

between observed and calculated structure factors showed no dependence on amplitude and resolution.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINT* (Siemens, 1994a). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1994b). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1069). Services for accessing these data are described at the back of the journal.

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2,5-Diethoxy-1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene and its Tetrahydrofuran 0.33-Solvate

KHALIL A. ABBOUD, DAVID J. IRVIN AND JOHN R. REYNOLDS

Department of Chemistry, University of Florida,
 PO Box 117200, Gainesville, Florida 32611-7200, USA.
 E-mail: abboud@chem.ufl.edu

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Abstract

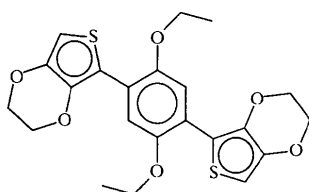
The crystal structures of the title compounds, 2,5-diethoxy-1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene, C₂₂H₂₂O₆S₂, (I), and its one-third tetrahydrofuran (THF)

solvate, C₂₂H₂₂O₆S₂· $\frac{1}{3}$ C₄H₈O, (II), were studied to determine the relative geometry of the benzene and thienyl rings. The dihedral angles between the benzene and thienyl rings are 6.04 (9) and 2.0 (1)° in (I) and (II), respectively, compared with 27.5 (2)° in the unsubstituted analog 1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene. The benzene and thienyl rings are more distorted in the title structures compared with the unsubstituted analog.

Comment

Thiophene-based polymers and oligomers have been the focus of much attention, due to their synthetic flexibility, environmental stability, and broad electrochemical stability range. However, one of the problems associated with direct thiophene electropolymerization is that the oxidation potential of the monomer is sufficiently high to degrade the polymer being formed, a process that has become known as overoxidation. We, and others, have overcome this problem by lowering the oxidation potential using electron-rich heterocyclic systems in combination with multi-ring conjugated monomers. The most interesting of these are 3,4-ethylenedioxythiophene (EDOT) derivatives (Jonas *et al.*, 1991; Kumar & Reynolds, 1996; Sankaran & Reynolds, 1997). We have developed a broad family of monomers such as the bis(2-heterocycle)benzenes (Reynolds *et al.*, 1993; 1994; Child *et al.*, 1995; Sozting *et al.*, 1996; Irvin & Reynolds, 1998), which lead to polymers with rationally controlled electronic properties.

In order for the polymer to stabilize charge carriers, the conjugated backbone must easily attain a fully planar conformation across a number of the heterocyclic and benzene rings. Previously (Reynolds *et al.*, 1991), we calculated the optimized geometry for two bis(2-thienyl)benzenes at the PRDDO level [partial retention of diatomic differential overlap (*CHEMX*; Chemical Design Ltd, 1988)], and found that the unsubstituted analog had a calculated dihedral angle of 24.3° between the planes of the benzene and thienyl rings. The 2,5-dimethoxy substituted compound had a calculated angle of 40°. In the previously determined crystal structure of 1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene, (III), the EDOT-to-benzene-ring angle was determined to be 27.5 (2)° (Sozting *et al.*, 1996). In analogy to the calculations carried out on the 2-thienyl derivative, we expected that with 2,5-disubstitution by the more sterically demanding ethoxy group, the dihedral angle would be increased. Thus the crystal structures of both 2,5-diethoxy-1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene, (I), and its tetrahydrofuran solvate, (II), were undertaken to determine the relative geometry of the EDOT ring (S, C1, C2, C5 and C6) with respect to the benzene ring (C7–C9 and their inversion counterparts). In contrast to our expectation, the 2,5-diethoxy substitution leads to an essentially planar compound, where the dihedral angles of (I) and (II) are 6.04 (9) and 2.0 (1)°,

(I) [(II) = (I)]₃C₄H₈O]

respectively. Other geometric differences in comparison with (III) appear in the benzene and thienyl rings: while all three molecules have similar asymmetric bonds to the S atom in the thienyl ring, C1—C2 bonds are longer than C5—C6 in (I) and (II), but are equal in (III) [C1—C2 = 1.362 (3) and C5—C6 = 1.350 (3) Å]. This is per-

