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# 2-[(trifluoroacetyl)amino]benzoquinone and the hydrochloride and perchlorate salts of 2-aminohydroquinone

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Hydrogen bonding parameters for the title materials are reported. 2-[(trifluoroacetyl)amino]benzoquinone crystallizes in the monoclinic space group $P2_1/c$, with $a = 18.195(4)$, $b = 5.110(1)$, $c = 9.635(2)$, $\beta = 104.22(3)^\circ$, $V = 868.4(3)$ Å$^3$, and $Z = 4$. This compound exhibits two weak intramolecular hydrogen bonds. The first is between a hydrogen atom of the quinone ring and the carbonyl oxygen of the trifluoroacetamide group; it has a distance of 2.24 Å and a C–H···O angle of 122°. The second is between the hydrogen atom of the trifluoroacetamide group and a quinone carbonyl group; it has a distance of 2.26 Å and a N–H···O angle of 107°. 2-Aminohydroquinone hydrochloride crystallizes in the orthorhombic space group $Pca2_1$, with $a = 16.220(3)$, $b = 5.211(1)$, $c = 8.719(2)$, $V = 737.0(2)$ Å$^3$, and $Z = 4$. 2-Aminohydroquinone perchlorate crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 7.110(1)$, $b = 7.139(1)$, $c = 18.043(4)$, $V = 915.8(3)$ Å$^3$, and $Z = 4$. All active hydrogens of the two salts exhibit intermolecular hydrogen bonds that serve to organize a three-dimensional framework for each case.

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**KEY WORDS:** Crystal structure; intermolecular hydrogen bonds; 2-[(trifluoroacetyl)amino]benzoquinone; 2-aminohydroquinone.

## Introduction

We are engaged in the synthesis of donor/acceptor molecules for electron-transfer studies that will feature ammonium quinone acceptors; our initial focus was on preparing materials in which the ammonium moiety is directly attached to the quinone skeleton. We sought materials that had no substituents (parent quinone) other than the ammonium group as well as substituted quinones (additional substituents could be halogen, methyl, nitrile, etc.). In the course of this work, we have prepared 2-[(trifluoroacetyl)amino]benzoquinone **1** by the method of Aulinger, Arnold, and Steglich.[1] Deprotection of the intermediate hydroquinone by dry methanolic hydrogen chloride afforded 2-aminohydroquinone hydrochloride **2**. Finally, metathesis of the chloride anion to the perchlorate salt **3** was accomplished with silver perchlorate (Note: caution should be used when handling this perchlorate salt since it is potentially shock sensitive). The chloride salt **2** is known as a partially deuterated material,[2] while perchlorate **3** is previously unreported.

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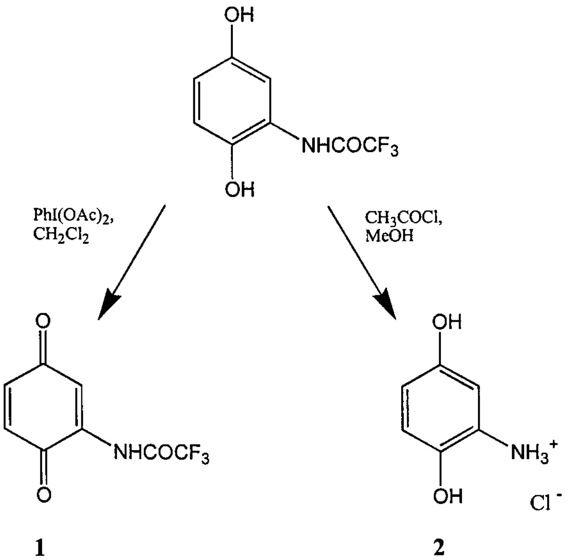

**1** **2**

We now report solid-state intramolecular hydrogen bonding in compound **1** as well as the structures of the salts **2** and **3**. Trifluoroacetamide **1** features two solid-state intramolecular hydrogen bonds: the first is a hydrogen bond between the carbonyl oxygen of the acetamide group and a hydrogen of the quinone ring, while the second is between the N–H of the acetamide and one of the quinone carbonyl oxygens. Salts **2** and **3** exhibit hydrogen bonds between active hydrogens and the relevant counterions.

