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Spontaneous oxidation of organic donors to their cation radicals using Brønsted acids. Identification of the elusive oxidant†

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Various electron-rich aromatic and olefinic donors (**D**) are readily converted to their cation radicals ($\mathbf{D}^{+\bullet}$) in the presence of strong protic acids, even in nonpolar solvents such as dichloromethane. By using the three prototypical organic donors octamethylbiphenylene (**OMB**), adamantylideneadamantane (**AA**) and the isomeric fused homoadamantene (**FHA**), we identify the protonated donor (**D**-H$^+$) as the effective oxidant for electron transfer from the organic donor (*i.e.*, $\mathbf{D}\text{-H}^+ + \mathbf{D} \longrightarrow \mathbf{D}\text{-H}^\bullet + \mathbf{D}^{+\bullet}$). The subsequent reduction of (**D**-H$^\bullet$) to the dihydro product **D**-H$_2$ is demonstrated by the isolation of 2,2′-biadamantane, the structure of which is established by X-ray crystallography.

Introduction

The one-electron oxidation of a variety of electron-rich organic donors (**D**) by dissolution in Brønsted acids such as sulfuric acid, trifluoromethanesulfonic acid, fluorosulfonic acid, perchloric acid, methanesulfonic acid, trichloroacetic acid, trifluoroacetic acid, *etc.* has been a well-accepted method for the production of cation radicals ($\mathbf{D}^{+\bullet}$) in solution, especially for EPR spectroscopy.[1–3] The Brønsted acids are also utilized for the quantitative isolation of the cation radical salts in the presence of quinones, ketones, carboxylic acids, *etc.* as sacrificial oxidants.[4,5]

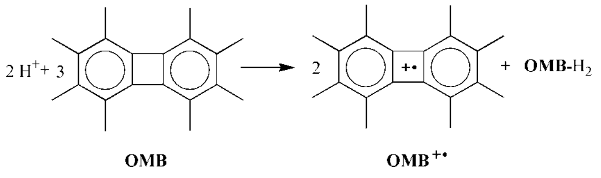
The oxidation process with Brønsted acids is often attributed to the presence of adventitious oxygen.[6] However, Illuminati *et al.*[7] showed that easily oxidizable organometallic donors such as ferrocene ($E^\circ_{ox} = 0.45$ V *vs.* SCE) and decamethylferrocene ($E^\circ_{ox} = 0.01$ V *vs.* SCE) undergo rapid one-electron oxidation to the corresponding ferricinium cations even in the absence of oxygen. Moreover, they also showed, by careful experimentation,[7] that hydrogen gas was not evolved during the oxidation of ferrocenes with various acids. Hart and co-workers[8] indicated that the protonated aromatic donor (**D**-H$^+$) itself can act as a one-electron oxidant towards **D**. Recently, Eberson and Radner[9] suggested that the oxidation of electron-rich anthracene derivatives to the corresponding cation radicals, particularly in trifluoroacetic acid, may be accelerated by light.

Despite the extensive use of acids to generate the cation radicals in solution, experimental evidence for how the oxidation actually occurs is singularly lacking.[4] Accordingly in this report, we utilize the three prototypical electron donors octamethylbiphenylene (**OMB**), adamantylideneadamantane (**AA**), and the isomeric fused homoadamantene (**FHA**) with $E^\circ_{ox} = 0.78$, 1.46, and 1.34 V *vs.* SCE, respectively, to show that carbocations **D**-H$^+$ (arising from the protonation of the donor molecule) act as oxidants for the production of cation radicals in various protic acids. Moreover, the isolation of the reduced product (*i.e.* **D**-H$_2$) from adamantylideneadamantane with various acids forms the basis for the discussion of the mechanism of oxidation of organic donors in the presence of Brønsted acids.

