New Tetrathiafulvalene–π-Spacer–Acceptor Derivatives: Synthesis, Crystal Structure, Optical and Electrochemical Properties

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4-[2-tetrathiafulvalenyl-ethenyl]pyridine (**1**) has been prepared from a Wittig reaction between formyltetrathiafulvalene and 4-picolyltriphenylphosphonium chloride hydrochloride. Conversion of the pyridine moiety of **1** by reaction with methyl iodide leads to 4-[2-tetrathiafulvalenyl-ethenyl]-1-methylpyridinium iodide (**2a**). Neutralization of **1** with a large excess of l-tartaric acid affords 4-[2-tetrathiafulvalenyl-ethenyl]-1-methylpyridinium hydrogen tartrate (**3**). These TTF-π-spacer-acceptor compounds have been characterized by elemental analysis, and IR and ^{1}H NMR spectroscopy. The crystal structure of **2a** has been determined by X-ray diffraction. The cation is essentially planar. Examination of the bond lengths in **2a**, UV/Vis spectra and CV data, and calculations indicate that an intramolecular charge transfer occurs in the studied compounds, although it is rather limited, and larger in **2a** and **3** than in **1**.

Introduction

TTF and its derivatives have been widely used as electron donor components in the preparation of charge-transfer complexes and radical ion salts which exhibit interesting conducting behavior in the solid state.[1] TTF is also much utilized as a versatile functionalized building block. However, the possible use of TTF as a donor in *intramolecular* charge-transfer (ICT) molecules has only been recently developed.[2] These ICT systems are of interest for several applications (see refs. 8–15 in[2]) including, for example, the preparation of single-component conductors,[3] and nonlinear optics (NLO).[4,5]

Several authors have studied TTF-spacer-A systems in which the acceptor subunits A were pyridinium cations,[6] bipyridinium dications[7] (see also ref. 44 in[2]), or *p*-benzoquinone.[8] In these cases, the TTF moiety and the acceptor group are linked by a σ-spacer, and these authors have studied the extent of intramolecular charge transfer as a function of the spacer's structure.

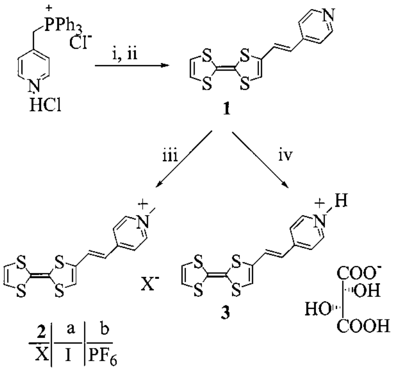
In this context, we have been interested in linking TTF to an *N*-methylpyridinium moiety, which is among the strongest electron acceptors commonly used, through an ethenyl π-spacer which should allow additional extended conjugation. We report here on the synthesis of 4-[2-tetrathiafulvalenyl-ethenyl]pyridine (**1**), 4-[2-tetrathiafulvalenyl-ethenyl]-1-methylpyridinium iodide (**2a**), and 4-[2-tetrathiafulvalenyl-ethenyl]-1-methylpyridinium hydrogen tartrate (**3**) (See Scheme 1).

We also present the crystal structure of **2a**, which is one of the very few single-crystal X-ray structures reported for 1 any TTF-spacer-A compound.[8] Finally, we discuss the extent of the intramolecular charge transfer from UV/Vis spectroscopic and cyclic voltammetric (CV) studies, and an analysis of the bond lengths in compound **2a**.

Results and Discussion

Synthesis

A Wittig reaction[9] between formyltetrathiafulvalene[10] and 4-picolyltriphenylphosphonium chloride hydrochloride[11] affords compound **1** as an orange solid (Scheme 1).



Scheme 1. Synthesis of compounds **1–3**. (i) BuLi 2.5 M, THF–CH_3CN, –80 °C; (ii) TTF–CHO; (iii) CH_3I, acetone, reflux; (iv) L-tartaric acid, abs. EtOH.

For the synthesis of **2a**, the pyridine moiety of **1** is converted into the pyridinium salt by reaction with a large excess of methyl iodide in dry acetone in the dark. It is interesting to note that this route makes various TTF-ethenyl-pyridinium salts accessible, depending on the alkyl iodide used in the synthetic procedure. Neutralization of **1** with a large excess of L-tartaric acid affords the 1:1 salt **3**. Chiral L-tartaric acid was selected to ensure a noncentrosymmetrical environment in **3**.

