

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.152$ $S = 1.093$

3642 reflections

219 parameters

H-atom parameters
constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0976P)^2 + 0.3939P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = -0.005$$

$$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

S1—C5	1.741 (2)	N3—C23	1.471 (3)
S1—C2	1.774 (2)	C4—C5	1.476 (3)
C2—N3	1.370 (3)	C5—C8	1.342 (2)
N3—C4	1.387 (2)	C8—C9	1.451 (2)
C5—S1—C2	91.77 (10)	N3—C4—C5	111.0 (2)
N3—C2—S1	110.80 (14)	C4—C5—S1	110.26 (15)
C2—N3—C4	116.2 (2)		
S1—C5—C8—C9	−2.3 (3)		
C5—C8—C9—C18	−13.5 (3)		
C16—C11—C12—C132	−14.7 (3)		
C11—C12—C132—C142	47.6 (5)		
C12—C132—C142—C15	−69.8 (5)		
C132—C142—C15—C16	53.0 (4)		
C12—C11—C16—C15	1.4 (3)		
C142—C15—C16—C11	−20.7 (3)		
C4—N3—C23—C24	74.1 (3)		

Disorder was identified in the adjacent methylene groups and modelled in terms of two components – C131 and C141 with occupancy 0.467 (7), and C132 and C142 with occupancy 0.533 (7). Except for the disordered atoms, non-H atoms were refined anisotropically. U_{iso} values for the disordered atoms refined in the range 0.060–0.070 \AA^2 . H atoms were fixed in idealized positions with common U_{iso} values for chemically related groups (range 0.066–0.126 \AA^2).

Data collection: *Collect Software* (Nonius BV, 1998). Cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). Data reduction: *DENZO* and *SCALEPACK*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: *SHELXL93* and *PARST95* (Nardelli, 1995).

MRC thanks the University of Cape Town and the FRD (Pretoria) for financial assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1315). Services for accessing these data are described at the back of the journal.

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- Acta Cryst.* (1999). **C55**, 1029–1031

3-(2-Hydroxyphenylamino)-5,5-dimethyl-cyclohex-2-enone

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(Received 10 March 1999; accepted 22 March 1999)

Abstract

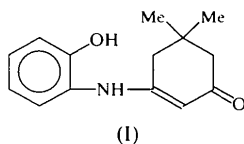
In the title compound, $\text{C}_{14}\text{H}_{17}\text{NO}_2$, the molecules are linked through two hydrogen bonds to form a two-dimensional network in the (100) plane. The carbonyl-O atom is involved in two intermolecular hydrogen

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bonds, one with the amino group and the other with the hydroxy group. The cyclohexenone ring is disordered into two distorted half-chair conformations. The phenyl and cyclohexenone moieties are not coplanar.

Comment

The reaction of amino compounds with acyclic β -dicarbonyl compounds (García & Gómez, 1965) has been used to prepare a variety of pyrrole derivatives, in some cases, in high yields. The extension of these reactions to cyclohexane-1,3-diones (Gómez *et al.*, 1974) also provides a convenient synthesis of 1,5,6,7-tetrahydroindol-4-ones. We reported briefly (Suárez *et al.*, 1991) on the synthesis of 2-hydroxy-6-oxo-8,8-dimethyl-6,7,8,9-tetrahydro-1*H*-carbazole *via* a two-path reaction from *o*-aminophenol and 5,5-dimethylcyclohexane-1,3-dione (dimedone). The primary product of this reaction was the enamine 3-(2-hydroxyphenylamino)-5,5-dimethyl-2-cyclohexenone, (I), which was obtained as a crystalline solid in good yield. This compound proved to be a useful intermediate in the synthesis of fused-heterocyclic compounds. It has been found that cyclohexanone rings fused to the 1,4-dihydropyridine moiety produce a striking effect on the entry of calcium ions into the intracellular space (calcium-agonist effect) (Meyer *et al.*, 1976).



