Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NS1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Int. Comput. Sci.* **31**, 187–204.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1358–1367.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hordvik, A. (1961). *Acta Chem. Scand.* **15**, 16–31.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kuma (1989). *Kuma KM-4 User's Guide.* Version 3.1. Kuma Diffraction, Wrocław, Poland.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sonntag, K. (1953). *Chem. Rev.* **52**, 231–416.

Takagi, S. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 3033–3040.

Wold, F. J. (1961). *J. Org. Chem.* **26**, 197–199.

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N-Acetyl-3-ethyl-2-phenyldecahydroquinolin-4-one, $C_{19}H_{25}NO_2$

A. Thiruvalluvar,[a] V. Parthasarathi,[a]* D. Natarajan,[b] N. Bhavani[b] and Mohan Bhadbhade[c]

[a]*Department of Physics, Bharathidasan University, Tiruchirapalli 620 024, India,* [b]*Department of Chemistry, Annamalainagar 608 002, India, and* [c]*Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India*

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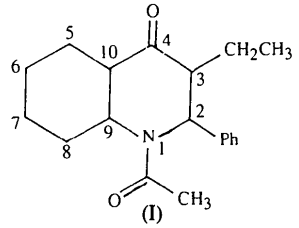
Abstract

The molecule of the title compound, $C_{19}H_{25}NO_2$, consists of a piperidin-4-one ring *trans* fused to a cyclohexane moiety. The piperidine ring has a twist conformation. The cyclohexane ring adopts the chair conformation.

Comment

The *trans*-decahydroquinoline framework forms part of many natural products. Baliah & Natarajan (1989) have reported that the introduction of methyl groups in the 1 and 3 positions of the decahydroquinoline system results in the distortion of the heterocyclic ring from a regular chair conformation. The present X-ray diffraction study was undertaken to determine how the conformation of the system is affected by the substitution of an acetyl group at the first position (N) and an ethyl group at the third position (C3) of the piperidine ring. A *PLUTO* (Motherwell & Clegg, 1978) drawing of the title molecule, (I), with the atomic numbering scheme is shown in Fig. 1.



(I)

The torsion angle H9—C9—C10—H10 [−178.2 (2)°] confirms the *trans* fusion of the title compound. The angles C2—N1—C11 [121.9 (2)°], C2—N1—C9 [118.2 (2)°] and C9—N1—C11 [117.1 (2)°] indicate a flattening of the piperidine ring at atom N1. The displacement of N1 from the plane defined by the atoms C2, C9 and C11 is 0.140 (2) Å. The displacements of N1, C2, C3, C4, C10 and C9 from the least-squares plane defined by N1, C3, C4 and C9 are 0.047 (2), 0.620 (2), −0.046 (2), 0.142 (3), 0.616 (2) and −0.046 (2) Å, respectively. This indicates that the piperidine ring adopts a flexible twist conformation (see Table 2 for torsion angles). In the cyclohexane ring, the displacements of atoms C6 and C9 from the least-squares plane of C5, C7, C8 and C10 are 0.627 (3) and −0.704 (2) Å, respectively, indicating a chair conformation. The atomic configuration around C11 is planar and the deviation from the plane defined by the atoms N1, C12 and O11 is 0.015 (2) Å.

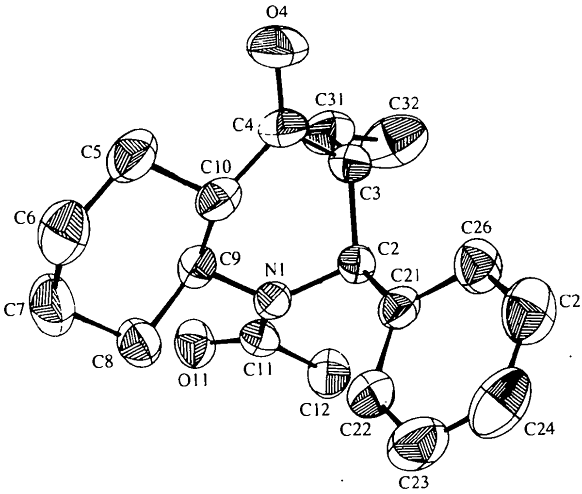


Fig. 1. Structure of the molecule of $C_{19}H_{25}NO_2$ showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms have been omitted for clarity.

Experimental

The method of Lynch & Cole (1966) was followed to prepare the title compound. The crude product was recrystallized from petroleum ether (333–353 K). Yield 2.5 g (78%); m.p. 408–409 K.