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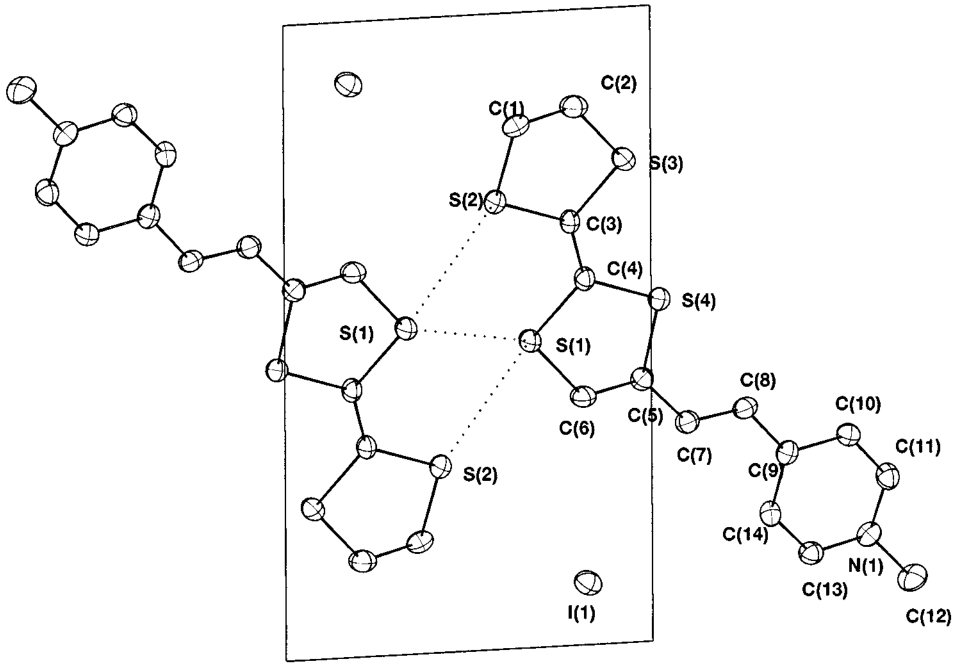

Figure 1. Atom numbering and molecular arrangement along the *a* axis in **2a**; H atoms are omitted for clarity; dotted lines indicate the short S···S van der Waals contacts (< 3.7 Å), with the symmetry operation (*i*) –*x*, 1 – *y*, 1 – *z*; S(1)–S(2)*i* = S(2)–S(1)*i* = 3.469(1) Å, S(1)–S(1)*i* = 3.430(1) Å

X-ray Crystal Structure

The crystal structure of **2a** (Figure 1) has been determined by X-ray diffraction (see Experimental Section for crystal data and data collection information).
Figure 1 shows the unit cell and atomic numbering scheme employed. The asymmetric unit contains one cation and one anion. The cation is planar, the largest deviation of 0.168 Å being observed at the C(7) atom. The molecular bond lengths are gathered in Table 1.

The most noticeable feature of the TTF moiety lies in the S(1)–C(6) bond length of 1.718(2) Å, which is significantly shorter than the corresponding S(2)–C(1) and S(3)–C(2) bond lengths in the other five-membered ring, 1.734(2) and 1.733(2) Å, respectively (Table 1). The C(5)–C(6) bond length is 1.345(3) Å, which is longer than the nonconjugated C(1)–C(2) bond [1.323(3) Å]. The value of 1.341(3) Å for the ethenyl C(7)–C(8) bond length is in the range (1.34–1.35 Å) reported for various compounds containing the related 4-[4-(dimethyl amino)-α-styryl]-1-methylpyridinium cation,[12–13] one of the most efficient second-order NLO systems.[14] This is also indicative of significant conjugation over the whole π-system in compound **2a**.

