis.

**Experimental.** The title compound was prepared by oximation of 4-methoxyindan-1-one (Barco, Benetti & Pollini, 1976) with hydroxylamine hydrochloride and pyridine. Recrystallization from methanol gave colourless prisms. A single crystal,  $0.8 \times 0.8 \times 0.8$  mm, was mounted on a Stoe Stadi-2 two-circle diffractometer equipped with graphite-monochromated Mo  $K\alpha$  X-radiation. Cell parameters were obtained from 12  $h0l$  and four  $0k0$  reflections

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Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|       | x            | y            | z            | U <sub>eq</sub> |
|-------|--------------|--------------|--------------|-----------------|
| C(1)  | 0.48089 (8)  | 0.33641 (15) | 0.69409 (14) | 0.0277 (6)      |
| C(2)  | 0.56120 (8)  | 0.28433 (15) | 0.61264 (14) | 0.0272 (6)      |
| C(3)  | 0.65684 (9)  | 0.28917 (18) | 0.67060 (16) | 0.0337 (6)      |
| C(4)  | 0.71849 (9)  | 0.23495 (18) | 0.56555 (17) | 0.0375 (7)      |
| C(5)  | 0.68758 (9)  | 0.17898 (18) | 0.40682 (17) | 0.0348 (7)      |
| C(6)  | 0.59222 (9)  | 0.17413 (16) | 0.35077 (15) | 0.0301 (6)      |
| C(7)  | 0.52885 (8)  | 0.22753 (15) | 0.45573 (14) | 0.0266 (6)      |
| C(8)  | 0.42391 (8)  | 0.23563 (17) | 0.41992 (15) | 0.0295 (6)      |
| C(9)  | 0.39192 (8)  | 0.30269 (17) | 0.58086 (15) | 0.0307 (6)      |
| N(11) | 0.49062 (7)  | 0.40374 (15) | 0.83719 (13) | 0.0334 (6)      |
| O(12) | 0.40330 (7)  | 0.44341 (15) | 0.88918 (13) | 0.0433 (6)      |
| O(61) | 0.55464 (7)  | 0.12023 (14) | 0.19907 (11) | 0.0407 (5)      |
| C(62) | 0.61744 (13) | 0.0763 (3)   | 0.08581 (20) | 0.0496 (9)      |

Table 2. Bond lengths (Å) and angles (°)

|                 |             |                  |             |
|-----------------|-------------|------------------|-------------|
| C(1)—C(2)       | 1.4661 (16) | C(5)—C(6)        | 1.3935 (18) |
| C(1)—C(9)       | 1.5081 (17) | C(6)—C(7)        | 1.3979 (17) |
| C(1)—N(11)      | 1.2767 (16) | C(6)—O(61)       | 1.3612 (16) |
| C(2)—C(3)       | 1.4006 (17) | O(61)—C(62)      | 1.4234 (21) |
| C(2)—C(7)       | 1.3871 (17) | C(7)—C(8)        | 1.5051 (17) |
| C(3)—C(4)       | 1.3821 (19) | C(8)—C(9)        | 1.5475 (17) |
| C(4)—C(5)       | 1.3944 (19) | N(11)—O(12)      | 1.4140 (15) |
| C(2)—C(1)—C(9)  | 109.25 (10) | C(5)—C(6)—O(61)  | 124.87 (12) |
| C(2)—C(1)—N(11) | 122.15 (11) | C(7)—C(6)—O(61)  | 116.27 (11) |
| C(9)—C(1)—N(11) | 128.57 (11) | C(6)—O(61)—C(62) | 117.62 (11) |
| C(1)—C(2)—C(3)  | 129.61 (11) | C(2)—C(7)—C(6)   | 120.04 (11) |
| C(1)—C(2)—C(7)  | 108.74 (10) | C(2)—C(7)—C(8)   | 112.28 (10) |
| C(3)—C(2)—C(7)  | 121.64 (11) | C(6)—C(7)—C(8)   | 127.67 (11) |
| C(2)—C(3)—C(4)  | 117.56 (12) | C(7)—C(8)—C(9)   | 104.38 (10) |
| C(3)—C(4)—C(5)  | 121.77 (13) | C(1)—C(9)—C(8)   | 205.27 (10) |
| C(4)—C(5)—C(6)  | 120.12 (12) | C(1)—N(11)—O(12) | 111.68 (10) |
| C(5)—C(6)—C(7)  | 118.86 (11) |                  |             |

