The Reaction of 3,4-Dinitrothiophene with Grignard Reagents: Formation of 2-(3-Amino-4-nitrothiophen-2-yl)phenols

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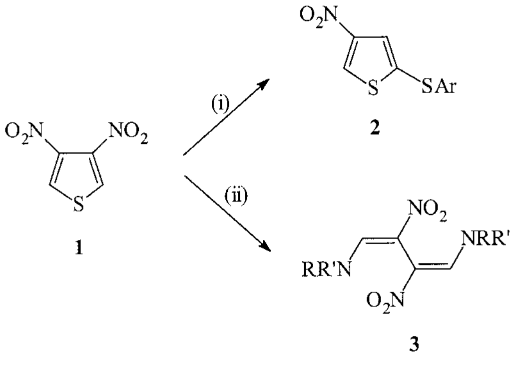
The treatment of 3,4-dinitrothiophene with an aryl Grignard reagent results in the reduction of one nitro group accompanied by the ipso-substitution of a hydrogen atom by an *ortho*-phenolic group on the ring carbon adjacent to the reduced nitro group. A Claisen-type intramolecular rearrangement is proposed as the pivotal step of a rather complex mechanism, followed by proton-transfer aromatizing steps. This work shows yet another facet of the variegated reactivity of 3,4-dinitrothiophene towards nucleophiles.

The multi-faceted chemical behaviour of the thiophene ring is clearly exemplified by the reactivity of nitrothiophenes towards nucleophiles. In particular, the reactivity of 3,4-dinitrothiophene (**1**) has been investigated extensively in our laboratories, encompassing (Scheme 1) observations such as *cine*-substitution (with arenethiolates)[1] or ring-opening accompanied by sulfur extrusion (with both primary and secondary amines),[2] the latter leading to the appealing substituted 2,3-dinitro-1,3-butadiene building blocks, such as **3**, and further derivatives of these following their manipulation.[3]



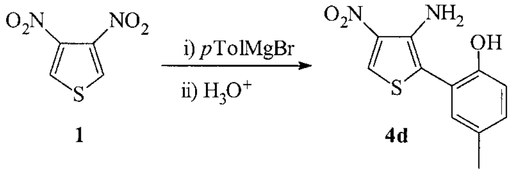
(i) ArS^-, ArSH, EtOH; (ii) RR'NH, EtOH.

Scheme 1

Herein we report on the reaction between 3,4-dinitrothiophene and aryl Grignard reagents, which unveils another facet of the variegated behaviour of this interesting heterocyclic compound.

Results and Discussion

The reactions between **1** and two molar equivalents of aryl Grignard reagents were carried out typically in THF at −78 °C, leading to rather complex final product mixtures from which compounds **4** could be isolated as main products (typified by the reaction of *p*-tolylmagnesium bromide as shown in Scheme 2) together with some unreacted substrate. The results are summarized in Table 1. Yields of isolated products and/or overall balances are generally rather low, but they should be definitely considered in light of the rather complex multi-step process discussed below. At this point, it should be noted that higher reagent to substrate molar ratios (3:1 or 6:1) were found not to lead to appreciable yield improvements.



Scheme 2

The structural assignment of compounds **4** is based on the single-crystal X-ray analysis of the model derivative **4d** (Figure 1, see later in the text) and on good agreement between the spectroscopic data (^1H and ^{13}C NMR, IR) of the latter and those of the other compounds **4**.

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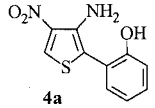
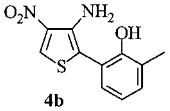
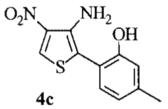
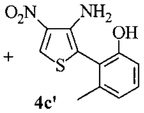
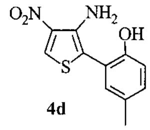
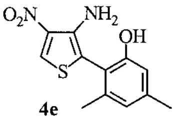
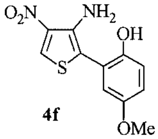
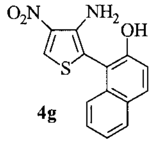
Table 1. Yields of **4** from the reactions of **1** with arylmagnesium bromides (ArMgBr). [a]

