C11—Si1—C12	108.45 (9)	C2—C1—C2'	124.1 (2)
C11—Si1—C13	110.49 (9)	C1—C2—C2"	117.95 (9)
C12—Si1—C13	109.06 (9)	C1—C2—C10	119.30 (13)
C11—Si1—C10	110.06 (7)	C2"—C2—C10	122.69 (8)
C12—Si1—C10	109.96 (8)	C2—C10—Si1	113.19 (10)
C13—Si1—C10	108.82 (8)		
C1—C2—C10—Si1	82.40 (14)	C12—Si1—C10—C2	−72.52 (13)
C11—Si1—C10—C2	46.89 (13)	C13—Si1—C10—C2	168.09 (11)

Symmetry codes: (i) $\frac{1}{4} - x, \frac{5}{4} - y, z$; (ii) $\frac{1}{4} - x, y, \frac{5}{4} - z$.

Data were corrected for Lorentz and polarization effects. All C and Si centres were refined anisotropically, and all hydrogens were located from the difference map and placed in idealized positions using a riding model; C—H$_{phenyl}$ = 0.95, C—H$_{methylene}$ = 0.99 and C—H$_{methyl}$ = 0.98 Å. The torsion of the methyl hydrogens and the isotropic displacement parameters of all H centres were refined (methyl and methylene moieties were treated as rigid groups).

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

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3,5-Dinitro-2-{[(R)-(−)-1-phenylethyl]-amino}pyridine

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Abstract

The synthesis and crystal structure of the title compound, $C_{13}H_{12}N_4O_4$, is reported. The compound displayed second harmonic generation and the results are reported. The molecular packing is described in conjunction with an investigation of the phase-matching ability of the compound.

Comment

Developments in organic non-linear optical (NLO) materials over the past 20 years have triggered a prolific interest in this area of research. In particular, second harmonic generation (SHG) measurements of organic NLO compounds have already produced results which by far exceed those obtained from all known inorganic materials, *e.g.* LiNbO$_3$. Moreover, the much broader scope in molecular design of organic materials compared to inorganics provides greater possibilities for improving the SHG response. For example, many pyridine derivatives have shown great promise in terms of SHG efficiency (Twieg, Azema, Jain & Cheng, 1982). The title complex, (I), was therefore studied for its NLO potential.

(I)
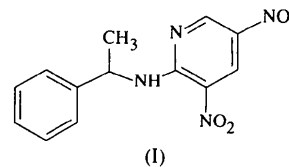
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The two planar six-membered rings in the molecule are linked *via* a twisted -CH(CH$_3$)—NH— unit, showing a twist angle between the two rings of 106.5 (1)°. The maximum deviations from planarity for the benzyl and pyridyl rings are 0.013 (4) (C6) and 0.018 (4) Å (C13), respectively. However, the two -NO$_2$ pyridyl substituents deviate from the pyridyl mean plane by 9.1 (2) (*p*-NO$_2$) and 13.2 (2)° (*o*-NO$_2$) which, in turn, leads to a nitro–nitro dihedral angle of 16.6 (4)°. The twist of the *o*-NO$_2$ group results from the intramolecular hydrogen bonds, O1$\cdots$H1N—N1 [2.06 (5) Å] and O2$\cdots$H11—C11 [2.35 (4) Å], and the weak intermolecular hydrogen bond, C3—H3$\cdots$O1 [2.63 (5) Å] (symmetry operator: $-x-1$, $y-\frac{1}{2}$, $2-z$) may also play a marginal role in the extent of the twist. Hydrogen bonding also seems to be responsible for the twist of the *p*-NO$_2$ group, although here there are one intramolecular and two intermolecular interactions. The C13—H13$\cdots$O4 [2.45 (4) Å] and O4$\cdots$H1N—N1 [2.51 (6) Å] (symmetry operator: $x-1$, y, z) contacts force the NO$_2$ group out of the pyridyl mean plane, while the slightly weaker hydrogen bond C5—H5$\cdots$O3 [2.55 (6) Å] (symmetry operator: $x-1$, y, $z+1$) counteracts this and turns the substituent back into the plane. The slight difference in deviation of the two NO$_2$ groups from the pyridyl mean plane is assumed to be a result of the balancing of different hydrogen bonds.