Crystal data

$C_{19}H_{25}NO_2$
$M_r = 299.4$
Orthorhombic
Pbca
$a = 10.683 (2)$ Å
$b = 16.996 (5)$ Å
$c = 18.770 (3)$ Å
$V = 3408 (1)$ Å^3
$Z = 8$
$D_x = 1.167$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 15\text{–}20°$
$\mu = 0.56$ mm^{-1}
$T = 295$ K
Plate
0.32 × 0.26 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2874 measured reflections
1984 independent reflections
1983 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.03$
$\theta_{\rm max} = 65°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 22$
3 standard reflections monitored every 200 reflections
intensity decay: negligible

Refinement

Refinement on F
$R = 0.045$
$wR = 0.053$
$S = 1.57$
1983 reflections
200 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: $F^* = F[1 - (0.0001\chi \times F^2/\sin\theta)]$
Extinction coefficient: $\chi = 0.0036$
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O4	0.3187 (2)	0.9749 (2)	0.5361 (1)	0.093 (1)
O11	0.0445 (2)	1.0239 (1)	0.2781 (1)	0.058 (1)
N1	0.2060 (2)	0.9604 (1)	0.3298 (1)	0.039 (1)
C2	0.3421 (2)	0.9582 (1)	0.3430 (1)	0.038 (1)
C3	0.3679 (2)	0.9986 (1)	0.4153 (1)	0.046 (1)
C4	0.2965 (2)	0.9598 (2)	0.4746 (1)	0.053 (1)
C5	0.1025 (3)	0.8844 (2)	0.5131 (1)	0.063 (1)
C6	0.0022 (3)	0.8272 (2)	0.4900 (2)	0.075 (1)
C7	−0.0649 (3)	0.8553 (2)	0.4240 (2)	0.076 (1)
C8	0.0259 (2)	0.8748 (2)	0.3639 (1)	0.055 (1)
C9	0.1210 (2)	0.9361 (1)	0.3882 (1)	0.043 (1)
C10	0.1931 (2)	0.9045 (1)	0.4528 (1)	0.047 (1)
C11	0.1555 (2)	1.0041 (1)	0.2762 (1)	0.043 (1)
C12	0.2352 (3)	1.0254 (2)	0.2137 (1)	0.062 (1)
C21	0.3976 (2)	0.8763 (1)	0.3343 (1)	0.041 (1)
C22	0.3364 (2)	0.8184 (1)	0.2959 (1)	0.054 (1)
C23	0.3905 (3)	0.7449 (2)	0.2859 (2)	0.069 (1)
C24	0.5067 (3)	0.7286 (2)	0.3125 (2)	0.073 (1)
C25	0.5695 (3)	0.7854 (2)	0.3489 (2)	0.070 (1)
C26	0.5171 (2)	0.8587 (1)	0.3599 (1)	0.054 (1)
C31	0.3359 (3)	1.0866 (2)	0.4148 (1)	0.068 (1)
C32	0.4254 (4)	1.1351 (2)	0.3720 (2)	0.101 (2)

Table 2. *Selected geometric parameters* (Å, °)

O4—C4	1.206 (3)	C4—C10	1.507 (3)
O11—C11	1.233 (3)	C5—C6	1.510 (5)
N1—C2	1.475 (3)	C5—C10	1.528 (3)
N1—C9	1.482 (3)	C6—C7	1.509 (5)
N1—C11	1.362 (3)	C7—C8	1.524 (4)
C2—C3	1.546 (3)	C8—C9	1.525 (3)
C2—C21	1.522 (3)	C9—C10	1.534 (3)
C3—C4	1.502 (3)	C11—C12	1.494 (3)
C3—C31	1.534 (4)	C31—C32	1.496 (5)
N1—C2—C21	112.9 (2)	C7—C8—C9	110.6 (2)
N1—C2—C3	108.2 (2)	N1—C9—C8	112.2 (2)
C3—C2—C21	115.5 (2)	C8—C9—C10	109.4 (2)
C2—C3—C31	112.8 (2)	N1—C9—C10	112.0 (2)
C2—C3—C4	111.4 (2)	C5—C10—C9	110.2 (2)
C4—C3—C31	108.6 (2)	C4—C10—C9	111.4 (2)
O4—C4—C3	121.1 (2)	C4—C10—C5	113.7 (2)
C3—C4—C10	116.4 (2)	O11—C11—N1	120.6 (2)
O4—C4—C10	122.5 (2)	N1—C11—C12	119.1 (2)
C6—C5—C10	112.4 (2)	O11—C11—C12	120.3 (2)
C5—C6—C7	111.7 (3)	C3—C31—C32	113.5 (3)
C6—C7—C8	112.0 (3)		
N1—C2—C3—C4	57.2 (2)	C5—C6—C7—C8	53.1 (4)
C2—C3—C4—C10	−14.1 (3)	C6—C7—C8—C9	−56.7 (3)
C3—C4—C10—C9	−39.2 (3)	C7—C8—C9—C10	58.8 (3)
N1—C9—C10—C4	49.7 (2)	C8—C9—C10—C5	−58.1 (2)
C2—N1—C9—C10	−5.3 (3)	C6—C5—C10—C9	55.7 (3)
C9—N1—C2—C3	−47.7 (2)	C10—C5—C6—C7	−52.9 (3)