Results and discussion

Oxidation of octamethylbiphenylene with Brønsted acids

When a 0.12 mM solution of octamethylbiphenylene (**OMB**) in a mixture of dichloromethane and methanesulfonic acid (~10%), was vigorously stirred under a pure argon atmosphere at 25 °C, it immediately turned bright blue. The UV-vis spectral analysis of the blue solution (see Fig. 1) confirmed the formation of octamethylbiphenylene cation radical ($\mathbf{OMB}^{+\bullet}$) [$\lambda_{max} = 602$ and 550(sh) nm, $\varepsilon_{602} = 12000$ M^{-1} cm^{-1}].[4,10] A careful spectrophotometric (UV-vis) quantification revealed that the $\mathbf{OMB}^{+\bullet}$ was rapidly formed in 66% yield within 1 min (see Fig. 1), and essentially no further absorbance change (at $\lambda_{mon} = 602$ nm) was observed during the course of the next 30 min. Such a rapid formation of $\mathbf{OMB}^{+\bullet}$ to attain a critical conversion of 66% was diagnostic of a 3:2 stoichiometry (eqn. (1)). Similarly,



OMB $\mathbf{OMB}^{+\bullet}$

(1)

the oxidation of **OMB** to its cation radical in eqn. (1) can also be effected with other protic acids, such as tetrafluoroboric acid (HBF$_4$), trifluoromethanesulfonic acid (CF$_3$SO$_3$H), or sulfuric acid (H$_2$SO$_4$) in dichloromethane at 25 °C. [Note that upon standing for prolonged periods (~10 h), the above dark blue solution (from eqn. (1)) eventually produces $\mathbf{OMB}^{+\bullet}$ in nearly quantitative yield, as shown pictorially in Fig. 1.]

In order to confirm the 3:2 stoichiometry in eqn. (1), we attempted the isolation and characterization of the reduced dihydro product (*i.e.* **OMB**-H$_2$) as follows. A 0.1 M solution of octamethylbiphenylene (**OMB**) in dichloromethane containing either methanesulfonic acid (~10%) or tetrafluoroboric acid (10%) was stirred under a rigorously oxygen-free argon atmosphere at 25 °C. The resultant bright blue solution was analyzed by UV-vis spectroscopy to show that a 63% yield of **OMB** cation radical was produced during the course of 5 min. The dark blue solution was rapidly quenched (with solid sodium carbonate and excess zinc dust) and the resulting mixture was stirred for an additional 5 min and filtered. The GC and

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† Dedicated in memoriam to Lennart Eberson, a friend to whom this problem was a source of continuing beguilement.

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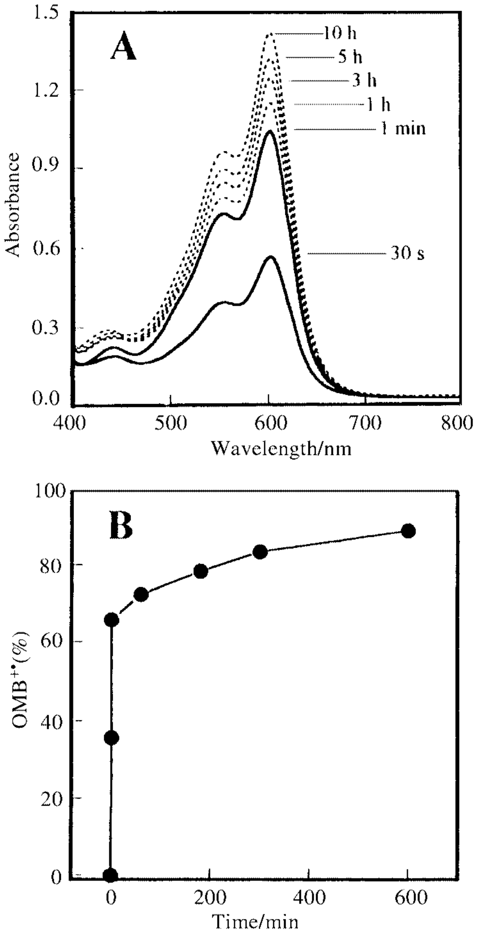


Fig. 1 A. Progressive oxidation of octamethylbiphenylene (0.12 mM) in dichloromethane containing methanesulfonic acid (~10%, v/v). B. The biphasic rate of growth of the cation radical **OMB**$^{+•}$.

