*ORTEP*II (Johnson, 1976). 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: CF1279). Services for accessing these data are described at the back of the journal.

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4′-(Dimethylamino)-2-nitroazobenzene†

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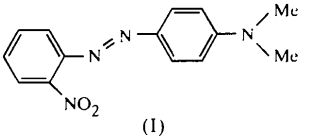
Abstract

The title compound, $C_{14}H_{14}N_4O_2$, has *trans* geometry about the azo linkage. The dihedral angle between the two phenyl rings is 5.3 (2)° and the twist angle for the nitro group is 63.9 (2)°. Excluding the nitro group, the molecular skeleton is almost planar, which may enhance the photostability of the compound. Within the crystal structure, molecules related by a glide plane are connected by weak intermolecular hydrogen bonding and form zigzag chains in the [001] direction. The polar molecular chains, which are arranged anti-parallel, are packed into stacks in the [101] direction through $\pi\cdots\pi$ interactions; the interstack forces are mainly van der Waals interactions.

Comment

Dyes based on 4-aminoazobenzene, containing a donor-acceptor chromogen, are important for use on polyester fibres, owing to their desirable colour and satisfactory light-fastness properties (Jan *et al.*, 1984; Oh & Kim, 1995). Some push-pull azobenzene compounds are second- or third-order nonlinear optical materials (Kang *et al.*, 1995; Shen *et al.*, 1992) and have potential applications in photonic devices. Technical interest prompted us to undertake a systematic study (Zhang *et al.*, 1997), during the course of which we synthesized the title compound, (I), and confirmed its structure by X-ray analysis.



(I)

The bond distances in (I) are essentially the same when compared with those in 4′-(diethylamino)-2-nitroazobenzene [(II); Zhang *et al.*, 1997] and 4′-[bis(β-hydroxyethyl)amino]-2-nitroazobenzene [(III); McIntosh *et al.*, 1989)], apart from the short N1—O2 link [1.190 (3), 1.217 (2) and 1.221 (2) Å for (I), (II) and

† IUPAC name: (4-dimethylaminophenyl)(2-nitrophenyl)diazene.

(III), respectively]. However, some bond angles in (I) (Table 1) are different from those in (II) and (III). While the twist angle of the nitro group relative to the phenyl ring is 63.9 (2)° [24.4 (3) in (II) and 27.8 (3)° in (III)], the dihedral angle between the two phenyl rings is 5.3 (2)° [47.1 (5) in (II) and 42.2 (3)° in (III)]. The deviations of N4, C13 and C14 from the mean plane of the C7–C12 ring are 0.030 (1), 0.065 (3) and 0.075 (2) Å, respectively, with torsion angles (Table 1) that show that the skeleton, except for the nitro group, is essentially planar.

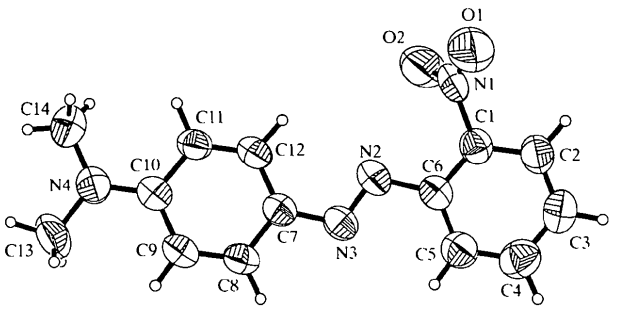


Fig. 1. The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

The O2···N2 distance of 2.926 (3) Å is longer than those in the related compounds [(II); 2.647 (5) Å] and [(III); 2.648 (3) Å], which is consistent with no azoxy intermediate being formed. This possibly results from the intermolecular hydrogen bonds and from the packing requirements. Therefore, the negatively charged O atoms of the *ortho*-nitro group of (I) inhibit delocalization of the electrons between the azo-N atoms to a lesser extent than those of (II) and (III) (Freeman & McIntosh, 1989), and (I) should have a higher photostability than (II) and (III).

In the crystal structure of (I), the molecules are held together by weak C—H···O hydrogen bonds {C2^{i}—H2^{i}···O1 3.278 (3) Å and 129.1 (3)°; C3^{ii}—H3^{ii}···O2 3.331 (2) Å and 131.3 (2)° [symmetry codes: (i) $2-x$, $1-y$, $2-z$; (ii) x, $\frac{1}{2}-y$, $z-\frac{1}{2}$]}, by $\pi\cdots\pi$ interactions of parallel-stacked phenyl rings (Table 2), and by normal van der Waals interactions.

Experimental

Sodium nitrite (0.35 g, 5.1 mmol) was added to a solution formed by dissolving 2-nitroaniline (0.69 g, 5.0 mmol) in a mixture of water (5 ml) and HCl (2 ml) cooled below 273 K. The solution was stirred for 15 min and then cooled to below 278 K, then *N*,*N*-dimethylaniline (0.65 ml, 5.0 mmol) and HCl (1 ml) were added. After addition of dry sodium acetate (3 g), the reaction proceeded for 20 min at ambient temperature, yielding a red product. The product was recrystallized twice from ethanol/water (1:1). Crystals were obtained by slow evaporation from dichloromethane/tetrahydrofuran over 4 d.