Bond distances and angles of the title compound are in agreement with those of related structures reported previously (Bolte & Scholtysik, 1997; Lynch *et al.*, 1989). The crystal structure is stabilized by two hydrogen bonds (Table 2). The molecules are linked, forming an infinite two-dimensional network,

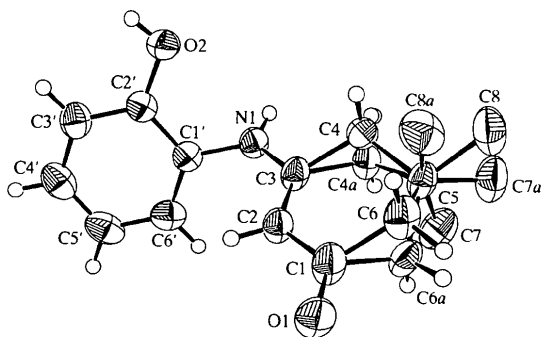


Fig. 1. A plot showing the atomic numbering scheme and the disordered cyclohexenone ring of (I). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. The H atoms of the methyl groups have been omitted for clarity.

with base vectors [010] and [001]. The disordered cyclohexenone ring exhibits a distorted half-chair conformation, with puckering parameters (Cremer & Pople, 1975) for the disordered conformations of $Q = 0.501(5) \text{ \AA}$, $\theta = 32.5(3)^\circ$ and $\varphi = 135(1)^\circ$ (for C3–C4–C5–C6–C1–C2), and $Q = 0.506(5) \text{ \AA}$, $\theta = 137.8(3)^\circ$ and $\varphi = -140.5(8)^\circ$ (for C6a–C5–C4a–C3–C2–C1). The phenyl and cyclohexenone moieties are not coplanar, the dihedral angle between their respective least-squares planes is $56.5(2)^\circ$.

Experimental

A mixture of *o*-aminophenol (0.9 mol) and dimedone (0.9 mmol) in benzene was heated for 6 h. The solid that precipitated was collected by filtration and further purified by recrystallization from ethanol (yield 93%; m.p. 409–410 K). UV (EtOH, nm): 232, 303; IR (KBr, cm^{-1}): 3220, 3180, 1630, 1600; ¹H NMR (DMSO- d_6): δ 9.12 (*s*, 1H, NH), 7.09 (*m*, 2H), 6.90 (*m*, 1H), 6.77 (*m*, 1H), 5.12 (*s*, 1H, CH), 3.51 (*s*, 1H, OH), 2.36 (*s*, 2H, CH₂), 2.08 (*s*, 2H, CH₂), 1.20 (*s*, 6H, CH₃); ¹³C NMR (DMSO): δ 195.4 (C1), 155.1 (C2'), 148.5 (C1'), 130.5 (C3), 125.3 (C5'), 123.2 (C4'), 122.4 (C6'), 121.4 (C3'), 96.0 (C2), 50.2 (C4), 42.2 (C6), 32.3 (C5), 27.9 (CH₃).

Crystal data

C₁₄H₁₇NO₂
 $M_r = 231.29$
 Monoclinic
Pc
 $a = 7.208(2) \text{ \AA}$
 $b = 6.291(4) \text{ \AA}$
 $c = 14.432(5) \text{ \AA}$
 $\beta = 104.04(2)^\circ$
 $V = 634.9(5) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.210 \text{ Mg m}^{-3}$
 D_m not measured

Cu K α radiation
 $\lambda = 1.54184 \text{ \AA}$
 Cell parameters from 33 reflections
 $\theta = 12.74\text{--}35.96^\circ$
 $\mu = 0.650 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prism
 $0.50 \times 0.40 \times 0.30 \text{ mm}$
 Light yellow

Data collection

Siemens P4 four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.751$, $T_{\max} = 0.823$
 1812 measured reflections
 1404 independent reflections

1381 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.018$
 $\theta_{\max} = 70^\circ$
 $h = -1 \rightarrow 8$
 $k = -7 \rightarrow 1$
 $l = -17 \rightarrow 17$
 3 standard reflections every 100 reflections
 intensity decay: 0.5%

Refinement

Refinement on F^2
 $R(F) = 0.043$
 $wR(F^2) = 0.133$
 $S = 1.139$
 1404 reflections
 197 parameters
 H-atom parameters constrained