Table 1. Selected bond lengths (Å) for **2a**

Bond	Length [Å]	Bond	Length [Å]
S(1)–C(4)	1.755(2)	C(5)–C(7)	1.434(3)
S(1)–C(6)	1.718(2)	C(7)–C(8)	1.340(3)
S(2)–C(1)	1.734(2)	C(8)–C(9)	1.443(3)
S(2)–C(3)	1.762(2)	C(9)–C(10)	1.407(3)
S(3)–C(2)	1.733(3)	C(9)–C(14)	1.394(3)
S(3)–C(3)	1.752(2)	C(10)–C(11)	1.364(3)
S(4)–C(4)	1.760(2)	C(11)–N(1)	1.339(3)
S(4)–C(5)	1.758(2)	C(12)–N(1)	1.475(3)
C(1)–C(2)	1.323(3)	C(13)–C(14)	1.358(3)
C(3)–C(4)	1.332(3)	C(13)–N(1)	1.345(3)
C(5)–C(6)	1.345(3)		

These observations would suggest a substantial mesomeric effect of the methylpyridinium moiety, and indicates that there may be some ground-state contribution from a dipolar resonance form with a hypothetical positive charge on sulfur atom S(1). This behaviour has already been observed in other conjugated carbonyl,[15] ester,[16] and thioamide–TTF derivatives.[17] On the other hand, however, the charge of TTF being reflected in bond lengths,[18] it is clear that the averaged value for the C(3)–S(2), C(3)–S(3), C(4)–S(1) and C(4)–S(4) bond lengths of 1.757(3) Å in the structure of **2a** is typical of a neutral TTF species,[19] as well as the 0.758(3) Å value for the *a*/*b* ratio (*a* is the central C=C bond length and *b* that of the adjacent C–S bond).[18b] Consequently, this indicates that the positive charge in **2a** is primarily carried by the pyridinium moiety. Mulliken charge distributions, calculated using the PM3 Hamiltonian implemented in the MOPAC-6.0 system of programs,[20] confirm that most of the positive charge (0.735) is located on the pyridine moiety, while the TTF fragment remains basically neutral. The frontier-orbital topologies of **2a** are shown in Figure 2.

The atomic coefficients of the LUMO are larger on the *N*-methylpyridinium moiety, while the TTF donor fragment bears most of the electron density of the HOMO. It is interesting to note that 96% of the electron density of **2a** is located on the TTF fragment. This feature suggests that the

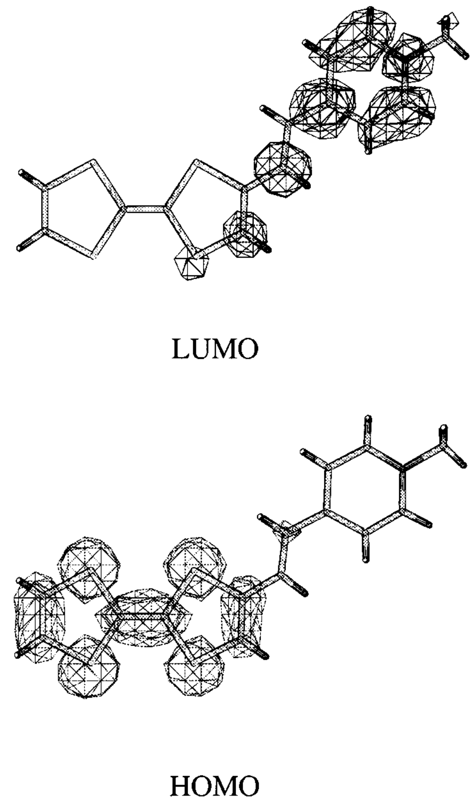

Figure 2. Frontier orbitals of **2a** calculated with the PM3 Hamiltonian

electrochemical properties of **2a** could be closely related to those of the parent TTF (vide infra).

UV/Vis Spectra

Compound **2a** shows a very broad, red-shifted band located at 580 nm (ε = 8000 mol^{-1} L cm^{-1}), and exhibits a strong negative solvatochromism, i.e., a blue shift when the solvent polarity is increased (Table 2), indicating intramolecular charge transfer.

Table 2. Absorption maxima (λ_{max} in nm) of the lowest energy optical transition in solvents of different polarities for **1** and **2a**

Solvent	Compound **1**	Compound **2a**
$CHCl_3$	454	638
pyridine	452	590
EtOH	457	580
MeOH	454	566
acetone	440	554
acetonitrile	438	552
DMSO	446	552
H_2O	unsoluble	538

The UV/Vis spectra of **1** in ethanol containing various amount of tartaric acid show a low-lying transition at 457 nm (ε = 5500 mol^{-1} L cm^{-1}) in pure ethanol, while it is strongly red shifted to 560 nm (ε = 6200 mol^{-1} L cm^{-1}) in concentrated solutions of tartaric acid, in a range of magnitude close to that of **2a**. Thus, the intramolecular charge transfer is larger in **2a** and **3** than in **1** due to the stronger acceptor character of the substituent. Indeed, the charge transfer observed in **1** must be small, as indicated by an almost vanishingly small solvatochromism (Table 2). In the presence of tartaric acid, the lowered transition energy suggests an enlarged charge transfer and an increase of the withdrawing effect of the pyridine. This strongly indicates protonation of the pyridine moiety once embodied in tartrate lattices in compound **3**, which is further confirmed by a comparison of the^{1}H NMR spectra of **2a**, **3** versus **1**.