Hydrogen bonds play a central role in the chemistry of biological systems and can markedly influence conformation.[3,4] The intramolecular hydrogen bonding subset occurs when a proton donor is oriented properly to interact with a proximal acceptor species. The most common acceptors are hard electron-rich species such as carbonyl oxygens, ether or alcohol oxygens, and amine nitrogens. Systems in which the atoms that behave as the proton donor and the acceptor are both highly electronegative can have different hydrogen-bond strengths depending on the distance involved.[5] The hydrogen bond in **1** between the N–H of the acetamide and a quinone oxygen can be classified as a weak hydrogen bond, since the distance involved is 2.26 Å. The second hydrogen bond in **1**, that between the carbonyl oxygen of the acetamide group and a hydrogen of the quinone ring, is less typical; nonbonded contacts of this type are considered to be weak hydrogen bonds since the proton donor involves a hydrogen–carbon bond.[5]

## Experimental section

### *General*

Methanol was dried over 3 Å molecular sieves. Melting points were determined on a Mel-Temp II apparatus and are uncorrected. NMR spectra were obtained with a Bruker AC-300 spectrometer. Tetramethylsilane was used as reference for proton spectra in CDCl$_3$ and DMSO-$d_6$, while for pyridine-$d_5$ the residual proton absorption at $\delta$ 8.71 was used. For carbon spectra the CDCl$_3$ absorption at $\delta$ 77.0, the DMSO-$d_6$ absorption at $\delta$ 39.5, or the pyridine-$d_5$ absorption at $\delta$ 149.9 were used as references. Assignments were made with the aid of coupled spectra and SFORD.

*2-[(trifluoroacetyl)amino]hydroquinone* was prepared according to Aulinger, Arnold, and Steglich.[1]

*2-[(trifluoroacetyl)amino]-1,4-benzoquinone* **1** was isolated from oxidation of the above hydroquinone using iodosobenzene diacetate as reported by Aulinger, Arnold, and Steglich.[1] However, in our hands concomitant deprotection of the amino group did not occur. The red-orange crystalline product gave the following spectra: $^1$H NMR (CDCl$_3$, $\delta$): 8.77 (1H, br, N$H$), 7.62 (1H, d, $J = 2.2$ Hz, $H$-3), 6.91 (1H, d, $J = 9.9$ Hz, $H$-6), 6.84 (1H, dd, $J = 9.9$, 2.2 Hz, $H$-5). $^{13}$C NMR (CDCl$_3$, $\delta$): 186.8 ($C$-4), 181.2 ($C$-1), 155.5 (q, $J_{CF} = 39.2$ Hz, $C$OCF$_3$), 138.3 ($C$-5), 136.5 ($C$-2), 133.4 ($C$-6), 117.6 ($C$-3), 114.7 (q, $J_{CF} = 288.3$ Hz, CO$C$F$_3$).

### *2-Aminohydroquinone hydrochloride **2***

Acetyl chloride (5 mL) was added rapidly dropwise to 50 mL of dry methanol cooled in ice and stirred under nitrogen. After 30 min 1.0 g (4.5 mmol) of the hydroquinone of **1**[1] was added and stirring was continued for 2 days at room temperature. Volatiles were removed on the rotary evaporator followed by high-vacuum drying. The resulting pale yellow-green crystalline solid was recrystallized from absolute ethanol giving dark green plates, mp 219–221 °C with decomposition. $^{1}$H NMR (DMSO-$d_6$, $\delta$): 9.89 (4H, br, $\mathrm{O}H + \mathrm{N}H_3$), 9.28 (1H, br, $\mathrm{O}H$), 6.85 (1H, d, $J = 8.5$ Hz, $H$-6), 6.84 (1H, d, $J = 2.9$ Hz, $H$-3), 6.63 (1H, dd, $J = 8.8$, 2.9 Hz, $H$-5). $^{1}$H NMR (pyridine-$d_5$, $\delta$): 9.86 (5 H, br, $\mathrm{O}H + \mathrm{N}H_{2-3}$), 7.14 (1H, d, $J = 2.9$ Hz, $H$-3), 7.12 (1H, d, $J = 8.8$ Hz, $H$-6), 6.63 (1H, dd, $J = 8.5$, 2.9 Hz, $H$-5). $^{13}$C NMR (DMSO-$d_6$, $\delta$): 150.0 ($C$-4), 143.0 ($C$-1), 118.9 ($C$-2), 116.9 ($C$-6), 115.6 ($C$-5), 110.9 ($C$-3). $^{13}$C NMR (pyridine-$d_5$, $\delta$): 152.8 ($C$-4), 140.4 ($C$-1), 135.1 ($C$-2), 117.1 ($C$-6), 107.5 ($C$-5), 106.2 ($C$-3). For a similar preparation of partially deuterated material see Gould, Shen, and Whittle.[2]

