Acta Cryst. (1999). C55, 1676–1677

1′,2′,3′,4′-Tetrahydro-1,3-diphenyl-4-*p*-tolyl-spiro[2-pyrazoline-5,2′-naphthalen]-1′-one

R. KRISHNA,[a] D. VELMURUGAN,[a] R. MURUGESAN,[b] M. SHANMUGA SUNDARAM[c] AND R. RAGHUNATHAN[c]

[a]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India,* [b]*Regional Sophisticated Instrumentation Center, Indian Institute of Technology, Chennai, India, and* [c]*Department Of Organic Chemistry, University Of Madras, Guindy Campus, Chennai 600 025, India. E-mail: crystal@giasmd01.vsnl.net.in*

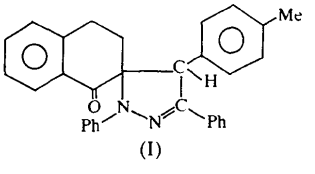
Abstract

In the title compound, $C_{31}H_{26}N_2O$, the pyrazoline ring is in a distorted sofa conformation, the cyclohexanone ring of the tetralone moiety is in a half-chair conformation and the other aromatic rings are planar.

Comment

Pyrazoline compounds have many important pharmacological properties, finding use as, for example, anti-inflammatory agents, herbicides, analgesic agents, antibacterial agents, moderate non-toxic local anaesthetics and antifungal agents (Gusar *et al.*, 1995; Sharma *et al.*, 1993; Ankhiwala *et al.*, 1996). They are also effective scintillation solutes and lubrication oil antioxidants (Beher *et al.*, 1967).

Fig. 1 shows the *ZORTEP* (Zsolnai, 1997) diagram of the title molecule, (I), with the atomic numbering scheme. The structure consists of a pyrazoline ring



(I)

connected with three aromatic rings (rings 2, 3 and 4) at N1, C19 and C11, respectively, and a tetralone moiety at C2. The pyrazoline ring is in a distorted sofa conformation. The cyclohexanone of the tetralone moiety is in the half-chair conformation. All aromatic rings connected to the pyrazoline ring are perfectly planar. With respect to the pyrazoline ring the two aromatic rings (ring 2 and ring 3) are tilted with dihedral angles of 20.9 (1) and 19.5 (1)°, respectively. The aromatic ring (ring 4) and tetralone moiety are perpendicular to the pyrazoline ring with dihedral angles of 82.6 (1) and 81.4 (1)°, respectively.

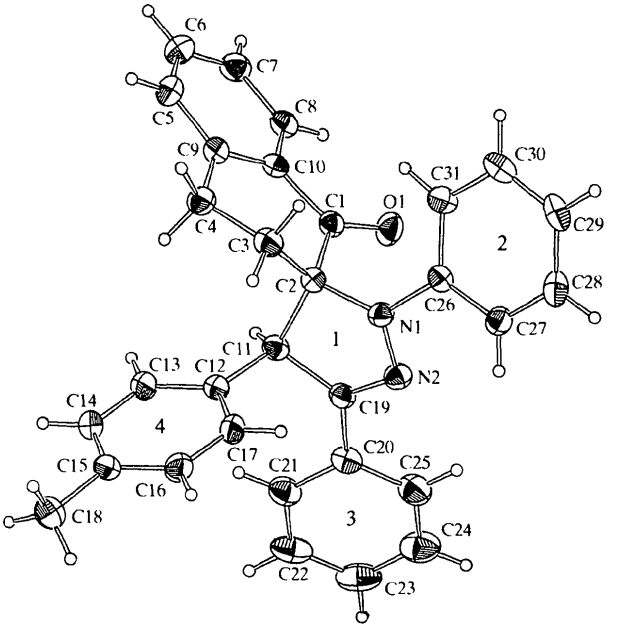


Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids.

The bond lengths and bond angles in the pyrazoline ring are compared with the corresponding values of two other similar spiro compounds [(II) (Jorgensen *et al.*, 1986) and (III) (Khalil *et al.*, 1996)] and are given in Table 1. The N—N bond shows single-bond character [1.385 (4) Å] when N has phenyl substitution (present study), a much shortened length [1.311 (3) Å] when N has hydroxyl substitution [compound (II)] and a pure N=N double bond character [1.234 (8) Å] when N has no substitution [compound (III)]. The effect of this aspect reflects on the N—C bond also. The smaller tilting [20.9 (1)°] of ring 2 with the pyrazoline ring may assist the delocalization in the pyrazoline ring.

There are a number of intermolecular contacts just below the sum of the relevant van der Waals radii, including C14—H14···C8($-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+\frac{1}{2}+1$) (H···C 2.67 Å) and C8—H8···C29($x+\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$) (H···C 2.75 Å).