Crystal data

$C_{14}H_{14}N_4O_2$
M_r = 270.29
Monoclinic
$P2_1/c$
a = 12.556 (2) Å
b = 7.618 (1) Å
c = 15.260 (2) Å
β = 109.76 (1)°
V = 1373.7 (3) Å^3
Z = 4
D_x = 1.307 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 33 reflections
θ = 3.03–15.85°
μ = 0.091 mm^{-1}
T = 295 (2) K
Prism
0.64 × 0.32 × 0.20 mm
Red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2851 measured reflections
2422 independent reflections
1014 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.96°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 9$
$l = -18 \rightarrow 17$
3 standard reflections
every 97 reflections
intensity decay: 1.05%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.130
S = 0.748
2421 reflections
238 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.003
$\Delta\rho_{max}$ = 0.108 e Å^{-3}
$\Delta\rho_{min}$ = −0.107 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0164 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—N1	1.211 (3)	N3—C7	1.400 (2)
O2—N1	1.190 (3)	N4—C10	1.362 (2)
N2—N3	1.263 (2)	C8—C9	1.370 (3)
N2—C6	1.420 (2)	C11—C12	1.357 (3)
O2—N1—O1	124.6 (3)	C5—C6—N2	126.0 (2)
O2—N1—C1	118.9 (3)	C1—C6—N2	117.2 (2)
O1—N1—C1	116.4 (3)	C12—C7—N3	125.9 (2)
C14—N4—C13	117.8 (3)	C8—C7—N3	116.0 (2)
C2—C1—N1	117.9 (2)	N4—C10—C9	121.7 (2)
C6—C1—N1	118.5 (2)	N4—C10—C11	121.3 (2)
C6—N2—N3—C7	−178.8 (2)	N2—N3—C7—C12	2.7 (3)
N3—N2—C6—C5	2.6 (3)	N2—N3—C7—C8	180.0 (2)
N3—N2—C6—C1	−176.0 (2)		

Table 2. *Intermolecular $\pi\cdots\pi$ interactions (kJ mol^{-1}, Å)*

E^a	DP^b	DC^c	Symmetry operation
−33.46 (5)	3.50 (3)	3.68 (3)	$1-x, -y, 1-z$
−7.32 (7)	3.67 (3)	4.70 (3)	$2-x, -y, 2-z$

Notes: (*a*) the interaction energy between the reference molecule and the molecule related by the symmetry operation, calculated by *OPEC* (Gavezzotti, 1983); (*b*) the shortest interplanar distance between the parallel ring planes; (*c*) the distance between the centres of the corresponding ring planes (C7–C12 and C1–C6, respectively, for the two rows).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1260). Services for accessing these data are described at the back of the journal.

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Three Isostructural Furosemide Prodrugs

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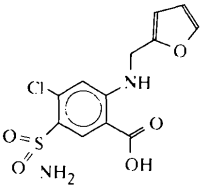
Abstract

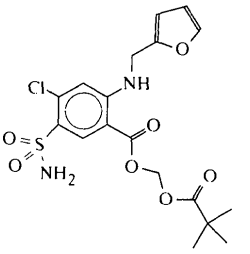
The structures of three furosemide prodrugs, pivaloyloxymethyl 4-chloro-*N*-furfuryl-5-sulfamoylanthranilate, $C_{18}H_{21}ClN_2O_7S$, butyryloxymethyl 4-chloro-*N*-furfuryl-5-sulfamoylanthranilate, $C_{17}H_{19}ClN_2O_7S$, and isobutyryloxymethyl 4-chloro-*N*-furfuryl-5-sulfamoylanthranilate, $C_{17}H_{19}ClN_2O_7S$, have been determined; the crystals have been shown to be isostructural. The crystal structures are described and compared with that of a related prodrug. The dihedral angle between the two planar rings of each prodrug is close to 70°. The space group is $P\bar{1}$ in each case, and the molecules pack as dimers in infinite chains along one of the crystallographic axes.

Comment

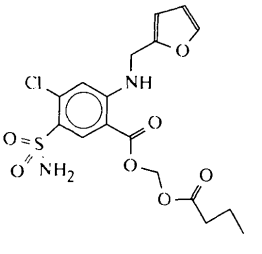
Furosemide (4-chloro-*N*-furfuryl-5-sulfamoylanthranilic acid), (I), is a strong diuretic agent used in hypertensive crisis. The compounds pivaloyloxymethyl 4-chloro-*N*-furfuryl-5-sulfamoylanthranilate, (II), butyryloxymethyl 4-chloro-*N*-furfuryl-5-sulfamoylanthranilate, (III), and isobutyryloxymethyl 4-chloro-*N*-furfuryl-5-sulfamoylanthranilate, (IV), were synthesized and characterized as furosemide prodrugs (Prandi, Fagiolino, Manta, Llera *et al.*, 1992). The therapeutic activity of these prodrugs has been studied (Prandi, Fagiolino, Manta & Llera, 1992).



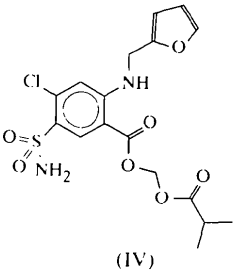
Furosemide (I)



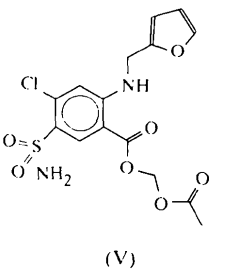
(II)



(III)



(IV)



(V)

The three molecules have the original furosemide skeleton in common, which contains a six-membered aromatic ring (atoms C1 to C6) with coplanar carboxylate and amine substituents (Lamotte *et al.*, 1978). The maximum deviations from this plane are for O1 in