The lack of π bonding in the branch between the two rings precludes any possible π conjugation across the whole molecule. The aromatic nature of the two rings is therefore localized within the rings and on their direct substituents.

The molecules are packed in a head-to-tail herringbone semi-layer-like fashion, linked by the hydrogen bonding described previously. The compound crystallizes in the non-centrosymmetric space group $P2_1$ and, by definition (Franken & Ward, 1963), the compound must exhibit a second harmonic response. Hence, the powder SHG efficiency was tested (using a Nd:YAG laser, reflection mode, fundamental 8 ns pulses, 3 Hz, < 1 mJ, $\lambda = 1.064$ μ) and gave a response of approximately four times that of urea.

The title compound's ability to be phase matched was also investigated. Studies have shown (Oudar & Zyss, 1982) that for the space group $P2_1$, optimal phase matching is achieved when the angle between the 2_1 axis and the charge-transfer axis is $\theta = 54.7°$. Because of the π localization within the rings, one can assume that the benzyl group plays a neutral role in the charge-transfer process; such an assumption was also made for the mono-nitro analogue (Bailey, Cruickshank, Pavlides, Pugh & Sherwood, 1991). Furthermore, because β_{zzz} (where z is along the molecular axis) is by far the most dominant tensorial component of the molecular hyperpolarizability, β (Lalama & Garito, 1979), one frequently approximates the charge-transfer axis to the molecular axis (assuming that charge transfer is the predominant intramolecular process affecting β). Hence, for (I), the charge-transfer axis was approximated to the molecular axis of the -NH—C$_5$N(NO$_2$)$_2$(H)$_2$ moiety and the angle was determined to be $\theta = 63°$. This is only +8.3° from the optimal angle and therefore suggests that the compound has high phase-matching potential.
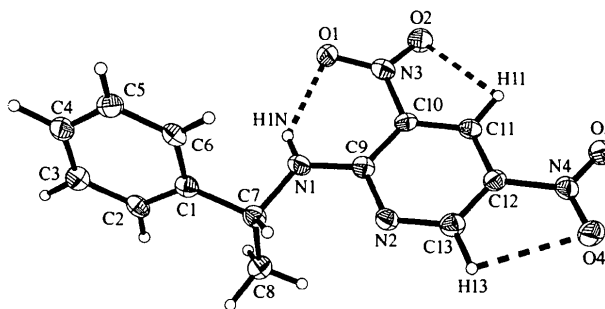

Fig. 1. A view of (I) with displacement ellipsoids drawn at the 50% probability level.
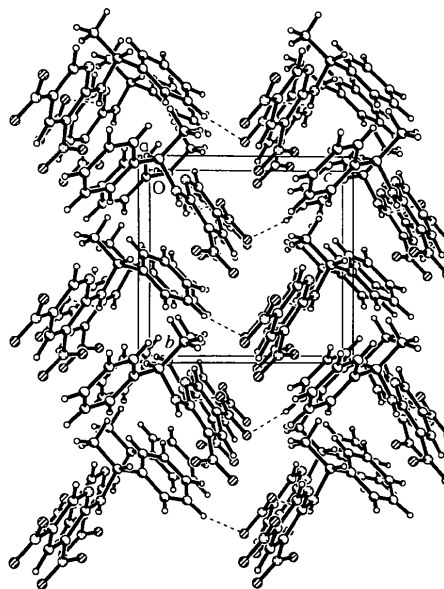

Fig. 2. The packing of (I) viewed down the x axis showing all H$\cdots$O intermolecular interactions.

Experimental

The starting materials, 2-chloro-3,5-dinitropyridine, (*R*)-(+)-1-phenylethylamine, triethylamine and all solvents were commercial materials used without further purification. The following synthetic conditions are milder than those used previously to prepare the mono-nitro analogue (Twieg, Jain, Cheng, Crowley & Azema, 1982). (*R*)-(+)-1-Phenylethylamine (0.60 g, 5 mmol) and 2-chloro-3,5-dinitropyridine (1.0 g,