Ar	Product	Yield (%)[b]
Ph	 **4a**	32 (59)
2-MeC$_6$H$_4$	 **4b**	9 (21)
3-MeC$_6$H$_4$	 **4c** +  **4c'**	27 (79)[c]
4-MeC$_6$H$_4$	 **4d**	33 (43)
3,5-Me$_2$C$_6$H$_3$	 **4e**	41 (52)
4-MeOC$_6$H$_4$	 **4f**	15 (25)
2-naphthyl	 **4g**	33 (58)

[a] ArMgBr: 2.0 mol equiv.; THF, −78 °C, 1 h, followed by 5% HCl(aq) quenching. [b] Isolated yields, based on 3,4-dinitrothiophene; figures in parentheses refer to the reacted substrate. [c] Ca. a 1:1 mixture (in ^{1}H NMR) of the two isomeric **4c** and **4c'**.

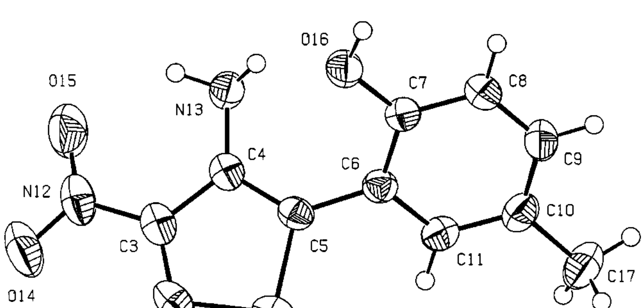


Figure 1. An ORTEP view of the molecule of **4d** in the crystal state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are on an arbitrary scale

It is immediately apparent from the process shown in Scheme 2 that ArMgX effectively behaves as a reductant towards one of the two nitro groups, with an oxidized Ar moiety subsequently replacing the H atom of the thiophene ring adjacent to the reduced nitro group.

In order to rationalize the results within a mechanistic scheme which could also properly account for the observed regioselectivity, it must be recalled first of all that reduction of a nitro to a nitroso group by Grignard reagents [Scheme 3, step (*a*)] is a well studied process[4−6] for which a radical pathway has also been recently proposed,[4b] with an initial one-electron transfer to the nitro group. In this work, it seems relevant that the addition of the Grignard reagent leads to an intense blue-green colour of the reaction solution, and is possible confirmation of the occurrence of a one-electron transfer process.

On the other hand, the proposed addition [step (*b*)] of a second molecule of Grignard reagent to the intermediate nitroso derivative **5** contrasts with an earlier report[5] where, in the case of Grignard reagents but not aryllithium reagents, binding of the aryl to the nitrogen atom (rather than to the oxygen) of the N=O double bond was assumed, in order to explain the identities of the isolated products. Nonetheless, more recent reports from other research groups do suggest an "inverse" addition of the Grignard reagent (either aromatic[6] or vinylic[4b]) to the nitroso group as the only conceivable route to the observed products.

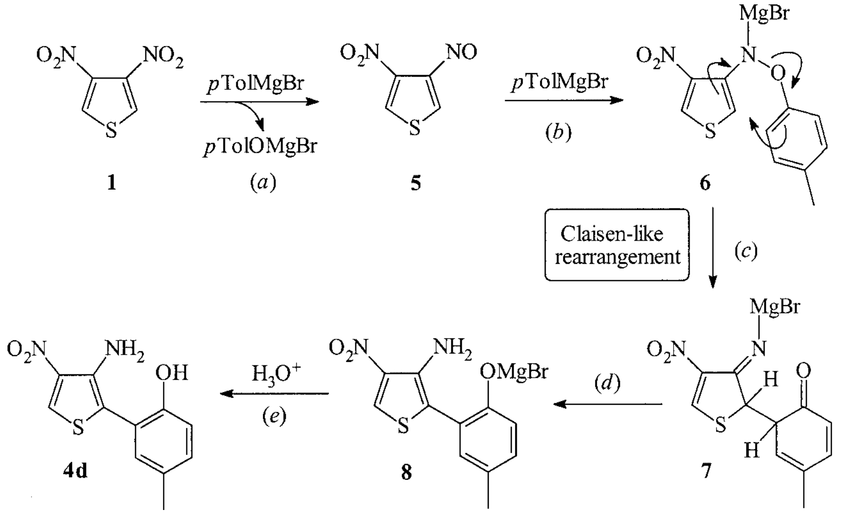
However it is formed,[7] **6** must be the key intermediate of the overall process, which is driven towards phenols **4** by means of the Claisen-like rearrangement of step (*c*),[4b] followed by the aromatization of the thiophene and benzene rings [step (*d*)] to give the final products **4** after acidic quenching [step (*e*)]. It should be pointed out that a [3,3]sigmatropic shift as depicted in step (*c*) has been already reported[4b] during the synthesis of indoles involving reactions of nitrobenzene derivatives with vinyl Grignard reagents. However, to the best of our knowledge, the example presented here is the first in which such a rearrangement involves π-electrons of the aryl moiety of an aromatic organometallic reagent, signifying a driving force which overcomes the concomitant loss of aromaticity of the two different π-systems.

