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2'-[1-(4-Fluorophenyl)ethyl]isonicotino-κN-hydrazide–Cyanoborane

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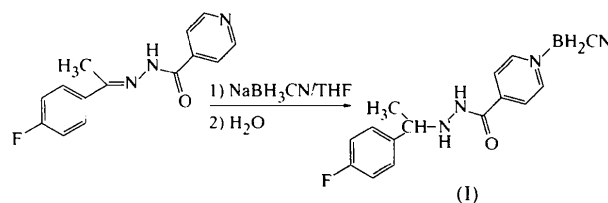
Abstract

The title compound, C₁₅H₁₆BFN₄O, is a cyanoborane adduct showing a butterfly-like conformation, with the fluorophenyl moiety disordered.

Comment

Interest in cyanoborane adducts stems from their extraordinary biological activities, *i.e.* anti-inflammatory (Hall *et al.*, 1980), anti-neoplastic (Sood *et al.*, 1991) and hypolipidemic (Hall *et al.*, 1981). By using known procedures (Calabretta *et al.*, 1991), an extensive series of cyanoborane adducts of aliphatic and aromatic isonicotinohydrazides has recently been prepared (Vigorita *et al.*, 1998). In particular, cyanoboranes derived from the primary antitubercular agent isoniazid (INH) should be of interest as potential anti-infective agents, in view of the current re-emergence of tuberculosis

and other AIDS-associated microbacterial diseases. The synthesis of the title isonicotinohydrazide–cyanoborane adduct, (I), was carried out by the treatment of 4'-fluoroacetophenone isonicotinoylhydrazone with an excess of sodium cyanoborohydride at pH 3–5 in anhydrous tetrahydrofuran.



However, since the title compound possesses at least two basic N atoms that might be in competition as sites coordinating BH₂CN (Calabretta *et al.*, 1991), the present X-ray diffraction analysis was required to determine the structure. This analysis shows that the packing is mainly determined by normal van der Waals interactions and intermolecular hydrogen bonds involving O1 and N1 (Table 2). Intermolecular hydrogen-bond interactions also occur in the disordered part of the molecule and involve the F atom (H...F distances range from 2.43 to 2.98 Å, whereas C—H...F angles range from 105 to 164°).

The cyanoborane group shows the typical tetrahedral geometry for the B atom [C1—B1—N2 = 109.2 (3)°], and distances and angles are in good agreement with those reported in the literature (Ferguson *et al.*, 1990). The angle between the N2—B1—C1—N1 moiety and the pyridine ring is 55.9 (2)°. The interplanar angle between the pyridine system and the O1—C7—N3—N4 moiety is 11.1 (1)°, showing that π-electron delocalization is not wide-ranging, since it is confined to the pyridine ring. The mutual orientation of the aromatic ring and the hydrazonic moiety is due to the presence of a weak intramolecular hydrogen-bond interaction involving C5 and O1 (Table 2).

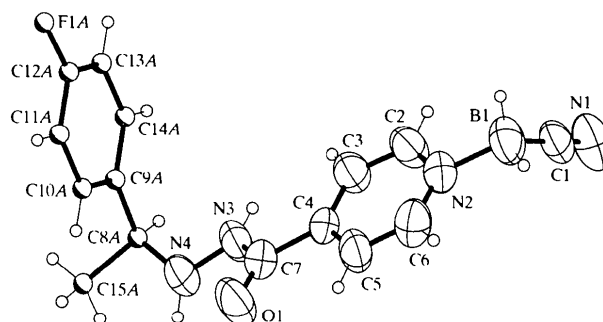


Fig. 1. View of the title compound showing the atomic numbering scheme, with displacement ellipsoids at 50% probability for non-H atoms. For clarity, only one position of the disordered moiety has been labelled.

All geometrical parameters concerning the hydrazonic fragment of the molecule agree with the values found in the literature (Okabe *et al.*, 1993; Simonsen, 1992), showing in particular a lengthening of the N3—N4 bond distance, which corresponds to a shortening of the C7—N3 bond length [1.413 (3) and 1.317 (4) Å, respectively]; the O1—C7—N3—N4 torsion angle of $-7.2(5)^\circ$ is indicative of sp^2 hybridization of both N atoms.