5 mmol) in ethanol (30 ml) were warmed to ca 333 K for 10 min and allowed to cool for 5 min before addition of triethylamine (0.7 ml, 5 mmol). After 20 h at room temperature, yellow irregular plates of (I) (1.21 g, 84%) formed. These were separated and washed with ethanol, raised to 369–369.5 K (m.p. 367–368 K) and recrystallized from propan-1-ol. Elemental analysis for $C_{13}H_{12}N_4O_4$ (288) found (required): C = 54.25 (54.15), H = 4.16 (4.19), N = 19.74 (19.44)%. IR data, principal bands (KBr, cm^{-1}): 3374 (NH str.), 1608 (s, NH bend); 1587 (py skel.); 1538, 1522 (asym. NO_2 str.); 1317 (sym. NO_2 str.); 1269, 1201 (C—NH—C str.). $[\alpha]_D^{22}$ (CHCl$_3$): −134°. ^{1}H NMR data (400 MHz, CDCl$_3$, 298 K): 1.70 (d, J_{CH} = 6.8 Hz,), 5.65 (dq, J_{CH} ca 7, 6 Hz), 7.30–7.40 (m, C_6H_5), 9.02 (br. d, J_{NH} ca 6 Hz), 9.21 and 9.22 (overlapping d, J = 2.4 Hz, py H$_\gamma$ and py H$_{\alpha'}$). ^{13}C NMR data (100.58 MHz, CDCl$_3$, 298 K): 22.39 (CH$_3$), 51.62 (alk. CH), 126.05, 127.85, 128.91 (C$_6$H$_5$, o, p, m), 131.35 (py C$_\gamma$), 134.04 (C$_6$H$_5$, $ipso$), 142.04 (py C$_\alpha$), 150.83 and 152.84 (py C$_\beta$ and C$_{\beta'}$), 151.19 (py C$_{\alpha'}$). ^{1}H–^{13}C HETCOR showed coupling between the following resonances (^{1}H–^{13}C): 1.70–22.39 (CH$_3$), 5.65–51.62 (alk. CH), ca 7.3–127.85 (C$_6$H$_5$, p), ca 7.4–126.05 and 128.91 (C$_6$H$_5$, o and m), 9.21–142.04 (py C$_\gamma$), 9.22–151.19 (py C$_\alpha$). λ_{max} (MeOH, nm, log ε): 330 (4.24), 380 (inflexion, 3.84).

Crystal data

$C_{13}H_{12}N_4O_4$
M_r = 288.27
Monoclinic
$P2_1$
a = 8.389 (1) Å
b = 8.580 (1) Å
c = 8.934 (1) Å
β = 93.689 (2)°
V = 641.7 (2) Å^3
Z = 2
D_x = 1.492 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 497 reflections
θ = 3.22–20.75°
μ = 0.114 mm^{-1}
T = 100 (2) K
Rectangular plate
0.45 × 0.35 × 0.10 mm
Yellow

Data collection

Siemens SMART–CCD diffractometer
ω scans
Absorption correction: none
2576 measured reflections
1723 independent reflections
1566 reflections with
  $I > 2\sigma(I)$

R_{int} = 0.0548
θ_{max} = 25.10°
$h = -9 \rightarrow 9$
$k = -7 \rightarrow 10$
$l = -8 \rightarrow 10$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0449
$wR(F^2)$ = 0.0971
S = 1.169
1713 reflections
226 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 0.5637P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.224 e Å^{-3}
$\Delta\rho_{min}$ = −0.228 e Å^{-3}
Extinction correction: none
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)
Absolute configuration:
  established by synthesis
  [Flack (1983) parameter
  not determinate]

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

O1—N3	1.238 (4)	N2—C9	1.359 (5)
O2—N3	1.234 (4)	N3—C10	1.452 (5)
O3—N4	1.229 (4)	N4—C12	1.452 (5)
O4—N4	1.240 (4)	C9—C10	1.436 (5)
N1—C9	1.345 (5)	C10—C11	1.363 (5)
N1—C7	1.476 (5)	C11—C12	1.388 (5)
N2—C13	1.327 (5)	C12—C13	1.382 (6)
C9—N1—C7	123.9 (3)	N1—C9—N2	116.1 (4)
O2—N3—O1	122.3 (3)	N1—C9—C10	123.8 (3)
O2—N3—C10	118.1 (3)	C11—C10—N3	117.5 (3)
O1—N3—C10	119.5 (3)	C9—C10—N3	122.1 (3)
O3—N4—O4	123.3 (3)	C13—C12—N4	120.5 (3)
O3—N4—C12	118.6 (3)	C11—C12—N4	119.3 (3)
O4—N4—C12	118.0 (3)		

The absolute configuration could not be determined reliably from the X-ray diffraction study. However, the molecule must be in the R configuration since the chiral centre in one of the starting material was carried through in the synthesis. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.004 cm. Coverage of the unique set is over 97% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. Positional and anisotropic displacement parameters for all non-H atoms and positional parameters of all H atoms were refined. Methyl H isotropic displacement parameters were constrained to be 150% of the equivalent isotropic displacement parameters of the ligated C atoms; all other H isotropic displacement parameters were set to be 120% of the equivalent isotropic displacement parameters of the ligated C atoms.

