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(5*S*,6*R*)-4,5-Dimethyl-6-phenyl-3-trimethylacetyl-2*H*-1,3,4-oxadiazinan-2-one

Gregory M. Ferrence,* Joel M. Esken, Jennifer R. Blackburn and Shawn R. Hitchcock

CB 4160, Department of Chemistry, Illinois State University, Normal, IL 61790-4160, USA

Correspondence e-mail: gferren@ilstu.edu

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.097
Data-to-parameter ratio = 9.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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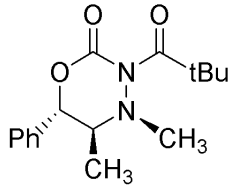
The crystal structure of the title compound, $C_{16}H_{22}N_2O_3$, was undertaken in the course of a study on an acylated pseudoephedrine-derived 1,3,4-oxadiazinan-2-one. The conformation adopted by this heterocycle is a contorted half-chair, in which the imide carbonyls are arranged with the carbonyl groups oriented approximately *syn* to each other. The torsion angle between the imide carbonyl groups is 37.6 (2)°.

Comment

Chiral, non-racemic, oxazolidin-2-ones serve as chiral auxiliaries in asymmetric transformations, most notably in the aldol addition reaction (Evans *et al.*, 2002; Crimmins *et al.*, 2001; Ager *et al.*, 1997); however, the related 1,3,4-oxadiazinan-2-one heterocycles have received little notice since their disclosure (Trepanier *et al.*, 1968). Recently, 1,3,4-oxadiazinan-2-ones were successfully employed as chiral auxiliaries in dipolar cycloadditions (Roussi *et al.*, 2000) and in diastereoselective alkylations (Roussi *et al.*, 1998). We have conducted synthetic (Hitchcock *et al.*, 2001) and conformational studies (Casper *et al.*, 2002) of 1,3,4-oxadiazinan-2-one derivatives.



(I)

Herein we report the X-ray structure of the N_3-trimethylacetylated pseudoephedrine-derived 1,3,4-oxadiazinan-2-one (I). The structure of (I) (Fig. 1) nominally exhibits *syn*–parallel carbonyls, consistent with our recently reported acetyl and propionyl variants. Crystallographic analysis of these latter two compounds revealed that these heterocycles adopt twist–boat conformations in which the imide carbonyl groups are arranged *syn*–parallel, as evidenced by the 3.1 (2) (acetyl) and 3.3 (1)° (propionyl) torsion angles between carbonyl groups (Casper *et al.*, 2002). Similarly, the N_3-trimethylacetyl derivative displays imide carbonyl groups tending towards a *syn*–parallel orientation, with an O21—C2—C15—O16 torsion angle of 37.6 (2)°. Remarkably, rather than maintaining the acetyl and propionyl derivatives' twist–boat conformation by allowing the trimetylacetyl carbonyl group to rotate to an antiparallel orientation, to alleviate N_4-methyl and *tert*-butyl steric interactions, compound (I) adopts a contorted half-chair conformation, in which the imide carbonyl groups remain arranged with the carbonyl groups oriented in the same

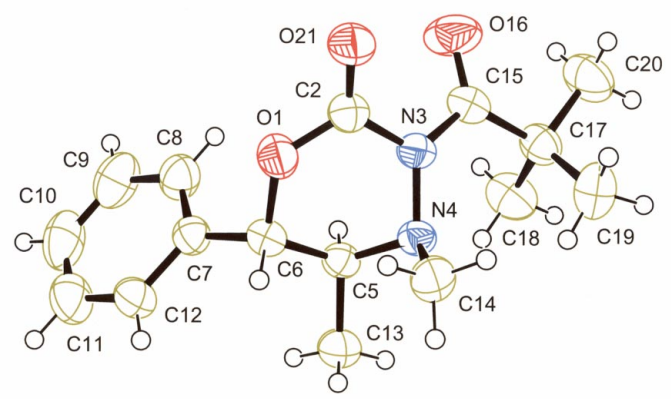


Figure 1
Perspective view of (I), showing the atom-labeling scheme. Non-H atoms are represented by ellipsoids at the 50% probability level. H atoms have been drawn arbitrarily small and are not labeled.