### *2-Aminohydroquinone perchlorate* **3**

A solution of 0.13 g (0.62 mmol) of silver perchlorate in 4 mL of dry methanol was added rapidly dropwise to a stirred solution of 0.10 g (0.62 mmol) of the hydrochloride **2** in 4 mL of methanol. A precipitate formed immediately. The suspension was stirred for 30 min under nitrogen, during which time the color lightened. The precipitated silver chloride was filtered off and washed with a little methanol. The combined filtrate and washings were rotary evaporated and high-vacuum dried leaving a quantitative yield of green crystalline perchlorate. Recrystallization from absolute ethanol gave mp 160-162°C with decomposition. NMR data very similar to the hydrochloride. Similar reactions were used to prepare the tetrafluoroborate and tosylate salts from the chloride.

### *Crystallography*

Single crystals of **1–3** were obtained by slow evaporation of their ethanol solutions. Suitable light yellow crystals of **1** and light grey crystals of **2** and **3** with approximate dimensions $0.55 \times 0.45 \times 0.20$, $0.30 \times 0.20 \times 0.10$, and $0.30 \times 0.25 \times 0.20$ mm were found. Diffraction data for **1–3** were collected at 25°C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Three standard reflections measured after every 97 reflections showed decay for **1** during the experiment, but there was no decay observed for **2** and **3**. For intensities and background, the individual reflection profiles were analyzed. The structures were solved by direct methods. It was found that the fluorine atoms of the trifluoromethyl group in **1** are disordered and occupy two different positions with a ratio of 2:1, which is a usual case for such a group.[6] Refinement was done by full-matrix least-squares first isotropically and then anisotropically for all non-H atoms using *SHELXTL97*.[7] Hydrogen atoms in all structures were placed in geometrically calculated positions and introduced in the refinements using the riding approximation. The final difference map showed no unusual features, with no significant peaks above the general background. Crystal and structure determination data for **1–3** are summarized in Table 1.

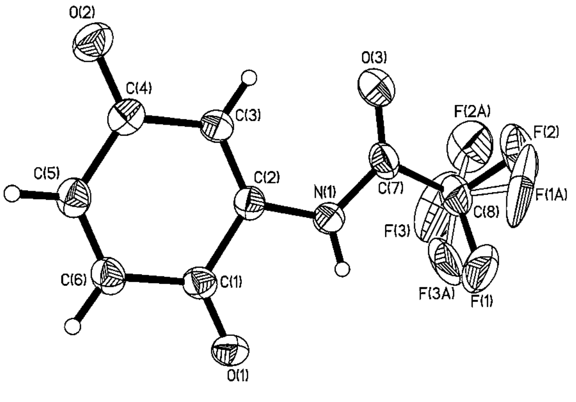

**Fig. 1.** General view of molecule **1**. Fluorine atoms are disordered and occupy two different positions. The non-H atoms are shown with thermal ellipsoids drawn at the 30% probability level.[7] H atoms are drawn as circles of arbitrary small radius for clarity.