Data collection: SMART system (Siemens, 1995). Cell refinement: SMART system. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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1,8-Dichloro-9,10-dihydro-9,10-ethenoanthracene

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Abstract

The title compound, $C_{16}H_{10}Cl_2$, presents a C=C bridge bond length of 1.312(3) Å and C—Cl distances of 1.741(2) and 1.744(2) Å. The dihedral angles between the aromatic rings and the plane formed by the ethene and the bridgehead C atoms are 121.79(8) and 120.76(6)°, and the two phenyl ring planes form a dihedral angle of 117.42(7)°.

Comment

We have been studying the activation of 1,8-dichloroanthracene derivatives towards nucleophilic substitution *via* π complexation to CpFe⁺ moieties (Cp = cyclopentadienyl) (Benites, Fronczek & Maverick, 1996). We found that π complexation was accompanied by reduction of the 1,8-dichloroanthracene moiety to 1,8-dichloro-9,10-dihydroanthracene. We were interested in the title compound, (1), because its central ring should no longer be subject to reduction.
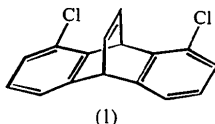
The bond length of the C=C bridge in compound (1) agrees well with the value of 1.316(3) Å reported for the equivalent C=C double bond in the par-

ent dibenzobarrelene (Trotter & Wireko, 1990) and is somewhat shorter than that in the 15,16-dicarbonitrile derivative [1.343(5) Å; Oliver, Fallon & Smith, 1986] and that in dimethyl 9,10-dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate [1.335(2) Å; Pokkuluri, Scheffer & Trotter, 1993]. The C—Cl distances in (1) [1.741(2) and 1.744(2) Å] are comparable to those in 1,8-dichloroanthracene [1.745(4) and 1.756(4) Å; Benites, Maverick & Fronczek, 1996], 1,8-dichloro-10-methylanthracene [1.749 Å; Desvergne, Gaultier & Hauw, 1970] and 1,8-dichloro-9-methylanthracene [1.726(7) Å; Dellaca, Penfold & Robinson, 1969]. The maximum deviation of the aromatic rings of (1) from planarity is 0.010(2) Å (for C11). The Cl atoms lie slightly out of these planes, with deviations of 0.0281(6) Å for Cl1 and 0.0166(5) Å for Cl2. The Cl—C11—C12 and C8—C13—C14 angles are smaller by an average of 2.3(2)° than C4—C12—C11 and C5—C14—C13, as a result of the Cl substitution. The structure of the molecule analogous to the title compound with methoxycarbonyl groups at C15 and C16 has been reported recently (Rettig, Scheffer, Trotter & Yang, 1995), and exhibits the same asymmetry, with a 2.6(2)° difference. This asymmetry is not present in the parent dibenzobarrelene (Trotter & Wireko, 1990). The benzene rings and the plane constituted by the ethene and the bridgehead C atoms (C9 and C10) of the title compound form dihedral angles of 120.76(6) and 121.79(8)°, whereas the aromatic rings make a dihedral angle of 117.42(7)°.
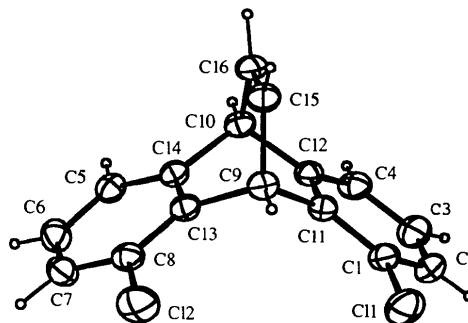

Fig. 1. Molecular structure showing 40% probability ellipsoids. H atoms are illustrated by circles of arbitrary radii.

Experimental