Electrochemical Behaviour

Compound **2b** (derived from **2a** by substituting the PF_6^- anion for the I^- anion) was examined by cyclic voltammetry (CV); compound **2a** was not used directly in order to avoid the oxidation reactions of iodide (Table 3). Measurements for **3** must be carried out in a saturated solution of L-tartaric acid to ensure full neutralization of the pyridine moiety.

Table 3. Cyclic voltammetry data for TTF-π-A compounds **1**, **2b,** **3** and TTF [mV]. $TBAPF_6$ 0.1 mol L^{-1} in acetonitrile, 100 mVs^{-1}, *vs.* SCE

Compound	E^1_{ox}	E^2_{ox}	E_{red}
1	441	804	–
2b	513	864	–872
3[a]	504	845	–808
TTF	382	768	–

[a] In 2 × 10^{-1} mol L^{-1} L-tartaric acid, 60 °C.

On the reduction side, **2b** (Figure 3) and **3** show an irreversible wave at –872 and –808 mV/SCE, respectively, corresponding to the pyridinium moiety. All compounds display two reversible single-electron oxidation waves, corresponding to the TTF fragment (formation of a radical cation and a radical dication, respectively).

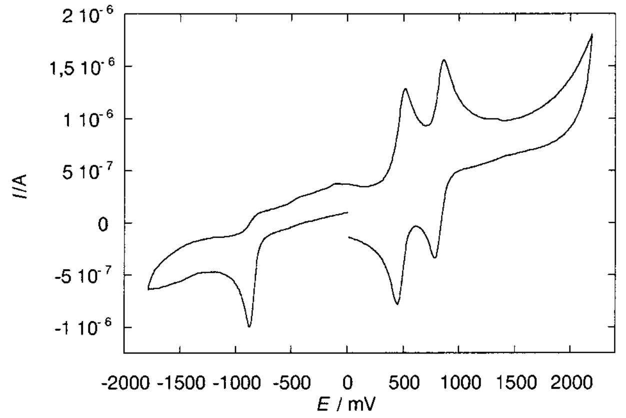

Figure 3. Cyclic voltammogram for **2b** (mV; $TBAPF_6$ 0.1 mol L^{-1} in acetonitrile; 100 mVs^{-1}; vs. SCE)

The potentials are shifted to higher positive values relative to the parent TTF due to partial electron transfer from the donor (TTF) to the acceptor moiety, and electrostatic repulsion, the proximity of one positive charge on nitrogen making the oxidation of TTF less favourable. These redox potential shifts [$\Delta E^1_{ox} = E^1_{ox} - E^1_{ox}$(TTF)] are similar to those of other TTF-pyridinium systems recently reported.[7a,7b]

This effect, which is more pronounced in **2b** and **3** (ΔE^{1}_{ox} = 131 and 122 mV, respectively) than in **1** (59 mV) due to larger intramolecular charge delocalization in the pyridinium derivatives, is consistent with the UV/Vis spectra. The same trend is observed for the second potential (E^{2}_{ox}), with smaller shifts (96, 77, and 36 mV for **2b, 3**, and **1**, respectively). Such shifts were not observed in other TTF-pyridinium systems,[6,7] but in those cases the TTF and pyridinium fragments were linked by saturated spacers.

Conclusion

The compounds described in this work are new examples illustrating a possible extension of the wide scope offered by TTF as a versatile building block for covalent attachment to a variety of TTF-spacer-acceptor systems. The novelty in compounds **1–3** is the nature of the spacer, which is a π-spacer (ethenyl); compounds with σ-spacers are more commonly used. Also the single-crystal X-ray structure of **2a** is one of the very few reported for any TTF-spacer-A compound.

An examination of the bond lengths in **2a**, UV/Vis spectra, CV data and calculations indicate that an intramolecular charge transfer occurs in the studied compounds, although it is rather limited, and, as expected, larger in **2a** and **3** than in **1**.