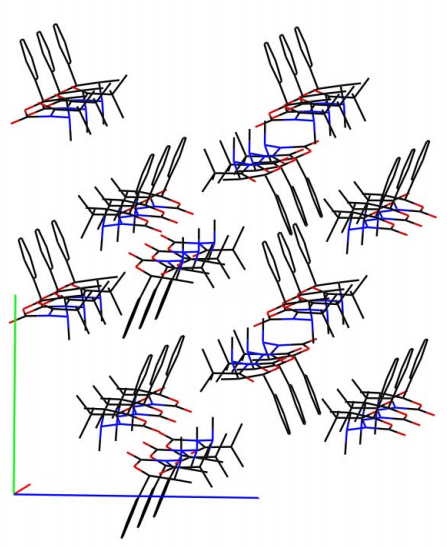


Figure 2
The molecular packing of (I), viewed along the *a* axis.

direction. Compound (I) displays a torsion angle of 154.2 (2)° for N4—N3—C2—O21, while values of 175.8 (2) and 178.6 (1)° are observed in the respective N_3-acetyl and the N_3-propionyl variants. Based on the amount of distortion of the π system and ^{13}C NMR analysis, it is possible this is not the structure adopted in solution. As noted in other oxadiazinanone systems, the N_3-substituent is rigidly held, while the N_4-methyl group must rearrange to relieve allylic strain (Casper *et al.*, 2002). Noteworthy is the X-ray structure of the ephedrine (C_6-epimer of related pseudoephedrine) based N_3-phenylacetylated oxadiazinanone, which also displays *syn*–parallel imide carbonyl groups, with a torsion angle of 19.5 (4)° (Hitchcock *et al.*, 2001). These four structures suggest the *syn*–parallel conformation is strongly preferred for the carbonyl moieties of 1,3,4-oxadiazinan-2-ones. The predominance of the parallel arrangement is remarkable in that the antiparallel conformation is observed in the related N_3-acyloxazolidin-2-ones (Evans & McGee, 1981) and should be energetically favorable, based on a reduced dipole moment.

The title compound crystallizes in the orthorhombic space group $P2_12_12_1$ (McArdle, 1996) and stacks with the phenyl substituents superimposed along and parallel with the stacking axis (Fig. 2). The closest intermolecular interactions are H6···O21^{i} of 2.46 Å and H18*A*···N4 of 2.45 Å [symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$]. Neither of these, nor other intermolecular interactions, seem particularly relevant to attributing packing arguments as explanation of the dicarbonyl conformation.

Experimental

The title compound was prepared by acylation of pseudoephedrine-derived 1,3,4-oxadiazinan-2-one using sodium hydride and trimethylacetylchloride (Casper *et al.*, 2002). Colorless clear single crystals were grown by vapor diffusion of cyclohexane into dichloromethane at 269 K. For data collection, a sample crystal was glued to the end of a glass fiber.

Crystal data

$C_{16}H_{22}N_2O_3$
M_r = 290.36
Orthorhombic, $P2_12_12_1$
a = 10.1079 (7) Å
b = 11.4087 (10) Å
c = 14.0354 (9) Å
V = 1618.5 (2) Å^3
Z = 4
D_x = 1.192 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 10.8–16.7°
μ = 0.08 mm^{-1}
T = 293 (2) K
Block, colorless
0.76 × 0.72 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.953, T_{max} = 0.967
3414 measured reflections
1792 independent reflections
1484 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 25.8°
$h = 0 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
S = 1.04
1792 reflections
195 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.0905P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.339 (3)	N3—C15	1.416 (3)
C2—O21	1.198 (3)	N3—N4	1.426 (2)
C2—N3	1.418 (3)	C15—O16	1.207 (3)
O21—C2—O1	119.31 (19)	C15—N3—N4	120.22 (16)
O21—C2—N3	123.8 (2)	C2—N3—N4	117.89 (16)
O1—C2—N3	116.80 (17)	O16—C15—N3	118.1 (2)
C15—N3—C2	120.33 (16)		
O1—C2—N3—C15	142.58 (19)	C14—N4—C5—C13	−63.9 (2)
O21—C2—N3—N4	154.2 (2)	N4—N3—C15—O16	160.0 (2)
O1—C2—N3—N4	−23.2 (3)	N4—N3—C15—C17	−18.8 (3)

All H atoms were included in the refinement in the riding model approximation, with isotropic displacement parameters fixed at 1.2U_{eq} of the parent atom. No evidence for disorder or included

solvents was identified through difference Fourier syntheses. While 1320 Friedel equivalent pairs were measured, the use of Mo radiation with the exclusively light atom sample precluded the calculation of a meaningful Flack parameter (Flack & Bernardinelli, 2000). The absolute configuraion was inferred from the chiral chemical precursors.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *MERCURY*1.1 (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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