Experimental

Trimethylamine (3.3 mmol) was added to a solution of *p*-Me-benzylidene-1-tetralone (3 mmol) and *N*-phenylbenzhydrazidoyl chloride (3 mmol) in dry chloroform. The reaction mixture was stirred at room temperature for 40 h. After the reaction was over, the solution was filtered to remove triethylamine hydrochloride and the was solvent evaporated under vacuum. The resulting crude product was purified by column chromatography. Crystals were grown from an aqueous solution of methanol by slow evaporation.

Crystal data

$C_{31}H_{26}N_2O$
M_r = 442.54
Monoclinic
$P2_1/n$
a = 10.58 (1) Å
b = 16.10 (2) Å
c = 13.954 (10) Å
β = 100.97 (1)°
V = 2334 (4) Å^3
Z = 4
D_x = 1.259 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 15 reflections
θ = 2–28°
μ = 0.592 mm^{-1}
T = 293 (2) K
Rectangular
0.25 × 0.20 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4382 measured reflections
4159 independent reflections
3081 reflections with $I > 2\sigma(I)$

R_{int} = 0.028
θ_{max} = 69.88°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 19$
$l = -16 \rightarrow 16$
3 standard reflections
every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.165
S = 1.099
4159 reflections
309 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 3.2P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.030
$\Delta\rho_{max}$ = 0.236 e Å^{-3}
$\Delta\rho_{min}$ = −0.213 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0037 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

	(I)[a]	(II)[b]	(III)[c]
N1—N2	1.385 (4)	1.311 (3)	1.234 (8)
N2—C19	1.288 (4)	1.443 (3)	1.461 (8)
N1—C2	1.475 (4)	1.490 (3)	1.516 (5)
C19—C11	1.516 (4)	1.491 (4)	1.535 (9)
C11—C2	1.579 (4)	1.308 (4)	1.507 (7)
N1—N2—C19	109.2 (3)	109.5 (2)	112.3 (5)
N2—C19—C11	113.5 (3)	108.2 (2)	105.7 (6)
C2—C11—C19	99.5 (2)	111.4 (2)	100.5 (4)
N1—C2—C11	100.6 (3)	100.4 (2)	104.5 (4)
N2—N1—C2	111.0 (2)	110.5 (2)	111.3 (4)

Notes: (*a*) present study; (*b*) 3,5,5-trimethyl-3-pyrazoline *N*,*N*′-dioxide; (*c*) a pyrazoline derivative of eunicin acetate.

H atoms were positioned geometrically using a riding model with C—H = 0.93, 0.96, 0.97 and 0.98 Å, but they were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

RK thanks UGC for a fellowship and DV thanks UGC (India) for providing funding under the UGC Career Award scheme.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1522). Services for accessing these data are described at the back of the journal.

References

Ankhiwala, M. D. & Hathi, M. V. (1996). *Indian J. Heterocycl. Chem.* **5**, 229–230.

Beher, L. C., Fusco, R. & Jufbose, C. H. (1967). *The Chemistry of Heterocyclic Compounds*. Vol 22, *Pyrazoles, Pyrazolidines, Indazoles and Condensed Rings*. Chichester: Wiley Interscience.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

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.

Gusar, N. I., Gulko, L. I., Gorodetskova, N. R. & Klebanov, B. M. (1995). *Chem. Abstr.* **122**, 290766f.

Jorgensen, P., Koksbang, R. & Lindhardt, P. (1986). *Acta Cryst.* C**42**, 1273–1274.

Khalil, S., Hossain, M. B. van der Helm, D., Alam, M. & Sanduja, R. (1996). *Acta Cryst.* C**52**, 1272–1274.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sharma, S. M., Osha, A. C. & Manohar, R. (1993). *Indian J. Biochem.* **2**, 63–65.

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

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Zsolnai, L. (1997). *ZORTEP. An Interactive ORTEP Program for Structure Illustration*. University of Heidelberg, Germany.

Acta Cryst. (1999). C**55**, 1677–1680

(+)-23,24-Dinor-3α,9α-epoxy-11-oxo-5β-cholan-22-oic acid: mutual carboxyl-to-ether dimeric hydrogen bonding in a steroidal carboxy–keto ether

HUGH W. THOMPSON, ANDREW P. J. BRUNSKILL AND ROGER A. LALANCETTE*

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA. E-mail: lalancette@hades.rutgers.edu

(*Received 8 February 1999; accepted 6 May 1999*)

Abstract

The title steroidal carboxy–keto ether, $C_{22}H_{32}O_4$, forms non-centrosymmetric dimers involving two distinct carboxyl-to-ether hydrogen bonds [O···O = 2.718 (3)