

Crystal structure of 2,4-dihydro-8-methoxy-4,4-dimethyl-2-*P*-tolyl-1*H*-[1]benzopyrano-[4,3,2-*cd*] indol-1-one

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Abstract. The crystal structure of 2,4-dihydro-8-methoxy-4,4-dimethyl-2-*P*-tolyl-1*H*-[1] benzopyrano-[4,3,2-*cd*] indol-1-one (C₂₄H₂₁NO₃) was determined from single crystal X-ray diffraction data. The crystal belongs to the triclinic, space group $P\bar{1}$, with $a = 6.060(2)$, $b = 12.276(5)$, $c = 12.889(5)$ Å, $\alpha = 92.63(4)$, $\beta = 90.78(4)$, $\gamma = 95.71(3)^\circ$, $M_r = 371.42$, $V = 952.92$ Å³, $Z = 2$, $D_{\text{cal}} = 1.29$ Mg·m⁻³, $D_m = 1.28$ Mg·m⁻³, $\lambda(\text{CuK}\alpha) = 1.54178$ Å, $\mu = 0.60$ mm⁻¹, $T = 293$ K, $F(000) = 392$. The crystal structure was solved by direct methods and refined by least-squares to $R = 0.038$ and $R_w = 0.043$ for 2257 independent reflections. The pyran ring assumes a distorted boat conformation.

Introduction

The title compound is a condensation product of 2-[(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-oxy]-6-methoxy-3 (2*H*)-benzofuranone with a 4-substituted aromatic amine (Chandrasekhar, 1989) in glacial acetic acid medium. As the structure of the compound could not be obtained unambiguously by analytical and spectral methods, X-ray analysis was undertaken.

Experimental

Pale yellow plate like single crystals were grown by slow evaporation of the compound in methanol. Density was measured by flotation. Intensity data

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses. $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N	0.5907(2)	0.6812(1)	0.7636(1)	0.053(1)
O1	0.4393(2)	0.7342(1)	0.9214(1)	0.069(1)
O2	0.1798(2)	0.9113(1)	0.5852(1)	0.069(1)
O3	-0.3611(2)	1.0759(1)	0.7706(1)	0.080(1)
C1	0.4517(3)	-0.7401(1)	0.8276(1)	0.055(1)
C3	0.6475(3)	0.6764(1)	0.5691(1)	0.057(1)
C4	0.5745(3)	0.7226(1)	0.4672(1)	0.058(1)
C5	0.4137(3)	0.8080(1)	0.4789(1)	0.065(1)
C7	-0.0879(3)	0.9898(1)	0.6844(1)	0.063(1)
C8	-0.1937(3)	1.0092(1)	0.7775(1)	0.061(1)
C9	-0.1312(3)	0.9621(1)	0.8664(1)	0.063(1)
C10	0.0412(3)	0.8955(1)	0.8629(1)	0.060(1)
C11	0.5665(3)	0.7101(1)	0.6594(1)	0.050(1)
C12	0.3334(3)	0.8361(1)	0.5709(1)	0.057(1)
C13	0.0835(3)	0.9257(1)	0.6822(1)	0.055(1)
C14	0.1543(3)	0.8762(1)	0.7719(1)	0.050(1)
C15	0.3317(3)	0.8064(1)	0.7575(1)	0.051(1)
C16	0.4074(3)	0.7881(1)	0.6618(1)	0.049(1)
C17	0.4588(4)	0.6262(2)	0.3996(1)	0.081(1)
C18	0.7806(3)	0.7709(2)	0.4115(1)	0.077(1)
C19	-0.4680(4)	1.1057(2)	0.8623(1)	0.083(1)
C20	0.7198(3)	0.5980(1)	0.7967(1)	0.050(1)
C21	0.6354(3)	0.5236(1)	0.8673(1)	0.058(1)
C22	0.7574(3)	0.4401(1)	0.8958(1)	0.062(1)
C23	0.9625(3)	0.4268(1)	0.8531(1)	0.060(1)
C24	1.0445(3)	0.5019(1)	0.7831(1)	0.063(1)
C25	0.9256(3)	0.5867(1)	0.7553(1)	0.059(1)
C26	1.0906(3)	0.3335(2)	0.8824(2)	0.083(1)

were collected from a crystal of approximate dimensions $0.2 \times 0.5 \times 0.3$ mm up to a maximum 2θ value of 140° with ω - 2θ scan using crystal monochromated $\text{CuK}\alpha$ radiation. Cell parameters were refined by least-square calculations from 20 reflections with $20^\circ < \theta < 40^\circ$ on an Enraf-Nonius CAD-4 automated diffractometer. Two strong reflections [1, 1, -7; 0, 4, 7] monitored periodically during data collection showed that the crystal was stable. Index range of unique data $-7 \leq h \leq 7$, $-14 \leq k \leq 14$, $0 \leq l \leq 15$. 4023 reflections were collected of which 2257 unique reflections with $I > 3\sigma(I)$ were considered in all subsequent calculations. The data were corrected for Lorentz and polarization effects. Absorption and extinction neglected.