Experimental

Crystals suitable for X-ray diffraction analysis were grown by evaporation from a mixture of ethyl acetate and light petroleum (313–333 K).

Crystal data

C₁₅H₁₆BFN₄O
M_r = 298.13
 Triclinic
*P*1
a = 7.049 (2) Å
b = 7.492 (4) Å
c = 15.077 (6) Å
 α = 91.57 (4)°
 β = 92.83 (3)°
 γ = 99.74 (3)°
V = 783.3 (5) Å³
Z = 2
D_x = 1.264 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 46 reflections
 θ = 5–13°
 μ = 0.090 mm⁻¹
T = 293 (2) K
 Prismatic
 0.30 × 0.17 × 0.06 mm
 Light yellow

Data collection

Siemens *R3m/V* diffractometer
 ω -2 θ scans
 Absorption correction: none
 3011 measured reflections
 2768 independent reflections
 1066 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.020
 θ_{\max} = 25.05°
h = 0 → 8
k = -8 → 8
l = -17 → 17
 3 standard reflections every 197 reflections
 intensity decay: 1.31%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.063
wR(*F*²) = 0.187
S = 0.820
 2768 reflections
 257 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.1043P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.169 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.199 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.029 (7)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|-------|-----------|-------|-----------|
| N1—C1 | 1.130 (4) | C4—C7 | 1.522 (4) |
| C1—B1 | 1.563 (6) | C7—O1 | 1.228 (4) |
| B1—N2 | 1.598 (4) | C7—N3 | 1.317 (4) |
| N2—C2 | 1.325 (4) | N3—N4 | 1.413 (3) |
| N2—C6 | 1.330 (4) | | |

| | | | |
|----------|-----------|-----------|-----------|
| N1—C1—B1 | 178.3 (4) | O1—C7—N3 | 123.1 (3) |
| C1—B1—N2 | 109.2 (3) | O1—C7—C4 | 120.5 (3) |
| C2—N2—C6 | 118.5 (3) | N3—C7—C4 | 116.5 (3) |
| C2—N2—B1 | 120.0 (3) | C7—N3—N4 | 119.9 (3) |
| C6—N2—B1 | 121.4 (3) | C8A—N4—N3 | 116.5 (4) |

Table 2. Hydrogen-bonding geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| N3—H7...N1 ⁱ | 0.86 | 2.20 | 2.954 (5) | 147 |
| C3—H3...N1 ⁱ | 0.93 | 2.53 | 3.335 (5) | 145 |
| C2—H2...O1 ⁱⁱ | 0.93 | 2.36 | 3.166 (5) | 145 |
| C5—H5...O1 | 0.93 | 2.46 | 2.778 (4) | 100 |

Symmetry codes: (i) 2 - *x*, -*y*, 2 - *z*; (ii) 1 + *x*, *y*, *z*.

Reflection intensities were evaluated by profile fitting (Diamond, 1969) of a 96-step peak scan (the fitting was performed by using different math curves depending on the 2 θ shells of the collected profiles and not a unique profile as usual), and then corrected for Lorentz-polarization effects. Standard uncertainties, σ (*I*), were estimated from counting statistics. All non-H atoms were refined anisotropically. H atoms were located on idealized positions and allowed to ride on their parent C atoms, with a common isotropic displacement parameter (*U*_{iso} = 0.08 Å²). Disorder problems have been handled by refining atoms in two staggered positions, having different site-occupancy factors (0.6 for part *A* and 0.4 for part *B*). Both disordered benzenic rings have been fitted to regular hexagons. All calculations were performed on a μ -VAX 3400 and on an AXP DecStation 3000/400.

Data collection: *P3/V* (Siemens, 1989). Cell refinement: *P3/V*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XPW* (Siemens, 1996). Software used to prepare material for publication: *PARST97* (Nardelli, 1995) and *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1320). Services for accessing these data are described at the back of the journal.