H atoms were located on difference Fourier maps and fixed at a distance of 0.95 Å, and were given isotropic temperature factors of $1.1U_{\rm eq}$ of their respective carrier atoms. H atoms were not refined but included as constant contributions to the structure factors. All computations were carried out on a MicroVAX II computer.

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baliah, V. & Natarajan, A. (1989). *Indian J. Chem.* **28A**, 609–611.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
Lynch, M. D. & Cole, W. (1966). *J. Org. Chem.* **31**, 3337–3342.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* University of Cambridge, England.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

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Dimethyl 2,6-Dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate, Diethyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate, and Diethyl 2,6-Dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate

KRISTIN R. ROWAN AND ELIZABETH M. HOLT

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@osucc.bitnet

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Abstract

The crystal structure of diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate, $C_{19}H_{22}N_2O_6$ (FR7534), a member of the 1,4-dihydropyridine class of calcium blockers, and the crystal structures of diethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate, $C_{19}H_{20}N_2O_6$, and dimethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate, $C_{17}H_{16}N_2O_6$, decomposition products of FR7534 and dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate, respectively, reveal that the decomposition products display conformational features associated with activity according to structure–activity relationships.

Comment

Compounds of the 1,4-dihydropyridine class exhibit calcium antagonistic activity, as they inhibit the influx of Ca^{2+} ions through plasma membrane channels (Núnez-Vergara, Sunkel & Squella, 1994). Compounds of this class are currently being used in the treatment of a variety of cardiovascular disorders, such as angina and hypertension (Triggle, Langs & Janis, 1989; Hurwitz, Partridge & Leach, 1991). Nifedipine [dimethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate], is the best known member of this class.

The basic 1,4-dihydropyridine (DHP) structure (Fig. 1) has been varied by (i) change of the alkyl groups at positions C2 and C6 to amide or extended alkyl amine groups (Arrowsmith, Campbell, Cross, Stubbs, Burges, Gardiner & Blackburn, 1986; Suzuki, Shiratori, Murayama, Harada, Miyano & Takeya, 1989), (ii) alteration of the ester groups at positions C3 and C5, or substitution of cyano and nitro groups at these positions, (iii) variation of the substituent on the phenyl ring and its position, and (iv) replacement of the H atom at N1 by alkyl or alkylcarboxylate groups (Triggle, Langs & Janis, 1989; Janis, Silver & Triggle, 1987).

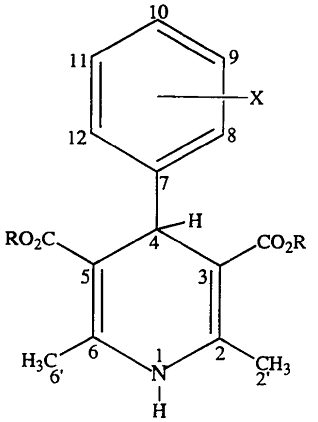

Fig. 1. 1,4-Dihydropyridine skeleton with our crystallographic numbering scheme.

The structure–activity relationships (SAR's) of a number of these compounds have been documented. Factors associated with high activity include the presence of (*a*) the 1,4-dihydropyridine moiety with an H atom on N1, (*b*) alkyl groups (preferably methyl) substituted at the 2 and 6 positions, (*c*) ester groups at the 3 and 5 positions, and (*d*) a phenyl ring at position 4 with a substituent (preference $o > m > p$). The three-dimensional characteristics that correspond to high activity in this class of compounds are a flattened boat conformation of the DHP ring and a near perpendicular orientation of the phenyl ring with respect to the plane of the base of the DHP ring (Triggle, Langs & Janis, 1989; Morad, Goldmann & Trentham, 1983; Loev, Goodman, Snader, Tedeschi & Macko, 1974; Janis, Silver & Triggle, 1987).

Nifedipine and some of its derivatives undergo a photodecomposition sequence to form nitroso-pyridine derivatives (Núnez-Vergara, Sunkel & Squella, 1994; Sadana & Ghogare, 1991; Hayase, Itagaki, Ogawa, Akutsu, Inagaki & Abiko, 1994), which are then oxidized to the nitro-pyridine form. We have analyzed the solid-state structures of two decomposition products of nifedipine and have observed that these structures dis-