As expected, in the case of (2,4,6-trimethylphenyl)magnesium bromide no product **4** was detected, since *ortho*- and *para*-substitution prevents the overall Claisen-like rearrangement although the substrate was consumed in processes which were not further investigated. The reaction with 1-naphthylmagnesium bromide met with a similar failure, possibly because of negative steric effects in the addition steps to the nitro and/or to the nitroso group.

X-ray Structural Determination of 4d

To the best of our knowledge, this is the first crystal structure determination of a non-condensed thiophene ring bonded to a phenyl group.

The ORTEP diagram[8] of compound **4d** is shown in Figure 1. In the molecule, two planar parts are connected by the central bond C5−C6 with their least-squares planes at



Scheme 3

an angle of 46.7°. Considering only non-hydrogen atoms, the 3-amino-4-nitrothiophene moiety is planar within 0.1Å (the largest deviation from planarity being due to atom O15), whereas the 2-hydroxy-5-methylbenzene moiety is planar within 0.005(2) Å. The atom N13 is involved in two intramolecular H bonds, N13−H131···O15 [H131···O15 2.07(2) Å, N13−H131···O15 132(2)°] and N13−H132···O16 [H132···O16 2.04(2) Å, N13−H132···O16 146(2)°], as well as in an intermolecular H bond (vide infra). N13 is pyramidal and its distance from the plane defined by C4, H131, H132 is 0.310(1) Å. The geometry of an isolated molecule of **4d** obtained from a theoretical calculation at the B3LYP/6-31G* level,[9] starting from final experimental coordinates, shows a pyramidality of 0.272 Å for N13.

In the crystal, a strong intermolecular hydrogen bond involving the lone pair of N13 [O16−H16···N13, N13 in $1 - x$, $-1/2 + y$, $3/2 - z$, H16···N13 1.88(2) Å, O16−H16···N13 171(2)°] connects the molecules parallel to the y axis. This feature could be responsible for the (albeit small) increase of pyramidality on going from the isolated molecule (0.272 Å) to the molecule in the crystal state (0.310 Å). The packing coefficient of Kitaigorodski[10] is K = 67.5.[8]

Conclusions

The results presented here reveal a peculiar reactivity of 3,4-dinitrothiophene towards aryl Grignard reagents. In fact, the latter basically acts as a reducing agent towards one of the nitro groups in a rather complex mechanism whose key step is a Claisen-type rearrangement [Scheme 3, step (*c*)], which follows the "inverse" addition of the Grignard reagent to the initially formed nitroso group. Overall, this process allows access to novel functionalized thiophene derivatives, and is yet another example of the multi-faceted reactivity of this interesting and versatile heterocycle towards nucleophiles.

The low degree of aromaticity of the thiophene ring most likely concurs to the driving force of a rearrangement which contemporaneously engages the π-electron systems of two aromatic moieties, an occurrence which is, to the best of our knowledge, hitherto unreported.

Finally, it should be stressed that the results presented here can be regarded as yet another example of the non-benzenoid behaviour of nitrothiophenes since, in our hands, *ortho*-dinitrobenzene failed to undergo an overall rearrangement analogous to that described in Scheme 3, when subjected to identical reaction conditions.[11]

Experimental Section

General Remarks: ^1H NMR and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz, respectively; chemical shifts (TMS as internal reference) are reported as δ ppm. Melting points were determined with a Büchi 535 apparatus and are uncorrected.