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A New Bis(dithioester): Methanediyl Bis(*N,N*-diethyldithiocarbamate), Derived from *cis*-Dichlorobis(*N,N*-diethyldithiocarbamato-*S,S'*)tin(IV)

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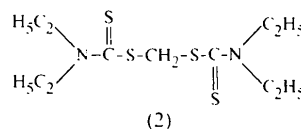
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Abstract

The title compound, C₁₁H₂₂N₂S₄ [or CH₂(Et₂DTC)₂, where DTC is dithiocarbamate], was unexpectedly obtained during studies on the reactivity of *cis*-dichlorobis(*N,N*-diethyldithiocarbamato-*S,S'*)tin(IV) {*cis*-[Cl₂Sn(Et₂DTC)₂]} with 2-thiouracil in dimethyl sulfoxide. The X-ray structural analysis of the title compound shows that two *N,N*-diethyldithiocarbamate units are linked together through a methylene C atom, so that the compound can be described as a dithioester, where the -CH₂(*N,N*-diethyldithiocarbamate) group itself constitutes the esteric organic radical. Structural parameters and IR spectra are in agreement with the crystal chemistry of this class of compounds. Of major interest is the methylene C atom, which presents an S—CH₂—S angle of 116.9(2)°, larger than the ideal tetrahedral value of 109.47°.

Comment

In the course of our work, which was undertaken to obtain a strong metal–nitrogen bond between metal complexes and DNA bases, particularly adenine (Marzotto *et al.*, 1993, 1995), we prepared *cis*-dichlorobis(*N,N*-diethyldithiocarbamato-*S,S'*)tin(IV) {*cis*-[Cl₂Sn(Et₂DTC)₂]} (1), in order to study its reactivity towards DNA bases. The interest in (1), whose molecular structure is already known (Bohra *et al.*, 1994; Selvaraju *et al.*, 1994), is due to its antitumor activity (Smith, 1978; Crowe & Smith, 1980; Crowe *et al.*, 1980; Oskarsson, 1983; Cardarelli & Libby, 1984). Then, during reactivity studies of (1) with 2-thiouracil [which exhibits a marked affinity for melanin-producing tissue (Wätjen *et al.*, 1982)], we unexpectedly obtained white crystals of the title compound, (2), identified as methanediyl bis(*N,N'*-diethyldithiocarbamate) by X-ray structure and IR spectroscopic analysis. It consists of two dithiocarbamate units, bridged by a methylene group, *i.e.* (C₂H₅)₂N—CS—S—CH₂—S—CS—N(C₂H₅)₂.



Compound (1), *cis*-[Cl₂Sn(Et₂DTC)₂], has been identified as hexacoordinate on the basis of the cell parameters, which are in agreement with those found by both Bohra *et al.* (1994) and Selvaraju *et al.* (1994). The subsequent interaction of (1) with 2-thiouracil in dimethyl sulfoxide yielded (together with other products which are under investigation) the title compound, methanediyl bis(*N,N*-diethyldithiocarbamate) [CH₂(Et₂DTC)₂, (2)], which has been characterized using X-ray diffraction and IR spectroscopy. The monoclinic cell contains two discrete molecules of methanediyl bis(*N,N*-diethyldithiocarbamate). In each molecule, the methylene carbon, C11, bridges two *N,N*-diethyldithiocarbamate moieties, which are closely related by a twofold molecular axis passing through C11 and the midpoint of the S1, S2, S3 and S4 atoms. This axis is nearly perpendicular [98.9(2)°] to the unique *b* axis, and also to the 2₁ screw axis, so that centrosymmetric (*P*2₁/*m*) or other space groups must be ruled out.

The atom joining the two dithiocarbamate units was identified as carbon by Fourier synthesis, which shows four positive maxima around it; the two highest peaks (0.43 and 0.41 e Å⁻³) occupy the positions expected for methylene H atoms, and the other two peaks (0.19 and 0.24 e Å⁻³) may be interpreted as bonding electrons. Three additional reasons support this choice: (i) the C11—S1 and C11—S2 distances of 1.792(3) and 1.789(3) Å, respectively, correspond exactly to a C_{sp³}—S single bond; (ii) the S1—C11—S2 angle of