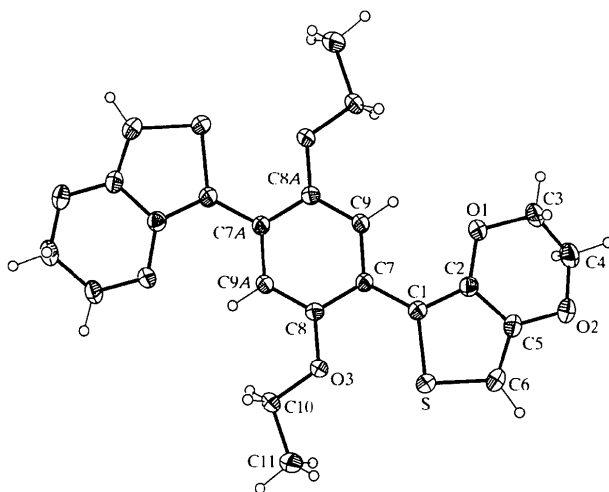


Fig. 1. Structure of a molecule of (I), showing ellipsoids at 50% probability and the atom-numbering scheme. The minor disorder at C3 and C4 is not shown.

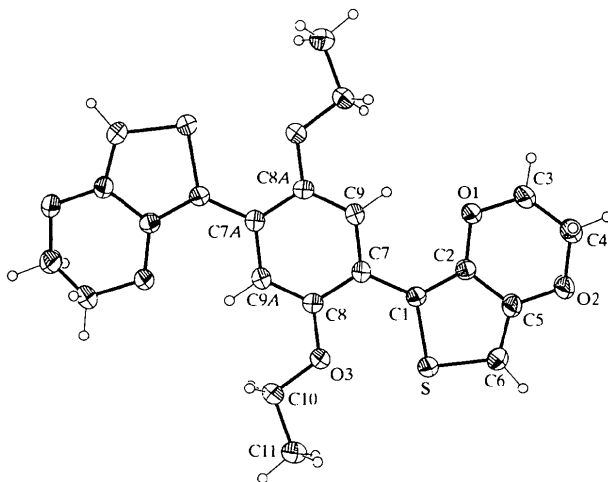


Fig. 2. Structure of a molecule of (II) without the solvate, showing ellipsoids at 50% probability and the atom-numbering scheme.

haps due to increased conjugation of the π electrons toward the benzene ring as a result of the ethoxy substitution. Additionally, the benzene ring is distorted in (I) and (II), with C8—C9ⁱ being shorter than C7—C8 and C7—C9 [symmetry code: (i) $-x, -y, -z$]; all three bonds are equivalent in (III) [1.388 (3), 1.399 (3) and 1.399 (3) Å, respectively]. A distortion of the C8—C7—C9 angle from ideal (120°) is observed in all three structures, but is more pronounced in (I) and (II) [$116.5(1)$ and $116.6(1)^\circ$, respectively] than in (III) [$118.2(2)^\circ$].

Experimental

The title compound was synthesized by a Negishi arylocoupling reaction (Knight, 1991). *n*-Butyllithium (19.8 ml of a 2.5 *M* solution in hexanes, 35.2 mmol) was slowly added to a stirred solution of 3,4-(ethylenedioxy)thiophene (7.00 g, 49.4 mmol) in THF (150 ml) at 195 K under argon. The yellow solution was stirred for 1 h. Anhydrous ZnCl₂ (21.6 ml of a 1.0 *M* solution in ether, 49.4 mmol) was added at 273 K. The mixture was stirred for 1 h, then 1,4-dibromo-2,5-diethoxybenzene (4.0 g, 12.3 mmol) and Pd(PPh₃)₄ (75 mg) were added. The yellow-brown solution was stirred at 323 K under argon for 96 h. It was then cooled to ambient temperature and quenched by pouring the mixture into 1 *M* HCl (500 ml). The THF was removed under vacuum, and the solid was collected by suction filtration and dried under vacuum. The crude solid was crystallized from THF at 263 K, to yield two types of orange-brown crystals, (I) and (II).

