

Table 5. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	D...A	D—H...A
N101—H101...O212 ⁱ	0.883 (8)	2.784 (10)	163.7
N103—H103...O311 ⁱⁱ	1.122 (12)	2.781 (16)	161.6
N201—H201...O112 ⁱⁱⁱ	0.855 (8)	2.794 (10)	169.0
N203—H203...O22	1.060 (12)	2.782 (16)	162.2

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, z$.

Since crystals of lumiflavinium nitrate degrade rapidly, the crystal selected for X-ray intensity data collection was sealed in a capillary with mother liquor to prevent degradation. Corrections for background, decay, Lorentz and polarization factors, and absorption effects, were included in the data reduction. The structure was solved by direct methods with the program *SIR92* (Altomare, Casciarano, Giacovazzo & Guagliardi, 1994), and resulted in reliable positions for all the non-H atoms. The initial model was refined with *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Two H atoms could not be located; they belong to two HNO₃ moieties. *PLATON* (Spek, 1990) was used for the generation of the Crystallographic Information File and geometry analysis.

Data collection: CAD-4 *EXPRESS*. Cell refinement: CAD-4 *EXPRESS*. Data reduction: *NRCVAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(E)-4-Nitrobenzaldehyde Phenylhydrazone

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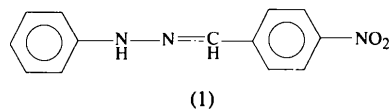
(Received 22 August 1994; accepted 2 November 1994)

Abstract

The title compound, C₁₃H₁₁N₃O₂, is found to be in the *E* conformation and the crystal structure is stabilized by intermolecular N—H...O hydrogen bonds. The dihedral angle between the planes of the phenyl and nitrophenyl rings is 15.55 (9)°.

Comment

In recent years the need to discover organic materials with large quadratic non-linear coefficients, for application in optical signal processing, has been recognized (Chemla & Zyss, 1987). The crystal structure determination of the title compound (1) forms part of our work on the discovery and properties of



non-linear optical organic materials. This compound shows nearly half the second harmonic generating capacity of urea (Mini, 1991). The N—O distances in the nitro group are asymmetrical [N16—O17 1.233 (4) and N16—O18 1.219 (4) Å]. The C6—N7 distance, 1.382 (4) Å, is well below the single-bond distance indicating electron delocalization over the region of the molecule [*cf.* other phenylhydrazone derivatives (Wiley & Drew, 1985) that have different substituents at C9]. The nitro group is tilted by 7.4 (2)° with respect to the plane of the phenyl ring. The structural conformation of the molecule is the *E* isomer, the most common conformation for benzaldehyde derivatives. Presumably, this conformation minimizes steric hindrance between the bulky phenyl and anilino groups lying across the C—N double bond [C9=N8 1.290 (4) Å]. The packing of the molecules in the unit cell is governed by N—H...O hydrogen bonds between N7 and O18 ($-x - 1/2, -y - 1, z + 1/2$) [N7—H7 1.02 (4), N7...O18 3.018 (4), H7...O18 2.00 (4) Å and N7—H7...O18 169 (3)°]. Vickery, Wiley & Drew

(1985) have studied the structure of various phenyl-hydrazone derivatives and established that the NH group participates in hydrogen bonding whenever possible, either intermolecular or intramolecular. The present study confirms this view.

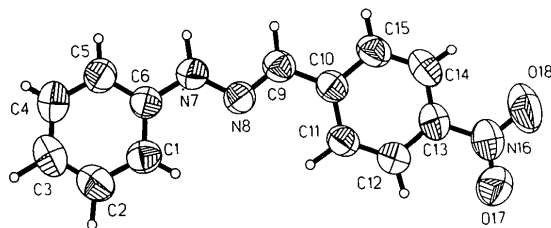


Fig. 1. Structure of the title compound showing 50% probability displacement ellipsoids.