Structure determination and refinement

The structure was solved by multisolution techniques using SHELXS-86 (Sheldrick, 1986) and refined on F by least squares methods with SHELX-

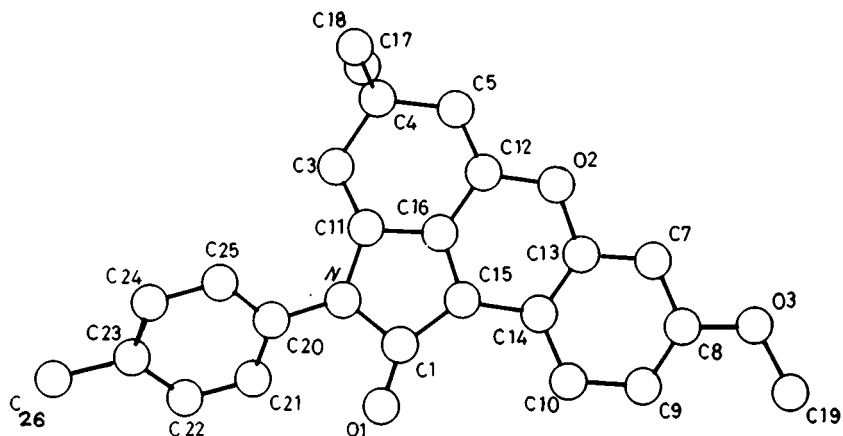


Fig. 1. PLUTO plot of the molecule.

76 (Sheldrick, 1976). H atom positions were obtained from difference Fourier maps at intermediate stages of refinement. Final refinement with non-H atoms anisotropically and H atoms isotropically converged to $R = 0.038$ and $R_w = 0.043$. The quantity minimized was $\sum W(|F_o| - K|F_c|)^2$ with $W = K' \{[\sigma(F_o)]^2 + 0.00118|F_o|^2\}^{-1}$ with $K' = 1.090$. $(\text{shift}/e.s.d.)_{\text{max}} = 0.061$. Maximum height in the final difference Fourier synthesis is $0.17 \text{ e}\text{\AA}^{-3}$. Atomic scattering factors were taken from SHELX-76 and the calculations were performed on a SIEMENS 7.580-E computer.

Results and discussion

The final atomic coordinates of the molecule are listed in Table 1 and the PLUTO (Motherwell and Clegg, 1978) plot of the molecule with atom numbering scheme is shown in Figure 1. The bond lengths, the bond angles and selected torsion angles involving non-H atoms are listed in Table 2. Figure 2 represents the packing of the molecules in a unit cell.

The bond lengths and bond angles are normal. In the heterocycle of the indole ring system, the values of $C_{(sp)^2} - N$ distances, $C(1) - N [= 1.414(2) \text{ \AA}]$ and $C(11) - N [= 1.414(1) \text{ \AA}]$ are not very different from the values reported for the same bond in 6,6-dimethyl-4-oxo-1, 2-diphenyl-4,5,6, 7-tetrahydroindole (Babu Varghese, Srinivasan, Padmanabhan and Ramadas, 1986) for the same bond.

The fused benzopyranoindole ring system is planar as seen from the endocyclic torsion angles. But the pyran ring has a larger distortion towards a boat conformation with the asymmetry parameter $\Delta C_s(O) [= 1.3(2)^\circ]$. A

Table 2. Bond lengths (Å) bond angles and torsion angles (°) with e.s.d.'s in parentheses.