for which  $30 < 2\theta < 40^\circ$ . Data were collected by  $\omega$  scans of width  $(1.5 + 0.8\sin\mu/\tan\theta)^\circ$ , for  $5 < 2\theta < 56^\circ$ ,  $h - 18 \rightarrow 18$ ,  $k 0 \rightarrow 8$ ,  $l 0 \rightarrow 10$ . 2283 reflections were collected. No significant crystal movement or decay were observed. No absorption correction was applied. After inter-layer scaling, 2131 unique reflections were obtained. Direct methods (SHELXS86; Sheldrick, 1986) revealed all non-H atoms. H atoms were refined riding on atoms to which they were attached. Refinement was by full-matrix least-squares on  $F$ , using SHELX76 (Sheldrick, 1976), and included anisotropic thermal parameters for C, O and N atoms, and isotropic for H atoms. At final convergence,  $R = 0.0385$ ,  $wR = 0.052$ ,  $S = 1.328$  for 163 parameters and 1770 reflections with  $F > 6\sigma(F)$ .  $(\Delta/\sigma)_{\max}$  in the final cycle was 0.011. Maximum and minimum residuals in the final  $\Delta F$  synthesis were 0.28 and  $-0.18 \text{ e \AA}^{-3}$ , respectively. A secondary-extinction parameter of 0.055 was applied. The weighting scheme  $w^{-1} = \sigma^2(F) + 0.00022F^2$  gave satisfactory agreement analyses. Three reflections with  $F_{\text{calc}} \gg F_{\text{obs}}$  were ignored. Scattering factors were inlaid (Sheldrick, 1976). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1 and bond lengths and angles appear in Table

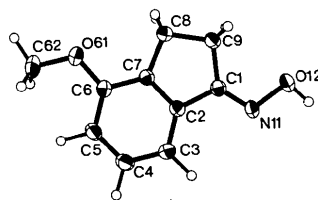


Fig. 1. A general view of the molecule showing the numbering scheme; the H atoms are numbered according to the atoms to which they are attached. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level. H-atom radii are 0.15 Å. In the crystal, a hydrogen bond is formed between O(11)—H(11) and O(10) of a neighbouring molecule producing a chain in the  $a$ -axis direction.

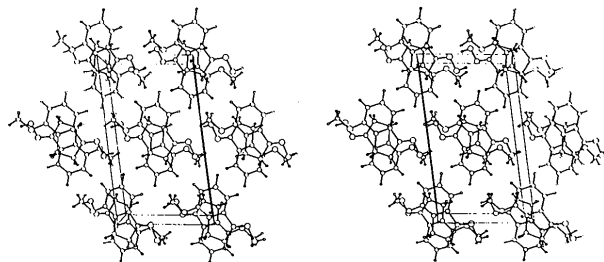


Fig. 2. A stereodiagram of the packing arrangement of the title molecule showing the sheets of planar molecules and the intermolecular hydrogen bonding.

2.\* The atomic numbering scheme is shown in Fig. 1 produced by the interactive version of ORTEPII included in the GX crystallographic program system (Mallinson & Muir, 1985), and the packing is shown in Fig. 2 produced by the program PLUTO (Motherwell, 1972). Molecular geometry calculations were performed using CALC (Gould & Taylor, 1983).

**Related literature.** The title compound arises from synthetic efforts to prepare aza analogues of 8-hydroxy-2-(di-*n*-propylamino)tetralin, which is the prototypical ligand for the 5HT<sub>1A</sub> neuroreceptor (Arvidsson *et al.*, 1981; Karlsson, Petterson, Sundell, Arvidsson & Hacksell, 1988; Mellin *et al.*, 1988).