Experimental

Single crystals of the title compound were obtained from methanol solution by slow evaporation at room temperature

Crystal data

C₁₃H₁₁N₃O₂
M_r = 241.25
 Orthorhombic
*P*2₁2₁2₁
a = 6.059 (1) Å
b = 11.598 (2) Å
c = 17.253 (4) Å
V = 1212.4 (4) Å³
Z = 4
D_x = 1.322 Mg m⁻³

Cu Kα radiation
 λ = 1.54180 Å
 Cell parameters from 25 reflections
 θ = 25–40°
 μ = 0.760 mm⁻¹
T = 293 (2) K
 Needle
 0.5 × 0.3 × 0.3 mm
 Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/2θ scans
 Absorption correction: none
 1198 measured reflections
 1198 independent reflections
 1087 observed reflections
 [*I* > 2σ(*I*)]

θ_{max} = 64.88°
h = 0 → 7
k = 0 → 13
l = 0 → 20
 2 standard reflections monitored every 100 reflections
 intensity decay: <2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.0368
wR(*F*²) = 0.1074
S = 1.099
 1198 reflections
 208 parameters
 All H-atom parameters refined
w = 1/[σ²(*F*_o²) + (0.0643*P*)² + 0.1528*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} = -0.087
 Δρ_{max} = 0.100 e Å⁻³
 Δρ_{min} = -0.111 e Å⁻³

Extinction correction:
*F*_c^{*} = *kF*_c[1 + (0.001χ × *F*_c²λ³/sin2θ)]^{-1/4}
 Extinction coefficient:
 χ = 0.0094 (13)
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	0.5723 (5)	-0.2300 (3)	-0.2271 (2)	0.0755 (8)
C2	0.7647 (6)	-0.1775 (3)	-0.2015 (2)	0.0909 (10)
C3	0.8446 (6)	-0.1960 (3)	-0.1280 (2)	0.0945 (10)
C4	0.7324 (6)	-0.2702 (3)	-0.0797 (2)	0.0907 (10)
C5	0.5433 (5)	-0.3241 (3)	-0.1041 (2)	0.0790 (8)
C6	0.4619 (4)	-0.3048 (2)	-0.1782 (2)	0.0670 (7)
N7	0.2713 (4)	-0.3617 (3)	-0.2001 (1)	0.0822 (7)
N8	0.1912 (4)	-0.3559 (2)	-0.2734 (1)	0.0711 (6)
C9	0.0005 (5)	-0.4027 (3)	-0.2841 (2)	0.0724 (7)
C10	-0.1000 (5)	-0.4069 (2)	-0.3601 (2)	0.0678 (7)
C11	0.0070 (5)	-0.3645 (2)	-0.4269 (2)	0.0722 (7)
C12	-0.0906 (5)	-0.3737 (3)	-0.4983 (2)	0.0751 (8)
C13	-0.2965 (5)	-0.4247 (3)	-0.5038 (2)	0.0755 (8)
C14	-0.4054 (6)	-0.4658 (3)	-0.4397 (2)	0.0831 (9)
C15	-0.3058 (5)	-0.4573 (3)	-0.3685 (2)	0.0789 (8)
N16	-0.4001 (5)	-0.4353 (2)	-0.5795 (2)	0.0911 (8)
O17	-0.2933 (5)	-0.4091 (3)	-0.6377 (2)	0.1136 (9)
O18	-0.5900 (5)	-0.4696 (3)	-0.5831 (2)	0.1270 (11)

Table 2. Geometric parameters (Å, °)

C1—C6	1.382 (4)	C10—C15	1.385 (4)
C1—C2	1.388 (4)	C10—C11	1.411 (4)
C2—C3	1.374 (5)	C11—C12	1.370 (4)
C3—C4	1.378 (5)	C12—C13	1.384 (4)
C4—C5	1.371 (5)	C13—C14	1.373 (4)
C5—C6	1.389 (4)	C13—N16	1.454 (4)
C6—N7	1.382 (4)	C14—C15	1.373 (5)
N7—N8	1.356 (3)	N16—O18	1.219 (4)
N8—C9	1.290 (4)	N16—O17	1.233 (4)
C9—C10	1.448 (4)		
C6—C1—C2	119.2 (3)	C15—C10—C9	119.2 (3)
C3—C2—C1	121.4 (4)	C11—C10—C9	122.3 (3)
C2—C3—C4	118.8 (3)	C12—C11—C10	120.6 (3)
C5—C4—C3	120.7 (3)	C11—C12—C13	119.0 (3)
C4—C5—C6	120.4 (3)	C14—C13—C12	121.7 (3)
C1—C6—N7	122.5 (3)	C14—C13—N16	119.1 (3)
C1—C6—C5	119.4 (3)	C12—C13—N16	119.2 (3)
N7—C6—C5	118.1 (3)	C13—C14—C15	119.0 (3)
N8—N7—C6	122.0 (2)	C14—C15—C10	121.3 (3)
C9—N8—N7	115.7 (2)	O18—N16—O17	122.4 (3)
N8—C9—C10	121.4 (3)	O18—N16—C13	118.7 (3)
C15—C10—C11	118.4 (3)	O17—N16—C13	118.9 (3)