C1--N	1.414(2)	C3--C11--C16	120.2(2)
C1--C15	1.474(2)	C4--C5--C12	121.8(2)
O1--C1	1.218(1)	C5--C4--C17	107.3(2)
N--C11	1.414(1)	C5--C4--C18	109.2(2)
N--C20	1.424(2)	C17--C4--C18	109.0(2)
C3--C4	1.531(2)	C5--C12--O2	124.0(2)
C3--C11	1.334(2)	C5--C12--C16	119.7(2)
C4--C5	1.505(2)	O2--C12--C16	116.3(2)
C4--C17	1.542(2)	C12--O2--C13	120.1(2)
C4--C18	1.531(2)	O2--C13--C7	115.4(2)
C5--C12	1.331(2)	O2--C13--C14	122.9(3)
O2--C12	1.384(2)	C7--C8--C9	120.7(3)
O2--C13	1.398(2)	C7--C8--O3	114.4(3)
C7--C8	1.390(2)	C8--C7--C13	119.6(3)
C7--C13	1.364(2)	C7--C13--C14	121.7(3)
C8--C9	1.372(2)	C8--C9--C10	119.3(3)
C8--O3	1.371(2)	C9--C8--O3	125.0(3)
C19--O3	1.406(2)	C8--O3--C19	118.3(3)
C9--C10	1.389(2)	C9--C10--C14	121.8(3)
C10--C14	1.389(2)	C10--C14--C13	117.0(3)
C11--C16	1.424(2)	C10--C14--C15	127.0(3)
C12--C16	1.423(2)	C11--C16--C12	122.7(2)
C13--C14	1.412(2)	C11--C16--C15	112.3(2)
C14--C15	1.449(2)	C12--C16--C15	125.0(2)
C15--C16	1.339(2)	C13--C14--C15	115.9(3)
C20--C21	1.386(1)	C14--C15--C16	119.2(3)
C20--C25	1.380(2)	C20--C21--C22	120.1(3)
C21--C22	1.382(2)	C21--C20--C25	119.0(2)
C22--C23	1.388(2)	C20--C25--C24	120.5(2)
C23--C24	1.381(1)	C21--C22--C23	121.4(3)
C24--C25	1.382(2)	C22--C23--C24	117.8(3)
C23--C26	1.506(2)	C23--C24--C25	121.3(2)
C1--N--C11	119.6(2)	C22--C23--C26	120.8(3)
C1--N--C20	125.4(3)	C24--C23--C26	121.4(3)
N--C1--C15	106.0(2)	C11--N--C20--C25	41.8(2)
C1--C15--C14	133.7(3)	O2--C13--C14--C15	-1.4(2)
C1--C15--C16	106.9(2)	C13--C14--C15--C16	-3.8(2)
N--C1--O1	124.9(3)	C14--C15--C16--C12	2.8(2)
C15--C1--O1	129.3(3)	C15--C16--C12--O2	3.4(2)
N--C11--C3	134.4(2)	C16--C12--O2--C13	-8.5(2)
N--C11--C16	105.2(2)	C12--O2--C13--C14	7.8(2)
C11--N--C20	124.8(2)	C3--C4--C5--C12	-3.4(2)
N--C20--C21	120.3(2)	C4--C5--C12--C16	2.7(2)
N--C20--C25	120.7(2)	C5--C12--C16--C11	0.2(2)
C3--C4--C5	115.0(2)	C12--C16--C11--C3	-2.2(2)
C3--C4--C17	107.4(2)	C16--C11--C3--C4	1.2(2)
C3--C4--C18	108.8(2)	C11--C3--C4--C5	1.4(2)
C4--C3--C11	120.5(2)		

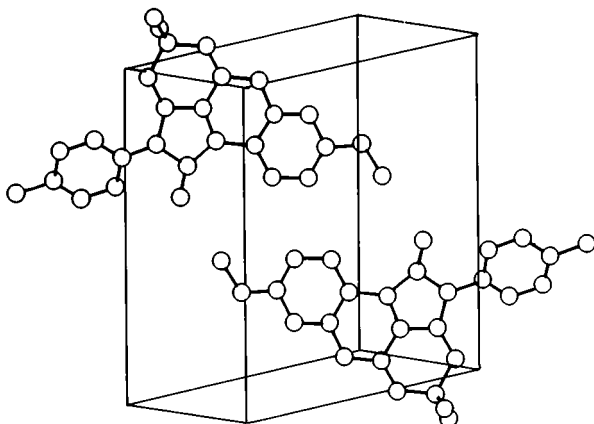


Fig. 2. Packing of the molecules in a unit cell.

similar conformation for the pyran ring has been reported in hexachloroxanthene (Soderholm et al., 1976).

The phenyl ring C(20)–C(21)–C(22)–C(23)–C(24)–C(25) is planar and is rotated from the plane of the five membered ring C(1)–N–C(11)–C(16)–C(15) about the N–C(20) bond by $41.8(2)^\circ$, to avoid the short nonbonded interactions between H(3) and H(25) [= 2.225 Å].

The dimethyl substitution at C(4) produces a distortion in the conformation of the 1,4-cyclohexadiene ring C(3)–C(4)–C(5)–C(12)–C(16)–C(11). The normal D_{2h} symmetry reported for this ring from Raman and IR spectral studies (Dale, 1978) is modified by the displacements of C(3) [= 0.041 Å] and C(4) [= 0.062 Å] from the plane formed by the atoms C(5), C(11), C(12) and C(16). These displacements avoid short intramolecular contacts between the hydrogen atoms of the methyl groups, and the neighbouring carbon atoms C(3) and C(5) [e.g. C(3)–H(171) = 2.593 Å, C(5)–H(181) = 2.653 Å].

The intermolecular contacts are Van der Waals. The shortest contact is between O(1) and C(19)* [= 3.329 Å].

* Symmetry code $-x, -y + 2, -z + 2$.

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