

Acta Cryst. (1997). **C53**, 1614–1615

o-Chlorobenzaldehyde 4,5-Diaza-9-fluorenylidenehydrazone

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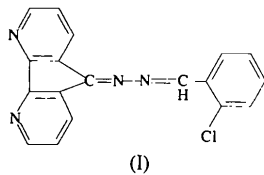
(Received 27 March 1997; accepted 30 May 1997)

Abstract

Molecules of the title compound, C₁₈H₁₁ClN₄, are essentially planar, with a highly conjugated π system. They stack in pairs about crystallographic inversion centres.

Comment

In recent years there has been considerable interest in the development of new materials with non-linear optical properties (Chemla & Zyss, 1987; Zhao, Samoc, Singh & Prasad, 1989; Prasad & Williams, 1991). It is known that molecules possessing extensively conjugated π -electron systems exhibit large optical non-linearity, especially of the third order, as described by the second hyperpolarizability, β . As part of our work in this area, we report the structure of the title compound, *o*-chlorobenzaldehyde 4,5-diaza-9-fluorenylidenehydrazone, (I).



The molecule is almost planar (Fig. 1). The dihedral angle between the planes of the diazafluorene and phenyl fragments is 6.88(6)°; these fragments make angles of 12.4(1) and 6.0(2)°, respectively, with the plane of the central hydrazone linkage. In the diazafluorene moiety, C16 shows the largest displacement

[−0.072(3) Å] from the mean plane. The C—N bond lengths in the hydrazone moiety are short compared with those observed in the related compound *p*-dimethylaminobenzaldehyde 4,5-diaza-9-fluorenylidenehydrazone monohydrate (Lu *et al.*, 1995). This may indicate a greater degree of conjugation in the present compound.

The crystal is stabilized by weak intramolecular C—H...N interactions.

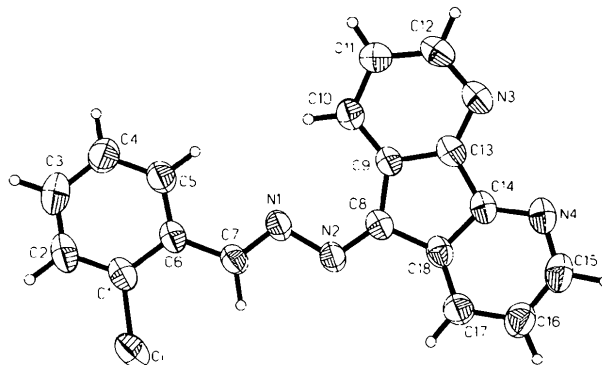


Fig. 1. A view of the title compound showing the numbering scheme and 50% probability ellipsoids.

Experimental

The compound was synthesized by reaction of *o*-chlorobenzaldehyde and 4,5-diazafluorene-9-hydrazine in ethanol solution under reflux for 3 h. Single crystals were obtained by recrystallization from ethanol.

Crystal data

C₁₈H₁₁ClN₄
M_r = 318.76
Monoclinic
*P*2₁/*c*
a = 8.028 (1) Å
b = 12.349 (2) Å
c = 14.922 (3) Å
 β = 92.20 (1)°
V = 1478.2 (4) Å³
Z = 4
D_x = 1.432 Mg m^{−3}
D_m not measured

Mo *K*α radiation

λ = 0.71073 Å
Cell parameters from 39 reflections
 θ = 5.42–12.43°
 μ = 0.263 mm^{−1}
T = 293 (2) K
Needle
0.70 × 0.32 × 0.30 mm
Orange

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
Absorption correction: none
4471 measured reflections
3388 independent reflections
1581 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

θ_{\max} = 27.51°
h = −1 → 10
k = −1 → 16
l = −19 → 19
3 standard reflections
every 97 reflections
intensity decay: <3%

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Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.102$
 $S = 0.808$
 3388 reflections
 252 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

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

C1—C1	1.739 (2)	N4—C14	1.330 (3)
N1—C7	1.267 (2)	N4—C15	1.345 (3)
N1—N2	1.406 (2)	C6—C7	1.460 (3)
N2—C8	1.286 (2)	C8—C18	1.474 (3)
N3—C13	1.329 (2)	C8—C9	1.484 (3)
N3—C12	1.341 (3)		
C7—N1—N2	111.0 (2)	N1—C7—C6	121.3 (2)
C8—N2—N1	113.9 (2)	N2—C8—C18	120.3 (2)
C13—N3—C12	114.2 (2)	N2—C8—C9	133.2 (2)
C14—N4—C15	114.2 (2)	C18—C8—C9	106.5 (2)

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from difference Fourier maps and refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Program used for geometrical calculations: PARST (Nardelli, 1983). Software used to prepare material for publication: SHELXL93.

The authors would like to thank the State Science and Technology Commission and National Nature Science Foundation of China for a grant for a major key project, and the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. One of the authors (KC) thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1327). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1615–1617

Two Substituted [1,2,4]Triazole Derivatives

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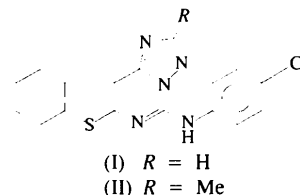
(Received 25 September 1996; accepted 26 March 1997)

Abstract

The structures of two 1,2,4-triazole derivatives, namely 5-(4-chlorophenyl)amino-8,9,10,11-tetrahydro[1]benzothieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine, C₁₇H₁₄ClN₅S, and its 2-methyl derivative, C₁₈H₁₆ClN₅S, have been determined. The cyclohexene ring in each compound shows disorder. Both molecules are nearly planar, with the chlorophenyl rings lying almost in the same plane as the rest of the structure. Both crystals are stabilized by N—H···N hydrogen bonds.

Comment

Condensed [1,2,4]triazoles are biologically important compounds (Kottke, Kuesmstedt, Hagen, Renner & Schnitzler, 1983; Francis & Gelette, 1988; Francis *et al.*, 1988). Our interest in the synthesis and characterization of these heterocyclic compounds, especially of thienopyrimidines, has led us to prepare a series of thieno[4,3-*a*][1,2,4]triazolo[3,2-*e*]pyrimidine derivatives. Some of these have been shown to exhibit excellent central-nervous-system depressant and skeletal-muscle relaxant activities through experiments on Swiss albino mice by the rota-rod method and by photoactometer. Previously, we reported the first crystal structure of a triazolo derivative (Velavan *et al.*, 1995); we now present two related structures, 5-(4-chlorophenyl)amino-8,9,10,11-tetrahydro[1]benzothieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine, (I), and its 2-methyl derivative, (II).



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