All the H atoms were located from difference Fourier maps and refined isotropically. *PARST* (Nardelli, 1983) was used for geometrical calculations.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: author's own program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Mesogenic Perfluorinated Compound

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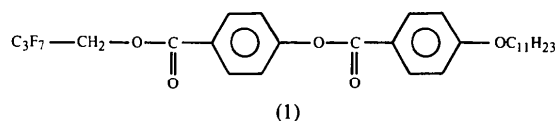
Abstract

The structure of 4-(2,2,3,3,4,4,4-heptafluorobutoxy-carbonyl)phenyl 4-undecyloxybenzoate, $C_{29}H_{33}F_7O_5$, adopts a slightly bent conformation. Molecules are aligned in the same direction and orientation as in an S_A smectic-like molecular arrangement. It is, therefore, a precursor of a ferroelectric phase.

Comment

Liquid crystals play an important role in a wide variety of electro-optical display devices and their development is currently of great interest (Kaneko, 1987). Recently, liquid crystals incorporating F atoms have shown very interesting results for such displays (Schad & Kelly, 1985; Goto, Ogawa, Sawada & Sugimori, 1991). There are numerous ways to introduce fluorine into liquid crystals; one is discussed in a recent paper regarding the 4-cyanophenyl 4-perfluoroheptylbenzoate with a cyano group on one side and a perfluoroheptyl chain on the

other (Kromm, Bideau, Cotrait, Destrade & Nguyen, 1994), which gives an S_{A2} -like arrangement. For the present compound, structural characterization shows that the material has a monolayer S_A phase. In order to clarify the precise relationship between the S_A structure and the molecular interactions, we solved the crystal structure of the present compound (1).



The molecule can be analysed as consisting of three parts, the alkoxy chain, the central core and the semi-perfluorinated chain. The title compound crystallizes in the $P1$ space group with two independent molecules in the cell, (I) and (II). The atom labelling, along with the molecular conformations, are given in a *SNOOP* drawing (Davies, 1983) (Fig. 1). Both alkoxy chains (O30–C41) for (I) and (O80–C91) for (II) are planar with torsion angles differing by less than 5° from 180° . Both semi-perfluorinated chains O18–C22 for (I) and O68–C72 for (II) are fully extended. The only conformational differences between molecules (I) and (II) are relative to the central core: C1–O18 and C51–O68 for (I) and (II), respectively. The torsion angles which differentiate molecules are as follows: C3–C4–C7–O9 -10.3 (12), C53–C54–C57–O59 -167.2 (7), C7–O9–C10–C11 -121.0 (9) and C57–O59–C60–C61 -71.1 (11) $^\circ$.

Both molecules are bent at the homologous C16 and C66 level: C(22)···C(16)···C(41) and C(72)···C(66)···C(91) are 131.7 and 127.8° , respectively. The two phenyl rings of the cores make angles of 52.5 and

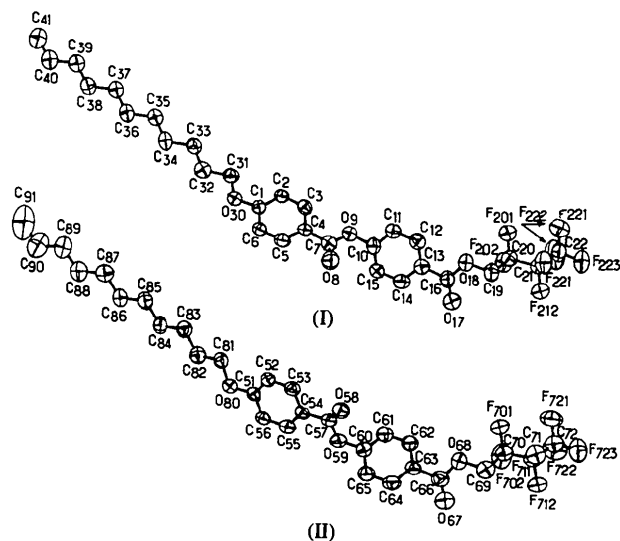


Fig. 1. View of $C_{29}H_{33}F_7O_5$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels (the projection of the structure is along the z axis).