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.12 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997a)
 Extinction coefficient: 0.096(7)

$w = 1/[\sigma^2(F_o^2) + (0.0988P)^2 + 0.0568P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.249 (4)	N1—C3	1.340 (3)
O2—C2'	1.356 (3)	N1—C1'	1.424 (3)
C1'—N1—C3	125.1 (2)	O2—C2'—C3'	123.0 (2)
O1—C1—C6	114.0 (4)	O2—C2'—C1'	117.8 (2)
O1—C1—C2	124.5 (3)	N1—C3—C2	125.0 (3)
O1—C1—C6a	117.0 (3)	N1—C3—C4a	113.7 (3)
N1—C1'—C2'	119.1 (2)	N1—C3—C4	112.3 (3)
N1—C1'—C6'	120.9 (2)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O1 ⁱ	0.86	2.17	2.984 (4)	158
O2—H2'...O1 ⁱⁱ	0.82	1.86	2.680 (3)	175

Symmetry codes: (i) $x, 2 - y, \frac{1}{2} + z$; (ii) $x, 1 - y, \frac{1}{2} + z$.

H atoms were calculated geometrically and included in the refinement, but were restrained to ride on their parent atoms. The isotropic displacement parameters of the H atoms were fixed at $1.3U_{eq}$ of their parent atoms. The C4 and C6 atoms of the cyclohexanone ring, as well as the C7 and C8 methyl groups, were located from the ΔF map and were found to be disordered. They were placed in positions of occupancy 0.588 (7).

Data collection: XSCANS (Siemens, 1996). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: DIAMOND (Bergerhoff, 1996). Software used to prepare material for publication: PLATON (Spek, 1990), PARST (Nardelli, 1983, 1995) and PARSTCIF (Nardelli, 1991).

This work was supported in part by the project 'Development of human resources and modern techniques for drug analysis in Cuba' (3M980032) from the Belgian Government (ABOS-AGCD) and KU Leuven.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1416). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1031–1034

Triterpenoide. XIV.† [2,3-*d*]Isoxazoltriterpenderivate

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(Eingegangen am 28. April 1998; angenommen am 4. Januar 1999)

Abstract

The X-ray crystal structure analyses of two triterpene isoxazoles, namely olean-2,12-dieno[2,3-*d*]isoxazol-28-oic acid methyl ester {methyl isoxazolo[4,5-*b*]olean-2,12-dien-28-oate, $C_{32}H_{47}NO_3$, (2a)} and 19 β ,28-epoxy-18 α -olean-2-eno[2,3-*d*]isoxazole {19 β ,28-epoxyisoxazolo[4,5-*b*]-18 α -olean-2-ene, $C_{31}H_{47}NO_2$, (4a)} are described. These compounds were obtained by treatment of 2-formyl- or 2-hydroxymethylene derivatives of 3-oxoolean-12-en-28-oic methyl ester, (1a) and (1b), and 19 β ,28-epoxy-18H α -oleanan-3-one, (3a) and (3b), with hydroxylamine hydrochloride according to the method described by Govardhan, Reddy, Ramaiah & Rao [*J. Indian Chem. Soc.* (1983), pp. 858–860] for the synthesis of ring-A-fused triterpene [3,2-*c*]isoxazoles. The structures of the obtained [2,3-*d*]isoxazoles, (2a) and (4a), were confirmed by the comparison of the bond lengths and bond angles found for the isoxazole rings of compounds (2a) and (4a) with the corresponding data given in the literature. The isoxazole rings in both compounds are planar. Ring A in (2a) and (4a) has a conformation between the half-chair and sofa form. Rings B, D and E in (2a), and B, C, D and E in (4a) have the chair conformation. Ring C in (2a) has a distorted sofa form. In (2a), the rings A/B, B/C and C/D are *trans*-fused and the rings D/E *cis*-fused. In (4a), the A/B, B/C, C/D and D/E ring junctions are *trans*. The axial O2 and C28 atoms

† Teil XIII: Gzella *et al.* (1998).