Materials: Silica gel 230−400 mesh was used for column chromatography, all solvents being distilled before use. Tetrahydrofuran (THF) was purified by standard methods and distilled from potassium benzophenone ketyl before use. 3,4-Dinitrothiophene (**1**) was synthesized as reported.[12] Commercial 1- and 2-bromonaphthalene were used after drying over molecular sieves (4 Å) or (for the latter) over P_2O_5 under vacuum. All other commercially available reagents were used as received.

Arylmagnesium Bromides: All the Grignard reagents were THF or Et_2O solutions and were titrated[13] just before use. Phenyl-, 2-, 3- and 4-methylphenyl- and 4-methoxyphenylmagnesium bromides were the commercially available solutions in THF or Et_2O. 3,5-Dimethylphenyl, 2,4,6-trimethyl-, 1-naphthyl- and 2-naphthylmagnesium bromides were prepared in THF by standard methods.

Reactions of Compound 1 with Aromatic Grignard Reagents: The Grignard reagent in THF (2.3 mmol) was slowly added by syringe to a solution of 3,4-dinitrothiophene (**1**) (0.2 g, 1.15 mmol) in THF (14 mL), cooled to −78 °C, under argon and with magnetic stirring. The reaction mixture was maintained with stirring for 1 h and then poured into ice-5% HCl (50 mL). The aqueous phase was extracted with dichloromethane (3 × 25 mL) and the organic extracts washed with 5% NaOH (2 × 25 mL), then water (2 × 20 mL), and dried with Na_2SO_4. After evaporation of the solvent under reduced pressure, unreacted 3,4-dinitrothiophene was recovered. 5% HCl(aq) was added to the alkaline extracts, the resulting solution was extracted with dichloromethane (3 × 25 mL) and the organic extracts were dried with Na_2SO_4. After concentration under vacuum, a crude product was obtained, which was purified by chromatography over silica gel (petroleum ether/diethyl ether gradients as eluent). Yields of compounds **4** are collected in Table 1.

2-(3-Amino-4-nitrothiophen-2-yl)phenol (4a): Yield: 87 mg (32%). Colorless crystals, m.p. 128.3−130.1 °C (light petroleum). IR (Nujol): nu (tilde) = 3378, 3266, 3121, 1566, 1351, 1291, 1189, 1109 cm^{-1}. ^1H NMR (CD_3SOCD_3): δ = 5.58 (s, 2 H, exch. D_2O), 6.90 (dt, *J* = 1.2, 7.6 Hz, 1 H), 6.98 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.23 (m, 1 H), 7.32 (dd, *J* = 1.5, 7.7 Hz, 1 H), 8.71 (s, 1 H), 10.21 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 118.46, 118.48, 119.25, 121.41, 128.25, 130.81, 130.86, 133.69, 138.81, 153.73 ppm. $C_{10}H_8N_2O_3S$ (236.251): calcd. C 50.84, H 3.41, N 11.86; found C 50.95, H 3.33, N 11.67.

2-(3-Amino-4-nitrothiophen-2-yl)-6-methylphenol (4b): Yield: 26 mg (9%). Colorless crystals, m.p. 136.5−138.1 °C (light petroleum). IR (Nujol): nu (tilde) = 3390, 3278, 3118, 1567, 1496, 1350, 1200, 1166 cm^1. ^1H NMR (CD_3SOCD_3): δ = 2.24 (s, 3 H), 5.57 (s, 2 H, exch. D_2O), 6.86 (t, *J* = 7.2 Hz, 1 H), 7.15 (d, *J* = 7.2 Hz, 2 H), 8.74 (s, 1 H), 8.96 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.44, 117.75, 119.24, 120.89, 127.41, 128.22, 128.51, 131.99, 133.62, 138.73, 152.01 ppm. $C_{11}H_{10}N_2O_3S$ (250.278): calcd. C 52.79, H 4.03, N 11.19; found C 52.97, H 4.20, N 10.91.

