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(*E*)-2-Buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]-binaphthalen-2-yl)propanimidate and (*E*)-2-Buten-1-yl (*S*)-*N*-(2′-Methoxy-3-methyl-[1,1′]binaphthalen-2-yl)propanimidate†

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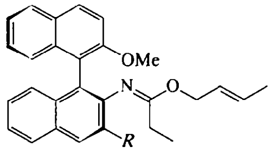
Abstract

In the structures of both of the title compounds, (*E*)-2-buten-1-yl (*S*)-*N*-(2′-methoxy-[1,1′]binaphthalen-2-yl)propanimidate, $C_{28}H_{27}NO_2$, (I), and it's methyl-substituted derivative, $C_{29}H_{29}NO_2$, (II), the C═N bond has an *E* configuration. In compound (II), the position of the additional methyl group is confirmed.

Comment

N-Arylimidates such as compound (I), derived from the axially chiral auxiliary (*S*)-2′-methoxy-[1,1′]binaphthalen-2-ylamine, are useful substrates for a highly diastereoselective and enantioselective Claisen rearrangement which produces, after hydrolysis, α,β-disubstituted γ,δ-unsaturated carboxylic acids with two new stereogenic centres (Metz & Hungerhoff, 1996). In order to optimize the inducing power of the auxiliary, we introduced a methyl group in the 3-position of the binaphthyl moiety. Details of the synthetic work have been published elsewhere (Metz & Hungerhoff, 1997).



(I) *R*=H
(II) *R*=Me

The crystals used in this work were obtained from petroleum ether/ether solutions. Structural studies of compounds (I) and (II) were undertaken in order to establish the geometry of the C═N bond. The X-ray crystal structures [compounds (I) and (II) are shown in Figs. 1 and 2, respectively] confirmed the anticipated *E* configuration. Related *N*-phenylimidates are also *E* configured, as shown by ^{1}H NMR NOE measurements (Metz & Linz, 1994). Furthermore, the structural investigation determined the correct position of the additional methyl substituent in the naphthyl moiety of (II).

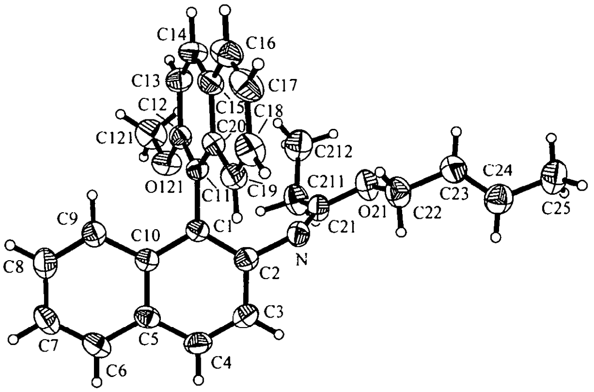


Fig. 1. *XP* (Siemens, 1990) (50% probability) plot of compound (I) with the atomic numbering scheme.

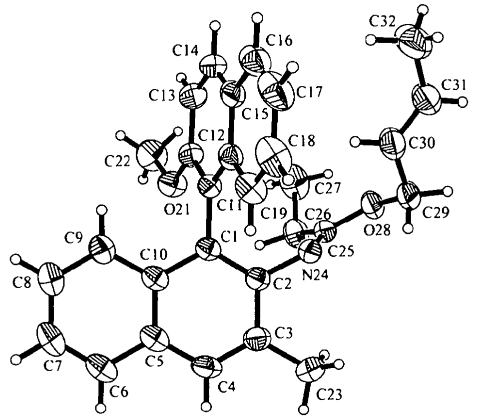


Fig. 2. *XP* (Siemens, 1990) (50% probability) plot of compound (II) with the atomic numbering scheme.

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† Dedicated to Dr Klaus Fleischmann on the occasion of his 60th birthday.

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The naphthyl groups in both molecules are very similar; the bond lengths are equal within 2σ. Also, the geometries of the two methoxy groups and of the N-bonded side chains are comparable; all bond lengths and angles are similar and show no deviations from the expected values. The influence of the methyl group in the 3-position of (II) on the torsion angles of the central bonds in the naphthyl moiety is also small, as shown by the angles C2—C1—C11—C12 [108.5 (2) in (I) and 105.7 (2)° in (II)] and C10—C1—C11—C20 [106.5 (2) in (I) and 104.8 (2)° in (II)].

In the crystal packing, no intermolecular contacts are shorter than normal van der Waals separations.

Experimental

The title compounds were prepared as described by Metz & Hungerhoff (1997) and crystals were obtained from petroleum ether/ether solutions.

Compound (I)

Crystal data

$C_{28}H_{27}NO_2$
$M_r = 409.51$
Monoclinic
$P2_1$
$a = 7.712 (1)$ Å
$b = 11.520 (1)$ Å
$c = 12.721 (1)$ Å
$\beta = 94.86 (1)°$
$V = 1126.1 (2)$ Å^3
$Z = 2$
$D_x = 1.208$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40.99$–$45.68°$
$\mu = 0.589$ mm^{-1}
$T = 223 (2)$ K
Plate
0.40 × 0.40 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical *via* ψ-scan data (*MolEN*; Fair, 1990)
$T_{\min} = 0.889$, $T_{\max} = 0.943$
2592 measured reflections
2413 independent reflections
2279 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$
$\theta_{\max} = 74.28°$
$h = -9 \rightarrow 0$
$k = -14 \rightarrow 0$
$l = -15 \rightarrow 15$
3 standard reflections every 250 reflections frequency: 120 min intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.109$
$S = 1.049$
2413 reflections
284 parameters
H atoms calculated and refined as riding atoms with $U_{\text{iso}} = (1.2$ or $1.5)U_{\text{eq}}$(host)
$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.0910P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.219$ e Å^{-3}
$\Delta\rho_{\min} = -0.176$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0070 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.0 (3)