The reversible redox behaviour of **2a**, which is similar to that of TTF, suggests that this compound could be used as a precursor to molecular conductors. BEDT–TTF derivatives [BEDT–TTF = bis(ethylenedithio)tetrathiafulvalene] bearing a pyridine group and their semi-conducting charge transfer complexes with TCNQ (TCNQ = tetracyanoquinodimethane) have recently been reported by Xu et al.[21] In our case, preliminary investigations showed that the metathesis reaction of **2a** with $Li^{+}TCNQ^{-}$ in acetonitrile results in the precipitation of a black microcrystalline salt with a 1:1 stoichiometry. The compacted powder conductivity of this salt ($< 10^{-6}$ S cm^{-1}) is very much lower than that of TTF·TCNQ.[1a] This may be explained either by the less appropriate adjustment of the redox potentials **2a** and TCNQ,[22] or by an inappropriate packing arrangement. The strong solvatochromism observed for **2a**,[23] and semi-empirical calculations of the hyperpolarizabilities in **2a** and **3**,[24] indicated a low-lying HOMO–LUMO electronic transition having sizable charge transfer, and therefore possible NLO capabilities for **2a** and **3** as second-order NLO chromophores. The structure of **2a** being centrosymmetric (space group $P\bar{1}$), it is not surprising that Kurtz-Perry powder tests[25] confirm that **2a** exhibits no efficiency in second-harmonic generation. Disappointingly, however, compound **3**, in which the protonated species of **1** was purposely embodied in the chiral L-tartaric acid lattice to ensure noncentrosymmetry, doesn't exhibit any efficiency either. This may be due either to a quasi antiparallel arrangement of the chromophores, which cancels out most of the effect of the hyperpolarizability, or to poor crystallinity of the sample.

Experimental Section

General Remarks: Infrared measurements were carried out in KBr pellets using a Perkin–Elmer 1725 X spectrometer. – Melting points were obtained with a melting point SMP1 (Stuart Scientific) apparatus and are uncorrected. – ^{1}H NMR spectra were recorded with a Bruker AM200 spectrometer operating at 200 MHz; δ values are given in ppm (relative to TMS) and *J* values in Hz. – Elemental analyses were performed by the "Service de Microanalyse du Laboratoire de Chimie de Coordination du C.N.R.S. (Toulouse, France)." – Electronic spectra were recorded with a Shimadzu UV 3100 spectrophotometer. – Cyclic voltammetry measurements were performed with a ISMP Model Elektrokemat 400 potentiostat, using Pt working and counter electrodes, and saturated calomel electrode (SCE) as a reference. The experiments were carried out under argon, in acetonitrile, with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 100 mV s^{-1}. Formyltetrathiafulvalene[10] and 4-picolyltriphenylphosphonium chloride hydrochloride[11] were prepared as previously described.

4-(2-Tetrathiafulvenyl-ethenyl)pyridine (1): Butyllithium (2.5 M solution in hexanes, 2.64 mL, 2.2 equiv.) was added dropwise to a stirred suspension of triphenyl-4-pyridylmethylphosphonium chloride hydrochloride (1.36 g, 1.1 equiv.) in a mixture of anhydrous THF (20 mL) and anhydrous acetonitrile (15 mL) at –78 °C under argon. Stirring was continued at –78 °C for a further hour. Into the resulting yellow solution was syringed a solution of formyltetrathiafulvalene (696 mg, 3 mmol) in anhydrous THF (15 mL), and slowly warmed to 20 °C over 12 hours. Solvent was evaporated, and CH_2Cl_2 was added (300 mL). The organic layer was washed with water (3 × 100 mL) and dried ($MgSO_4$). Solvent evaporation and chromatography (silica gel) using diethyl ether as eluent gave **1** as an orange solid in 862 mg 85% yield. M.p. 133 °C. – IR (KBr): $\tilde{\nu}$ = 1596 cm^{-1}. – ^{1}H NMR (CD_3OD): δ = 8.54 (d, *J* = 6.3 Hz, 2 H), 7.57 (d, *J* = 6.3 Hz, 2 H), 7.46 (d, *J* = 15.9 Hz, 1 H), 6.97 (s, 1 H), 6.61 (s, 2 H), 6.43 (d, *J* = 15.9 Hz, 1 H). – $C_{13}H_9NS_4$ (307.4): calcd. C 50.78, H 2.95, N 4.56; found C 50.15, H 2.71, N 4.25.