**Table 1.** Structure Determination Summary for **1–3**

| | **1** | **2** | **3** |
|---|---|---|---|
| CCDC deposit no. | 210968 | 210969 | 210970 |
| Empirical formula | $C_8H_4F_3NO_3$ | $C_6H_8ClNO_2$ | $C_6H_8ClNO_6$ |
| Formula weight | 219.12 | 161.58 | 225.58 |
| Diffractometer | Enraf-Nonius | Enraf-Nonius | Enraf-Nonius |
| Temperature, K | 298 | 298 | 298 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group; $Z$ | $P2_1/c$; 4 | $Pca2_1$; 4 | $P2_12_12_1$; 4 |
| $a$, Å | 18.195(4) | 16.220(3) | 7.110(1) |
| $b$, Å | 5.110(1) | 5.211(1) | 7.139(1) |
| $c$, Å | 9.635(2) | 8.719(2) | 18.043(4) |
| $\alpha$, ° | 90.00 | 90.00 | 90.00 |
| $\beta$, ° | 104.22(3) | 90.00 | 90.00 |
| $\gamma$, ° | 90.00 | 90.00 | 90.00 |
| Volume, Å$^3$ | 868.4(3) | 737.0(2) | 915.8(3) |
| Density (g/cm$^{-3}$) | 1.676 | 1.456 | 1.636 |
| $\theta$scan range | 2–26 | 3–28 | 2–28 |
| Absorbtion coeff. (mm$^{-1}$) | 0.170 | 0.450 | 0.42 |
| Indep. refls. | 1661 | 930 | 2185 |
| Obs. refls. | 932 | 399 | 847 |
| Final $R_1$ | 0.0965 | 0.0766 | 0.0780 |
| Final $wR_2$ | 0.2195 | 0.1645 | 0.1605 |
| Goodness of fit | 1.029 | 1.024 | 0.944 |

## Results and discussion

General views of the investigated molecules are shown in Figs. 1–3. Selected bond lengths for compounds **1**–**3** are listed in Table 2.

With the exception of the fluorine atoms, molecule **1** has an almost planar structure: the dihedral angle between the flat ring and the similarly flat portion of the trifluoroacetamide fragment is equal to 2.5°. The formation of an intramolecular non-bonded contact between the oxygen atom of

**Table 2.** Selected Bond Distances in the Molecule **1** and Cations **2** and **3**

| Bond | **1** | **2** | **3** |
|---|---|---|---|
| O(1)—C(1) | 1.212(4) | 1.35(1) | 1.341(9) |
| O(2)—C(4) | 1.227(5) | 1.37(1) | 1.387(8) |
| O(3)—C(7) | 1.202(6) | — | — |
| N(1)—C(2) | 1.391(5) | 1.45(2) | 1.458(7) |
| N1—C(7) | 1.361(5) | — | — |
| C(1)—C(2) | 1.484(5) | 1.40(2) | 1.380(9) |
| C(2)—C(3) | 1.329(5) | 1.38(2) | 1.375(9) |
| C(3)—C(4) | 1.456(5) | 1.37(1) | 1.351(9) |
| C(4)—C(5) | 1.463(6) | 1.39(2) | 1.369(9) |
| C(5)—C(6) | 1.317(5) | 1.38(2) | 1.383(9) |
| C(6)—C(1) | 1.470(5) | 1.36(2) | 1.36(1) |
| C(7)—C(8) | 1.501(7) | — | — |

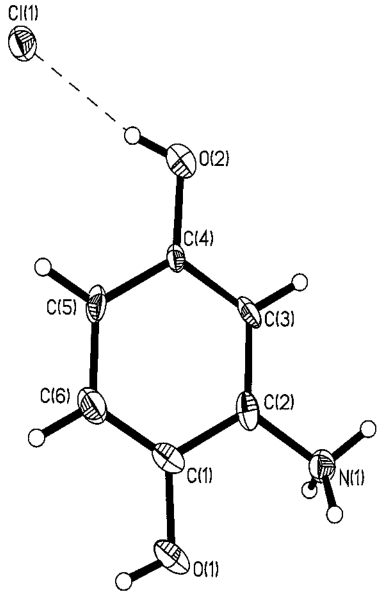

**Fig. 2.** General view of salt **2.** Cation and anion are linked by H-bond O–H···Cl. The non-H atoms are shown with thermal ellipsoids drawn at the 30% probability level.[7] H atoms are drawn as circles of arbitrary small radius for clarity.