2-(3-Amino-4-nitrothiophen-2-yl)-5-methylphenol (4c): Yield: 41 mg (14%). Colorless crystals, m.p. 129.9−131.4 °C (light petroleum). IR (Nujol): nu (tilde) = 3375, 3255, 3131, 3113, 1617, 1567, 1517, 1485, 1402, 1347, 1297, 1205, 1168, 1128, 1070 cm^{-1}. ^1H NMR (CD_3SOCD_3): δ = 2.27 (s, 3 H), 5.53 (s, 2 H, exch. D_2O), 6.73 (d, *J* = 7.8 Hz, 1 H), 6.80 (s, 1 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 8.68 (s, 1 H), 10.11 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.23, 115.46, 118.87, 119.41, 122.38, 127.87, 130.56, 133.45, 138.82, 141.42, 153.56 ppm. $C_{11}H_{10}N_2O_3S$ (250.278): calcd. C 52.79, H 4.03, N 11.19; found C 52.84, H 4.18, N 11.04.

2-(3-Amino-4-nitrothiophen-2-yl)-3-methylphenol (4c′): Yield: 38 mg (13%). Colorless crystals, m.p. 88.8−90.0 °C (light petroleum). IR (Nujol): nu (tilde) = 3377, 2946, 2931, 1572, 1409, 1340, 1291, 1154, 1068 cm^{-1}. ^1H NMR (CD_3SOCD_3): δ = 2.10 (s, 3 H), 5.23 (s, 2 H, exch. D_2O), 6.78 (d, *J* = 8.0 Hz, 2 H), 7.15 (app t, *J* = 8.0 Hz, 1 H), 8.72 (s, 1 H), 9.52 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.35, 107.95, 113.64, 115.86, 122.71, 129.03, 130.98, 138.17, 140.62, 155.03 (one pair of carbons are accidentally isochronous) ppm. ^{13}C NMR (CD_3SOCD_3): δ = 19.61, 110.06, 113.02, 116.73, 120.65, 127.99, 129.58, 137.18, 137.37, 139.93, 156.50 ppm. $C_{11}H_{10}N_2O_3S$ (250.278): calcd. C 52.79, H 4.03, N 11.19; found C 52.65, H 3.93, N 11.10.

2-(3-Amino-4-nitrothiophen-2-yl)-4-methylphenol (4d): Yield: 95 mg (33%). Colorless crystals, m.p. 158.6−159.6 °C (light petroleum/toluene). IR (Nujol): nu (tilde) = 3373, 3235, 3108, 2710, 1566, 1497, 1345, 1280, 1258, 1226, 1140, 1119 cm^{-1}. ^1H NMR (CD_3SOCD_3): δ = 2.24 (s, 3 H), 5.58 (s, 2 H, exch. D_2O), 6.88 (d, *J* = 8.2 Hz, 1 H), 7.03 (dd, *J* = 1.5, 8.2 Hz, 1 H), 7.11 (s, 1 H), 8.70 (s, 1 H), 9.98 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.41, 118.11, 118.31, 119.33, 128.04, 130.78, 130.99, 131.52, 133.64, 138.79, 151.48 ppm. $C_{11}H_{10}N_2O_3S$ (250.278): calcd. C 52.79, H 4.03, N 11.19; found C 52.88, H 4.00, N 11.02.

2-(3-Amino-4-nitrothiophen-2-yl)-3,5-dimethylphenol (4e): Yield: 124 mg (41%). Colorless crystals, m.p. 108.5−110.3 °C (light petroleum/toluene). IR (Nujol): nu (tilde) = 3499, 3373, 3314, 3075, 1616, 1591, 1566, 1503, 1462, 1405, 1335, 1271, 1159, 1047 cm^{-1}. ^1H NMR (CD_3SOCD_3): δ = 2.06 (s, 3 H), 2.22 (s, 3 H), 5.19 (s, 2 H, exch. D_2O), 6.60 (s, 2 H), 8.69 (s, 1 H), 9.38 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.23, 21.35, 108.24, 112.84, 114.17, 123.71, 128.86, 128.88, 138.20, 140.21, 141.44, 154.86 ppm. $C_{12}H_{12}N_2O_3S$ (264.305): calcd. C 54.53, H 4.58, N 10.60; found C 54.71, H 4.45, N 10.49.