GC-MS analysis of the pale yellow solution showed that it contained only the neutral octamethylbiphenylene (yield = 97%). We then conjectured that even if the dihydro-aromatic reduction product **OMB**-H$_2$ was formed in eqn. (1), it was too susceptible to oxidative aromatization, and not readily isolated.[11] In order to isolate the reduced product (**D**-H$_2$) in eqn. (1), we now employ a sterically hindered olefinic donor adamantylideneadamantane (**D**) using various Brønsted acids which leads to the isolation of reduced product (**D**-H$_2$) as follows.

Isolation and identification of the reduced donor using adamantylideneadamantane (AA)

To a solution of adamantylideneadamantane **AA** (100 mg, 0.3 mmol) in purified dichloromethane (10 mL) was added trifluoromethanesulfonic acid (1 ml, 10%) under an argon atmosphere at −10 °C. After stirring the reaction mixture for 3 h at ambient temperature, it was rapidly quenched with saturated aqueous sodium bicarbonate solution (25 mL), and the organic layer was separated, dried (with magnesium sulfate), and evaporated *in vacuo*. Chromatographic purification of the crude solid residue indicated that the mixture contained 2,2′-biadamantane (32%), adamantylideneadamantane 2,2′-oxide (21%), rearranged spiro[adamantane-2,2′-[2a]homoadamantan]-2′a-one (25%), together with small amounts of several unidentified products (see the Experimental section), *i.e.* (eqn. (2)).

It is important to note that in the reduction of **AA** to 2,2′-biadamantane, the donor moiety maintains its structural identity, as confirmed by X-ray structure analysis (see Fig. 2) of a single crystal of **AA**-H$_2$ grown from a 1 : 1 mixture of hexane and ethanol. Moreover, it is noteworthy that other acids such as sulfuric acid and fluorosulfonic acid gave similar yields of reduced biadamantane (**AA**-H$_2$) together with the oxygen-containing products in eqn. (2).[12] However, weaker acids (such as methanesulfonic acid and trifluoroacetic acid) produced only traces of 2,2′-biadamantane (**AA**-H$_2$) even after prolonged stirring (see the Experimental section).

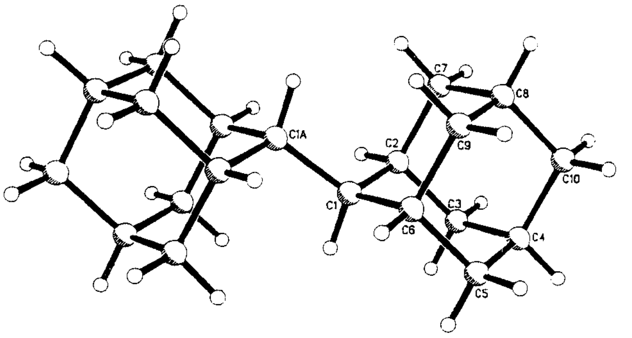
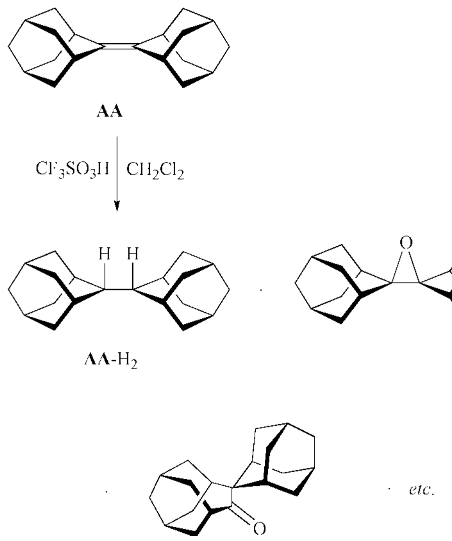


Fig. 2 X-Ray structure of reduced adamantylideneadamantane (**AA**-H$_2$).



(2)

In order to probe the source of the hydrogen atoms in the reduced biadamantane (**AA**-H$_2$), we carried out the reaction in dichloromethane-d$_2$ (CD_2Cl_2) containing trifluoromethanesulfonic acid. The reaction mixture was stirred for 3 h at 25 °C and was quenched with saturated solution of sodium carbonate in D_2O. A careful mass spectral analysis of the crude mixture showed no sign of deuterium incorporation into the reduced product. However, when the same reaction was carried out in the presence of trifluoromethanesulfonic acid-d (CF_3SO_3D), the resulting reduced product was identified by GC-MS and NMR spectroscopy to be 2,2′-deuterio-2,2′-biadamantane (**AA**-D$_2$). Thus, these experiments confirm that both protons in the reduced product (**AA**-H$_2$) derive from the acid rather than the solvent.

