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5'-[2-(*N*-*tert*-Butylethanal nitron)]-1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-*b*][1,4]oxazine]†

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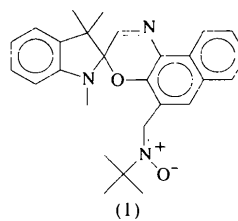
Abstract

The title compound, C₂₇H₂₉N₃O₂, is photochromic with spin-trapping properties.

Comment

Photochromic compounds are able to undergo light-induced reversible colour changes (Bertelson, 1971). One of the major problems encountered in their use is their irreversible degradation (Baillet *et al.*, 1993), probably involving radical species. In order to increase the life of these compounds, a spin trap (nitron) is added to the molecule (Campredon *et al.*, 1997).

† Alternative name: spiro[1,3,3-trimethylindoline-2,3'-naphtho[2,1-*b*][1,4]oxazine]-5'-methylidene-*tert*-butylamine *N*-oxide.



All geometric parameters of the title compound, (1), correspond to the expected values. The orientation of the nitron with respect to the phenyl ring is characterized by the torsion angle C8—C9—C11—N12 [168.6 (2)°].

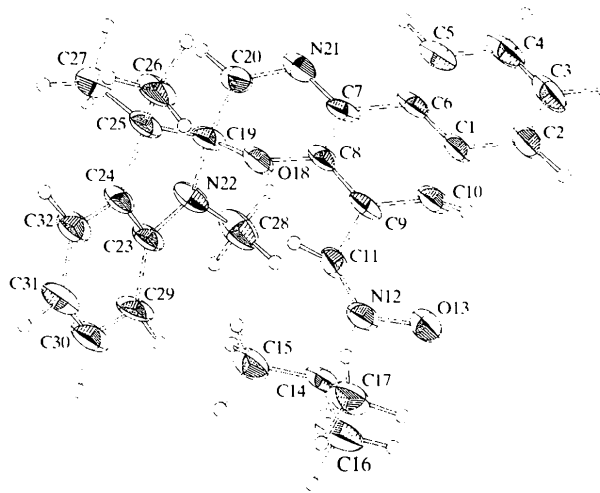


Fig. 1. ORTEPII (Johnson, 1976) drawing of (1) with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

Experimental

Nitron (1) was prepared (Campredon *et al.*, 1997) by oxidation of the corresponding hydroxymethyl derivative with 1,1,1-triacetoxy-1,1-dihydro-1,2-benzodioxol-3(1*H*)-one according to the Dess–Martin procedure (Dess & Martin, 1983) followed by condensation of the resulting aldehyde with *tert*-butylhydroxylamine (yield 41%). Colourless pseudo-hexagonal prismatic crystals were obtained by dissolving (1) in CH₂Cl₂ and saturating this solution with pentane to give a 5:95 mixed solvent.

Crystal data

C₂₇H₂₉N₃O₂
M_r = 427.53
 Monoclinic
*P*2₁/c
a = 8.580 (1) Å
b = 13.901 (2) Å
c = 19.977 (3) Å
 β = 98.57 (2)°
V = 2356.1 (6) Å³
Z = 4
D_x = 1.205 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 9–15°
 μ = 0.077 mm⁻¹
T = 293 (2) K
 Pseudo-hexagonal prism
 0.5 × 0.3 × 0.3 mm
 Colourless

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
4732 measured reflections
4732 independent reflections
2038 reflections with
 $I > 2\sigma(I)$

$\theta_{\max} = 29.95^\circ$
 $h = -10 \rightarrow 10$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity variation: <3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.066$
 $S = 0.923$
4732 reflections
376 parameters
H atoms refined with fixed
values for $d = 1 \text{ \AA}$ and
 $U = 0.05 \text{ \AA}^2$

$w = 1/[\sigma^2(F_o^2) + (0.0036P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.09 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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

C7—N21	1.371 (3)	C19—N22	1.464 (2)
C8—O18	1.366 (2)	C19—C20	1.497 (3)
C11—N12	1.287 (3)	C19—C25	1.515 (3)
N12—O13	1.277 (2)	C20—N21	1.311 (3)
O18—C19	1.452 (2)		
C8—C7—N21	123.0 (2)	C8—O18—C19	118.6 (2)
C7—C8—O18	118.6 (2)	O18—C19—C20	108.8 (2)
O13—N12—C11	125.3 (2)	N22—C19—C25	104.0 (2)
O13—N12—C14	113.4 (2)	C20—N21—C7	117.3 (2)
C11—N12—C14	121.2 (2)		
C8—C9—C11—N12	168.6 (2)	C9—C11—N12—C14	-168.0 (2)
C9—C11—N12—O13	8.2 (3)		

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *DATARED* (Pèpe, 1979). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1178). Services for accessing these data are described at the back of the journal.

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(2,5-Diméthylpyrrolidin-2-yl)phosphonate de Diisopropyle

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Abstract

The title compound, diisopropyl (2,5-dimethylpyrrolidin-2-yl)phosphonate, $C_{12}H_{26}NO_3P$, was isolated as colorless crystals during the synthesis of α -amino-alkenylphosphonates and their transformation to α -phosphorylated pyrrolidines via an aminomercuration–demercuration sequence. As the stereochemical selectivity of this type of reaction is difficult to predict because of its dependancy on experimental conditions, the crystal structure is reported here. X-ray analysis shows a *trans* stereochemistry of the two methyl groups.

Commentaire

La synthèse d'une série d' α -amino alkénylphosphonates et de leur transformation en pyrrolidines α -phosphorylées via une séquence aminomercuration–démercuration a déjà été décrite dans de précédents articles (Roubaud *et al.*, 1994, 1996; Fréjaville *et al.*, 1995). Elle est ici appliquée à la molécule (2,5-diméthylpyrrolidin-2-yl)phosphonate de diisopropyle, (I), selon le schéma. La dernière étape conduit à l'obtention de deux isomères géométriques *cis* et *trans*. La stéréosélectivité de ce type de réaction est difficile à prédire car elle dépend des conditions expérimentales. Cependant l'isomère *trans* (minoritaire) a pu être isolé par des recristallisations successives dans le *n*-pentane à 253 K. La structure de cet isomère a fait l'objet de notre étude cristallographique et a permis d'une part, de confirmer la position *trans* des