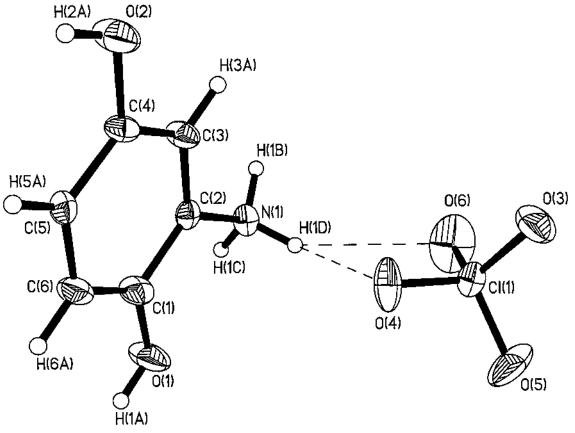

**Fig. 3.** General view of salt **3.** A fork H-bond links the cation and anion to each other. The non-H atoms are shown with thermal ellipsoids drawn at the 30% probability level.[7] H atoms are drawn as circles of arbitrary small radius for clarity.

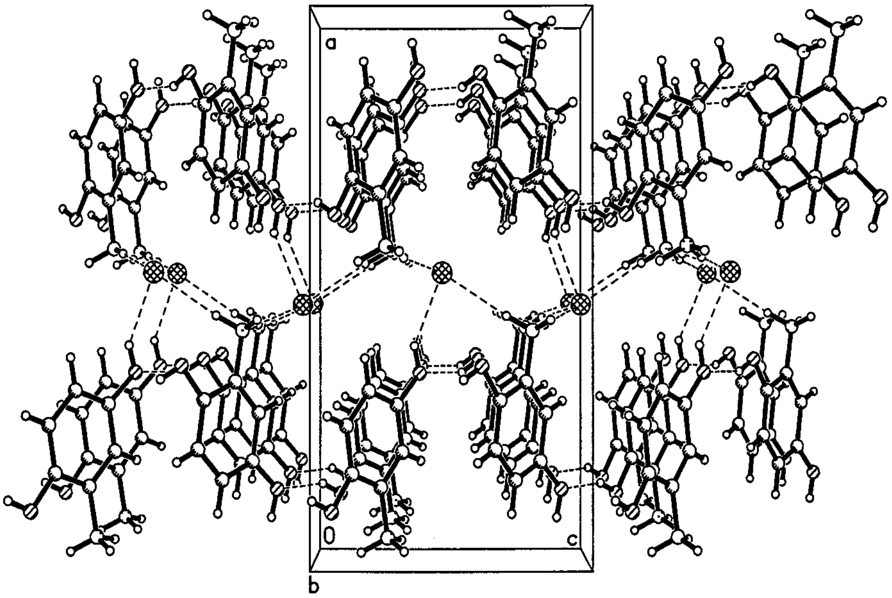

**Fig. 4.** A projection onto the *ac* plane showing the H-bonding scheme of salt **2**.

the carbonyl group of the acetamide group and the H3A atom of the quinone ring contributes to this arrangement. According to literature data describing C–H—O contacts,[5] a C—O distance of less than 3.25 Å is a conservative threshold for distinguishing weak hydrogen bond contacts from classical van der Waals contacts. In our case, the parameters for this contact in compound **1** are: C3–H3A 0.93 Å, H3A···O3 2.24 Å, C3···O3 2.843(6) Å, angle C3–H3A···O3 122°. Thus we assign this contact to be a weak intramolecular hydrogen bond rather than a classical van der Waals contact. That a six-membered ring forms likely facilitates hydrogen bond formation and the