4-(2-Tetrathiafulvenyl-ethenyl)-1-methylpyridinium Iodide (2a): A mixture of compound **1** (307 mg) and methyl iodide (2.12 mL, 20 equiv.) in dry acetone (40 mL) was refluxed under argon in the dark for six hours, until disappearance of the starting product. After cooling, a dark blue solid was isolated by filtration, washed with cold acetone and diethyl ether and dried. (86% yield). Recrystallization from methanol gave dark purple crystals. M.p. 210–214 °C. – IR (KBr): $\tilde{\nu}$ = 1599, 1501 cm^{-1}. – ^{1}H NMR (CD_3OD): δ = 8.77 (d, *J* = 6.8 Hz, 2 H), 8.14 (d, *J* = 6.8 Hz, 2 H), 7.85 (d, *J* = 15.6 Hz, 1 H), 7.33 (s, 1 H), 6.64 (s, 2 H), 6.61 (d, *J* = 15.6 Hz, 1 H), 4.37 (s, 3 H). – $C_{14}H_{12}INS_4$ (449.4): calcd. C 37.42, H 2.69, N 3.12; found C 37.40, H 2.48, N 3.50.

4-(2-Tetrathiafulvenyl-ethenyl)-1-methylpyridinium Hexafluorophosphate (2b): To a solution of 4-(2-tetrathiafulvenyl-ethenyl)-1-methyl pyridinium iodide **2a** (270 mg; 0.6 mmol) in a mixture of hot water/methanol (20:1) was added a water solution of potassium hexafluorophosphate (994 mg; 9 equiv.). After cooling, the purple dark solid was isolated by filtration and dried. Recrystallization from acetonitrile/ether gave compound **2b** (yield 70%). M.p. 170 °C. – $C_{14}H_{12}NPF_6S_4$ (467.4): calcd. C 35.97, H 2.57, N 3.00; found C 36.07, H 2.27, N 3.16.

4-(2-Tetrathiafulvenyl-ethenyl)pyridinium Hydrogen Tartrate (3): To a filtered solution of 4-(2-tetrathiafulvenyl-ethenyl)pyridine **(1)** (123 mg) in hot absolute ethanol (50 mL) was added a solution of L-(+)-tartaric acid (900 mg, 15 equiv.) in 50 mL of absolute ethanol. Slow evaporation in the dark afforded a purple crystalline solid, which was isolated by filtration, washed with a saturated solution of L-(+)-tartaric acid and dried. (Yield: 60%). M.p. 160 °C. – IR (KBr): $\tilde{\nu}$ = 3319, 1602 cm^{-1}. – ^{1}H NMR (CD_3OD): δ = 8.74 (d, J = 6.7 Hz, 2H), 8.07 (d, J = 6.7 Hz, 2 H), 7.78 (d, J = 15.7 Hz, 1 H), 7.28 (s, 1 H), 6.63 (s, 2 H), 6.58 (d, J = 15.7 Hz, 1 H). All attempts to recrystallize **3** from different solvents failed. – $C_{17}H_{15}NO_6S_4$ (457.4): calcd. C 44.64, H 3.31, N 3.06; found C 43.27, H 3.72, N 2.53.

X-ray Crystallographic Study for Compound 2a. Crystal Data: $C_{14}H_{12}INS_4$ (Mw = 449.4), triclinic $P\bar{1}$, Z = 2, a = 7.681(1) Å, b = 7.845(1) Å, c = 13.562(1) Å, α = 87.24(2)°, β = 89.09(2)°, γ = 86.95(2)°, V = 815.0 Å^3, d = 1.83 g.cm^{-3}. – **Data Collection:** X-ray diffraction data with 2.9° ≤ 2θ ≤ 48.4° were collected at 180 K with an STOE IPDS (imaging plate diffraction system) diffractometer using monochromatic Mo-K_α radiation (λ = 0.71013 Å), μ = 24.2 cm^{-1}. 6632 measured reflections, 2398 independent reflections with $I > 0\sigma(I)$. – **Structural Analysis and Refinement:** The structures were solved by direct methods (SHELXS-86),[26] and refined by least-square procedures. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. No absorption correction was considered. The structure was refined by full-matrix methods to R = 0.021, Rw = 0.016. The calculations were carried out with the CRYSTALS package programs,[27] running on a PC. The drawings of the molecular structures were obtained with the help of CAMERON.[28] The atomic scattering factors were taken from the International Tables for X-ray Crystallography.Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-119859. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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