Compound (I)

Crystal data

C₂₂H₂₂O₆S₂
M_r = 446.52
 Orthorhombic
Pbca
a = 12.0267 (2) Å
b = 11.3835 (2) Å
c = 14.5357 (2) Å
V = 1990.02 (6) Å³
Z = 4
D_x = 1.490 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 8192 reflections
 θ = 1.5–27.5°
 μ = 0.307 mm⁻¹
T = 173 (2) K
 Plate
 0.26 × 0.19 × 0.19 mm
 Orange-brown

Data collection

Siemens SMART platform/CCD diffractometer
 ω scans
 Absorption correction: empirical (Blessing, 1995)
 T_{\min} = 0.797, T_{\max} = 0.956
 30 066 measured reflections
 2292 independent reflections

2009 reflections with $I > 2\sigma(I)$
 R_{int} = 0.027
 θ_{max} = 27.5°
 h = -16 → 14
 k = -11 → 15
 l = -19 → 18

Refinement

Refinement on F^2
 $R(F)$ = 0.035
 $wR(F^2)$ = 0.099
 S = 1.074

$(\Delta/\sigma)_{\text{max}}$ = 0.003
 $\Delta\rho_{\text{max}}$ = 0.34 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.38 e Å⁻³
 Extinction correction: none

2292 reflections
155 parameters
H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 1.0729P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

subtracted from the full data set; the ratio of the molecules to THF was 3:1, with a full THF molecule on every $\bar{3}$ center. The new data set, with the solvent contribution removed, was used in the final refinement. The CH₂ units of C3 and C4 in (II) are disordered and were refined in two parts. Their site occupation factors were dependently refined to 0.844 (5) for the major part (C3, C4) and consequently 0.156 (5) for the minor part (C3', C4'). The C atoms of the major part were refined with anisotropic displacement parameters, while those of the minor part (C3', C4') were refined with isotropic displacement parameters. The H atoms were placed in idealized positions and refined riding on their parent atoms. C—H distances of 0.98, 0.99 and 0.95 Å were used for methyl-, secondary- and aromatic-C atoms, respectively. The displacement parameters of the H atoms were 1.2U_{eq} of the parent C, or 1.5U_{eq} for the methyl atoms. A hemisphere of frames, 0.3° in ω , was collected. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. Full data collection details are in the relevant section of the archived CIF and are also reported elsewhere (Abboud *et al.*, 1997).

Table 1. Selected geometric parameters (Å, °) for (I)

S—C6	1.709 (2)	C5—C6	1.356 (2)
S—C1	1.742 (2)	C7—C9	1.405 (2)
C1—C2	1.390 (2)	C7—C8	1.411 (2)
C2—C5	1.422 (2)	C8—C9	1.385 (2)
C6—S—C1	93.31 (7)	C6—C5—C2	112.8 (1)
C2—C1—S	108.5 (1)	C5—C6—S	111.5 (1)
C1—C2—C5	113.9 (1)		

Symmetry code: (i) $-x, -y, -z$.

Compound (II)

Crystal data

C₂₂H₂₂O₆S₂· $\frac{1}{3}$ C₄H₈O

$M_r = 470.55$

Trigonal

$R\bar{3}$

$a = 29.3123$ (1) Å

$c = 6.8706$ (1) Å

$V = 5112.40$ (7) Å³

$Z = 9$

$D_x = 1.376$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 8192 reflections

$\theta = 1.5$ – 27.5°

$\mu = 0.283$ mm⁻¹

$T = 173$ (2) K

Hexagonal needle

$0.30 \times 0.27 \times 0.27$ mm

Orange-brown

For both compounds, data collection: SMART (Siemens, 1995); cell refinement: SMART and SAINT (Siemens, 1995); data reduction: SHELXTL (Sheldrick, 1995); program(s) used to solve structures: SHELXL97 (Sheldrick, 1997); program(s) used to refine structures: SHELXL97; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXL97.

Data collection

Siemens SMART platform/CCD diffractometer

ω scans

Absorption correction:

empirical (Blessing, 1995)

$T_{\min} = 0.764$, $T_{\max} = 0.947$

13 329 measured reflections

2597 independent reflections

2309 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 27.5^\circ$

$h = -38 \rightarrow 34$

$k = -38 \rightarrow 35$

$l = -8 \rightarrow 8$

KAA wishes to acknowledge the National Science Foundation and the University of Florida for funding the purchase of the X-ray equipment. Funding from the AFOSR (F49620-96-1-0067) and the NSF (CHE-96-28954) is also acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1445). Services for accessing these data are described at the back of the journal.