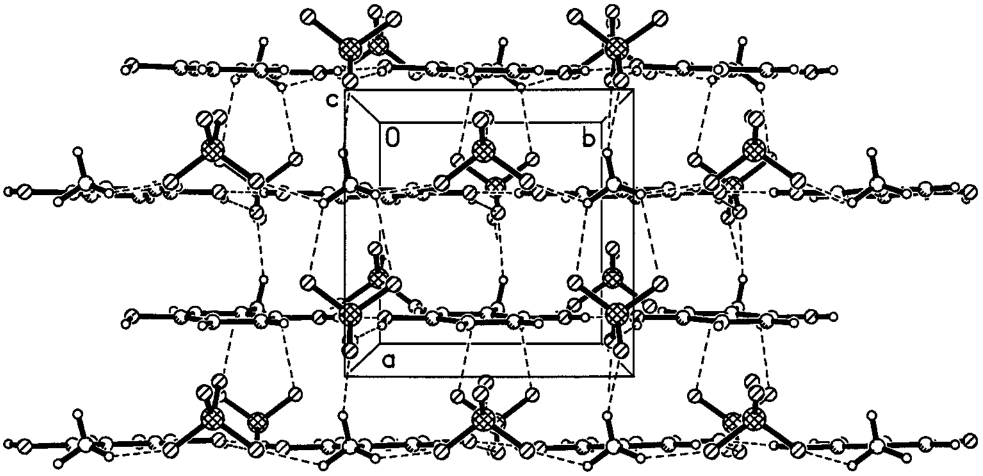

**Fig. 5.** A projection onto the *ab* plane showing the H-bonding scheme of salt **3**.

**Table 3.** Hydrogen-Bond Parameters for **2**

| D—H | $d$(D—H) | $d$(H···A) | ∠DHA | $d$(D···A) | $A$ |
|---|---|---|---|---|---|
| O1—H1A | 0.82 | 1.95 | 154 | 2.711 | O2 $[-x+1/2, y+1, z-1/2]$ |
| O2—H2A | 0.82 | 2.33 | 148 | 3.059 | Cl1 $[x, y, z]$ |
| N1—H1B | 0.89 | 2.28 | 173 | 3.170 | Cl1 $[x-1/2, -y, z]$ |
| N1—H1C | 0.89 | 2.28 | 168 | 3.200 | Cl1 $[-x+1/2, y, z-1/2]$ |
| N1—H1D | 0.89 | 2.28 | 168 | 3.143 | Cl1 $[x-1/2, -y+1, z]$ |

**Table 4.** Hydrogen-Bond Parameters for **3**

| D—H | $d$(D—H) | $d$(H···A) | ∠DHA | $d$(D···A) | $A$ |
|---|---|---|---|---|---|
| O1—H1A | 0.82 | 1.87 | 175 | 2.689 | O2 $[x, y+1, z]$ |
| O2—H2A | 0.82 | 1.95 | 160 | 2.734 | O4 $[x-1/2, -y-1/2, -z]$ |
| N1—H1B | 0.89 | 2.14 | 154 | 2.968 | O5$[-x+1, y-1/2, -z+1/2]$ |
| N1—H1B | 0.89 | 2.47 | 121 | 3.033 | O3 $[x-1, y, z]$ |
| N1—H1C | 0.89 | 2.28 | 137 | 2.987 | O5 $[x-1, y, z]$ |
| N1—H1C | 0.89 | 2.34 | 125 | 2.938 | O3 $[-x+1, y+1/2, -z+1/2]$ |
| N1—H1D | 0.89 | 2.10 | 147 | 2.885 | O4 $[x, y, z]$ |
| N1—H1D | 0.89 | 2.52 | 146 | 3.294 | O6 $[x, y, z]$ |

resulting arrangement leads to flattening of the molecule.

It should also be noted that hydrogen atom H1A of compound **1**, which is bonded to N1, forms a short intramolecular contact with O1 of the quinone ring with a distance of 2.26 Å. This is less than the sum of the van der Waals radii of these atoms.[8] The N1—O1 distance is 2.64 Å and the N1–H1A—O1 angle is 107°. This hydrogen bond creates a five-membered ring and also helps to flatten this portion of the molecule. The hydrogen bond parameters are consistent with a related N–H—O intramolecular hydrogen bond that we have recently described.[9]

In salts **2** and **3,** all active hydrogen atoms participate in hydrogen bond formation and link cations and anions into three-dimensional frameworks (Tables 3 and 4 and Figs. 4 and 5). We observed the following types of hydrogen bonds in these salts (refer to the figures for the exact structural elements involved): O–H—O, O–H—Cl, N–H—Cl, and N–H—O. Most of these hydrogen bonds can be considered to be weak. The remaining geometrical parameters in the investigated molecules have standard values.[10]

## Acknowledgment

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## Supplementary material

CCDC-210968-210970 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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