\* Lists of torsion angles, structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55466 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1004]

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## (4*E*,8*Z*,12*E*)-13,16-Dichloro-14-azabicyclo[10.4.0]hexadeca-4,8,12-trien-15-one: a Thermal Cycloaddition Product

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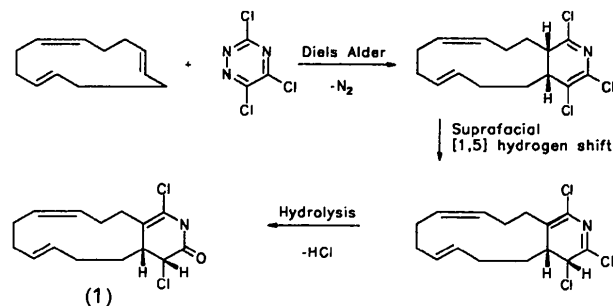
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**Abstract.**  $C_{15}H_{19}Cl_2NO$ ,  $M_r = 300.23$ , monoclinic,  $P2_1/c$ ,  $a = 13.978$  (8),  $b = 7.467$  (9),  $c = 16.452$  (9) Å,  $\beta = 114.11$  (4)°,  $V = 1567$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.272$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.41$  mm<sup>-1</sup>,  $F(000) = 632$ ,  $T = 293$  K,  $R = 0.052$ , 1468 unique reflexions [ $F \geq 4\sigma(F)$ ]. The 12-membered ring is sufficiently flexible to accommodate a planar *cis*-alkene link [C=C=C—C—2 (1)°]; however, the *trans*-alkene is distorted [C=C=C—C 171.2 (5)°]. The smaller ring adopts a twist conformation, severely flattened in part by the combined effect of a double bond and the amide group. Pairs of molecules are linked across an inversion centre by hydrogen bonds between the amide H atom and ketonic O atom [H···O = 2.06 (4) Å, N—H···O = 170.0 (4)°].

**Experimental.** A mixture of 3,5,6-trichloro-1,2,4-triazine (2.00 g, 10.8 mmol) and (1*E*,5*E*,9*Z*)-1,5,9-dodecatriene (6.15 g, 38.0 mmol) was sealed *in vacuo* in a Rotaflo tube (*ca* 50 ml) and heated at 343 K for 4 d. This gave a volatile mixture of hydrogen chloride (0.11 g, 3.0 mmol, 39%) and nitrogen together with a brown residue (7.5 g), which was extracted with diethyl ether (3 × 20 ml). The filtrate, on removal of the ether, gave a reddish oil (7.22 g), which was separated by DCFC (dry column flash chromatography) [silica (Merck Kiesegel 60 H); eluant CH<sub>2</sub>Cl<sub>2</sub> and *n*-C<sub>5</sub>H<sub>12</sub> (1:1 v/v)] to afford (i) unchanged triene (4.75 g, 29.3 mmol, 77%), (ii) a yellow oil ( $R_F$  0.63) comprising a mixture (0.91 g, 3.2 mmol, 42%) of (*E*,*Z*)- and (*Z*,*E*)-1,3-dichloro-

5,6,9,10,13,14-hexahydrododeca[*c*]pyridine, and (iii) a solid (1.22 g). The solid was sublimed *in vacuo* to give unchanged triazine (0.59 g, 3.2 mmol, 30% recovered) and a residue ( $R_F$  0.57; 0.62 g, 1.7 mmol, 22%; analysis found: C 60.0, H 6.4, N 4.7, Cl 23.6%;  $M^+$  299/301/303; analysis calculated for C<sub>15</sub>H<sub>19</sub>NOCl<sub>2</sub>: C 59.8, H 6.4, N 4.6, Cl 23.6%;  $M$  299/301/303) comprising two isomers in the ratio 4:1 (<sup>1</sup>H NMR). Recrystallization from chloroform produced a small amount of the title compound (major isomer) (1) {formed by hydrolysis of (4*E*,8*Z*,12*E*,14*E*)-13,15,16-trichloro-14-azabicyclo[10.4.0]hexadeca-4,8,12,14-tetraene}.



A colourless block crystal, 0.3 × 0.25 × 0.25 mm, was used for data collection on a Rigaku AFC-6S diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Unit-cell dimensions were determined from setting angles of 16 accurately centred reflections ( $20.2 \leq 2\theta \leq 24.1^\circ$ ). Data were