Refinement

Refinement on F^2

$R(F) = 0.035$

$wR(F^2) = 0.096$

$S = 1.060$

2597 reflections

137 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 5.9899P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.46$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Extinction correction:

SHELXL97

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 2. Selected geometric parameters (Å, °) for (II)

S—C6	1.710 (1)	C5—C6	1.352 (2)
S—C1	1.748 (1)	C7—C9	1.403 (2)
C1—C2	1.379 (2)	C7—C8	1.409 (2)
C2—C5	1.421 (2)	C8—C9	1.383 (2)
C6—S—C1	93.03 (7)	C6—C5—C2	113.2 (1)
C2—C1—S	108.7 (1)	C5—C6—S	111.3 (1)
C1—C2—C5	113.7 (1)		

Symmetry code: (i) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{4}{3} - z$.

The intensity contribution of the disordered THF molecule in (II) was calculated with SQUEEZE (PLATON; Spek, 1994) and

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1,1-Diamino-2,2-dinitroethylene:† a Novel Energetic Material with Infinite Layers in Two Dimensions

ULF BEMM AND HENRIC ÖSTMARK

Defence Research Establishment (FOA), Weapons and Protection Division, Energetic Materials Department, S-147 25 Tumba, Sweden. E-mail: ulfb@sto.foa.se

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Abstract

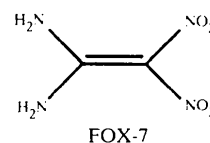
The title compound ($C_2H_4N_4O_4$) is a novel and interesting high explosive with high performance and low sensitivity. Single-crystal X-ray diffraction studies of the compound show that the molecules in the crystal structure have bond lengths and bond angles as expected for this type of push–pull ethylene. There are two intramolecular hydrogen bonds present between the nitro-O atoms and the amino-H atoms. The geometry of the molecule indicates that there is extensive π conjugation present. The molecular packing is built up by infinite two-dimensional wave-shaped layers, with extensive intermolecular hydrogen bonding within the layers and ordinary van der Waals interactions between the layers. The crystal packing explains some of the physico-chemical properties of the compound, such as the absence of a melting point, its low solubility, and its low sensitivity to friction and impact compared with the common high explosive RDX (1,3,5-triaza-1,3,5-trinitrocylohexane).

Comment

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel and interesting high explosive with high performance and low sensitivity (Östmark *et al.*, 1998). The compound is

† IUPAC name: 2,2-dinitroethylene-1,1-diamine.

a typical so-called push–pull ethylene, a group of compounds which has attracted interest for a long time because of their structural properties and stereochemistry, and since the 1970s a lot of work has been published in this area (*e.g.* Sandström, 1983; Baum, Bigelow *et al.*, 1992; Baum, Nguyen *et al.*, 1992).



The ethylene bond distance of 1.456(2) Å is intermediate between a single C—C bond (1.54 Å) and a double C=C bond (1.34 Å). The molecular configuration of the C and amino-N atoms is essentially planar, while the nitro-N atoms, especially N12, are out of plane (Fig. 1). This is also verified by *ab initio* calculations (Gaussian94; Frisch *et al.*, 1995). The configuration of the molecule was calculated using the B3LYP/6–31G(d,p) basis set which showed exactly the same deviation out of the plane of the two nitro-N atoms, especially N12, although no intermolecular interactions were included in the *ab initio* calculations (Bemm & Östmark, 1998). This indicates that the planarity of the molecule and the nitro groups is most probably affected by strong electrostatic repulsion forces between the two O atoms O11 and O22, and the intra- and intermolecular hydrogen bonds present are not believed to have any influence. The distance between O22 and O11 is only 2.575(2) Å giving rise to strong repulsion forces between the two nitro groups, thus introducing the twist of the two nitro groups. The N11 nitro group exhibits normal geometry, while the N12 nitro group deviates slightly from normal nitro-group geometry (Sadova & Vilkov, 1982). Two intramolecular hydrogen bonds are present between the amino groups and the nitro groups (Table 3). The above features indicate that the structure exhibits extensive π conjugation as expected. The FOX-7 molecule also possesses local symmetry in the form of an approximate twofold rotation axis through the two C atoms.

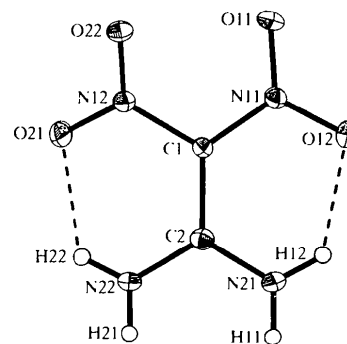


Fig. 1. Displacement ellipsoid (50% probability) drawing of FOX-7. Intramolecular hydrogen bonds are drawn as dashed lines.