2-(3-Amino-4-nitrothiophen-2-yl)-4-methoxyphenol (4f): Yield: 46 mg (15%). Colorless crystals, m.p. 171.6−173.1 °C (light petroleum/dichloromethane). IR (Nujol): nu (tilde) = 3360, 1566, 1457, 1349, 1277, 1252, 1221, 1181, 1027 cm^1. ^1H NMR (CD_3SOCD_3): δ = 3.71 (s, 3 H), 5.66 (s, 2 H, exch. D_2O), 6.81 (dd, *J* = 2.8, 8.4 Hz, 1 H), 6.89 (m, 2 H), 8.71 (s, 1 H), 9.76 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.31, 112.33, 114.81, 114.92, 116.94, 119.49, 128.25, 137.16, 137.23, 147.92, 152.26 ppm. $C_{11}H_{10}N_2O_4S$ (266.277): calcd. C 49.62, H 3.79, N 10.52; found C 49.50, H 3.52, N 10.35.

1-(3-Amino-4-nitrothiophen-2-yl)naphthalen-2-ol (4g): Yield: 108 mg (33%). Colorless crystals, m.p. 156.6−158.0 °C (light petroleum/toluene). IR (Nujol): nu (tilde) = 3378, 1566, 1334, 1204 cm^{-1}. ^1H NMR (CD_3SOCD_3): δ = 5.24 (s, 2 H, exch. D_2O), 7.36 (m, 4 H), 7.88 (m, 2 H), 8.83 (s, 1 H), 9.97 (s, 1 H, exch. D_2O) ppm. ^{13}C NMR ($CDCl_3$): δ = 108.17, 109.09, 118.37, 122.85, 123.70, 126.90, 128.05, 128.20, 128.87, 130.72, 133.72, 137.34, 138.50, 154.86 ppm. $C_{14}H_{10}N_2O_3S$ (286.311): calcd. C 58.73, H 3.52, N 9.78; found C 58.70, H 3.49, N 9.52.

X-ray Crystallographic Study of 4d: Transparent, orange single crystals were grown from toluene. After preliminary Laue photographs, X-ray data were recorded on an Enraf−Nonius Mach3 diffractometer with graphite monochromated Mo-K_α ($\lambda = 0.7107$ Å) radiation. Cell constants were determined by least-squares refinement of diffractometer angles for 25 automatically centered reflections. During the data collection the centering of six reflections was repeated periodically to test the crystal orientation, and two reflections were monitored every hour to check its stability. No decay of the crystal was observed.

Crystal Data: 2-(3-amino-4-nitrothiophen-2-yl)-4-methylphenol, **4d**, $C_{11}H_{10}N_2O_3S$, *M* = 250.3, m.p. 159 °C. Monoclinic, $a = 10.123(1)$, $b = 7.211(2)$, $c = 16.290(2)$ Å, $\beta = 102.35(1)°$, $V = 1161.6(4)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_{calcd.} = 1.431$ g·cm^{-3}, $F(000) = 520$. Prismatic crystal, 0.40 × 0.36 × 0.30 mm, $\mu = 0.276$ mm^{-1}; ω/θ scan mode, scan width 1.20°, scan speed 1.0−16.5° min^{-1}. 2653 unique reflections were measured ($2.5 \leq \theta \leq 27.5°$). An absorption correction was applied according to the method of North, Phillips and Mathews.[14]

Structure solution and Refinement: The structure was solved by direct methods using the SIR97 system of programs[15] and refined by full-matrix least-squares techniques,[16] including the whole data set of 2653 F_o^2 in the calculations. An extinction correction was needed; the corresponding coefficient[16] converged to 0.012(2). In the final refinement all heavier atoms were treated as anisotropic. All the hydrogen atoms were localized by means of difference Fourier syntheses and their positions and isotropic displacement parameters were refined without constraints.

Convergence was reached within a maximum shift-to-e.s.d. ratio of 0.006. The largest correlation matrix element was 0.522. Final reliability factors are $R_1 = 0.0349$ on 2223 $F_o \geq 4\sigma(F_o)$, $wR_2 = 0.0987$ for all 2653 F_o^2 and 195 parameters, with a goodness of fit $S = 1.047$. At the end of the refinement the difference Fourier map was essentially flat, the electron density ranging between 0.22 and -0.21 e·Å^{-3}.

Geometry calculations were performed using the program PARST.[17] Atomic coordinates, thermal parameters, bond lengths, bond angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre.[18]

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