Compound (II)

Crystal data

$C_{29}H_{29}NO_2$
$M_r = 423.53$
Monoclinic
$P2_1$
$a = 7.786 (1)$ Å
$b = 17.431 (1)$ Å
$c = 8.749 (1)$ Å
$\beta = 98.24 (1)°$
$V = 1175.1 (2)$ Å^3
$Z = 2$
$D_x = 1.197$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40.34$–$42.63°$
$\mu = 0.580$ mm^{-1}
$T = 223 (2)$ K
Block
0.60 × 0.50 × 0.50 mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical *via* ψ-scan data (*MolEN*; Fair, 1990)
$T_{\min} = 0.727$, $T_{\max} = 0.748$
2663 measured reflections
2484 independent reflections
2426 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$
$\theta_{\max} = 74.33°$
$h = -9 \rightarrow 0$
$k = -21 \rightarrow 0$
$l = -10 \rightarrow 10$
3 standard reflections every 250 reflections frequency: 120 min intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.095$
$S = 1.066$
2482 reflections
294 parameters
H atoms calculated and refined as riding atoms with $U_{\text{iso}} = (1.2$ or $1.5)U_{\text{eq}}$(host)
$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.0904P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.170$ e Å^{-3}
$\Delta\rho_{\min} = -0.134$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0093 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.0 (2)

For both compounds, data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Express*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1211). Services for accessing these data are described at the back of the journal.

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3-(*o*-Carboxyphenyl)-1-methyltriazene 1-Oxide†

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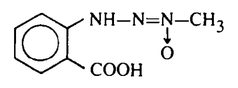
Abstract

The structure determination of the title compound, $C_8H_9N_3O_3$, establishes the *N*-oxide form of triazene. The overall molecular planarity and trigonal planar geometry of the triazene N atom bonded to the phenyl ring suggest a resonance interaction extending over adjacent atoms. The molecular conformation is stabilized by intramolecular hydrogen bonds and the crystal packing by intermolecular hydrogen bonds.

Comment

Substituted triazenes increasingly find applications as initiators of radical polymerization (Rapta *et al.*, 1996), as efficient chelating agents (Saha, Chakraborty, Roychaudhuri & Maji, 1992) and as antitumor drugs (Wilman, 1988). As part of our studies on the synthesis and characterization of triazene 1-oxide derivatives and to build up a hierarchy for such systems, the structure determination of 3-(*o*-carboxyphenyl)-1-methyltriazene 1-oxide, (I), was undertaken.



(I)

The results of the present X-ray analysis are in agreement with those of analyses of corresponding substituted phenyltriazene 1-oxide structures (Sarkar, Khalil, Saha & Talapatra, 1983; Samanta, De, Sarkar, Saha & Talapatra, 1985) and establish the tautomeric *N*-oxide form of triazene (Smith *et al.*, 1992). Torsion angles close to 0 and 180°, and the r.m.s deviation of 0.051 Å from the least-squares plane through the non-H atoms illustrate the overall molecular planarity. The essentially planar phenyl moiety and trigonal-planar geometry of the triazene N1 atom strongly suggest a resonance interaction extending over the C6, N1, N2 and N3 atoms. The short N2—N3 distance [1.263 (2) Å] indicates double-bond character and the N1—N2 distance [1.323 (2) Å] is shorter than a pure single bond. The deviation of O3 [0.122 (1) Å] from the molecular plane causes conjugation between N3 and C8 to be less effective and is reflected in the longer N3—C8 bond length [1.459 (2) Å] compared with the N1—C6 distance [1.390 (2) Å].

The almost planar conformation of the molecule is a result of intramolecular hydrogen bonding; there are two N—H···O interactions and two C—H···O interactions (see Table 2). Three of the resulting four pseudo-rings

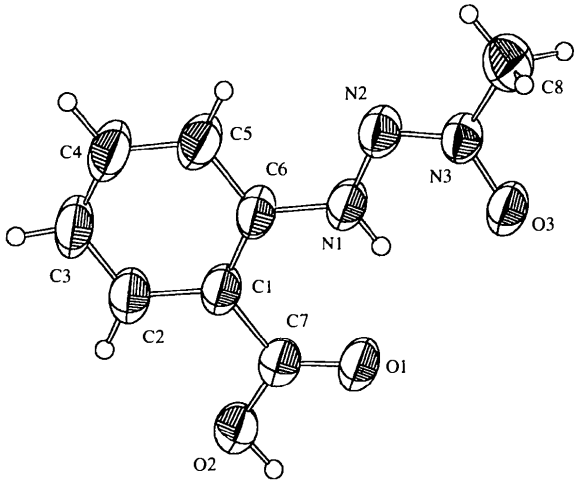


Fig. 1. *ORTEP*II (Johnson, 1976; Zsolnai, 1995) view (50% probability level) of the molecule showing the atom-labelling scheme.

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† Alternative name: *o*-(3-methyl-2-triazeno)benzoic acid N^3-oxide.