Mechanism of the oxidation of organic donors by Brønsted acids

Scheme 1 presents the mechanism of the oxidation of organic

$$\mathbf{D} + H^+ \rightleftharpoons \mathbf{D}\text{-}H^+ \qquad (3)$$

$$\mathbf{D}\text{-}H^+ + \mathbf{D} \rightleftharpoons \mathbf{D}\text{-}H^{\bullet} + \mathbf{D}^{+\bullet} \qquad (4)$$

Scheme 1

donors to the corresponding cation radicals based on the various experimental results described above. Thus, the oxidation of octamethylbiphenylene to its cation radical in the critical yield of 66% and the formation of the reduced dihydro-adamantylideneadamantane (**AA**-H$_2$) in 31% yield with various

Brønsted acids confirm the 3:2 stoichiometry in eqn. (1). We posit that the initial protonation of the organic donor (**D**) produces the carbocationic intermediate (**D**-H$^+$) which acts as the oxidant towards the neutral donor (**D**) (as presented in eqns. (3) and (4) in Scheme 1).

The resulting radical **D**-H$^\bullet$ can be converted to the reduced product (**D**-H$_2$) either in a series of proton transfer and electron transfer steps (*i.e.* eqns. (5) and (6)) or *via* a disproportionation mechanism (*i.e.* eqn. (7)). We cannot at this juncture distinguish

$$\mathbf{D}\text{-H}^\bullet + \text{H}^+ \rightleftharpoons \mathbf{D}\text{-H}_2^{+\bullet} \qquad (5)$$

$$\mathbf{D}\text{-H}_2^{+\bullet} + \mathbf{D} \rightleftharpoons \mathbf{D}\text{-H}_2 + \mathbf{D}^{+\bullet} \qquad (6)$$

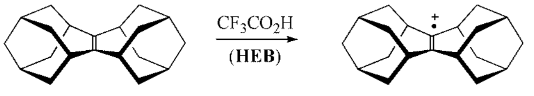
$$\mathbf{D}\text{-H}^\bullet + \mathbf{D}\text{-H}^\bullet \rightleftharpoons \mathbf{D} + \mathbf{D}\text{-H}_2 \qquad (7)$$

between the two mechanisms for the formation of the reduced products without undue speculation. However, the intermediacy of the carbocation as oxidant can be demonstrated by using the highly-hindered fused homoadamantene (**FHA**) as an electron donor, as described below.

Oxidation of the fused homoadamantene (FHA) with DDQ–CF_3COOH

We proceed from the fact that a mixture of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)–trifluoroacetic acid (CF_3COOH) in dichloromethane is known to readily oxidize a variety of organic donors ($E^\circ_{ox} \leq 1.7$ V *vs.* SCE) to the corresponding cation radicals in dichloromethane.[4,5] **FHA**[13] is such a readily oxidizable olefinic donor with $E^\circ_{ox} = 1.34$ V and it is known to form its stable red-colored cation radical. However the mixing of **FHA** with a solution of DDQ–trifluoroacetic acid in dichloromethane at −30 °C merely resulted in a pale yellow mixture. This solution was stable for several hours at −30 °C without any perceptible color change, as monitored by UV-vis spectroscopy (see the Experimental section).

The singular lack of formation of the cation radical of the fused homoadamantene from the DDQ–CF_3COOH mixture can be readily attributed to the fact that the highly-hindered **FHA** does not undergo protonation in trifluoroacetic acid.[13] However, the addition of another donor which is readily protonated by trifluoroacetic acid (such as hexaethylbenzene, **HEB** with $E^\circ_{ox} = 1.59$ V *vs.* SCE[14]) to the above pale yellow solution, immediately yields a dark red solution. The UV-vis spectral analysis of the red solution confirmed the formation of the cation radical **FHA**$^{+\bullet}$ (eqn. (8)) [$\lambda_{max} = 360$ and 485(sh) nm, $\varepsilon_{360} = 4000$ M^{-1} cm^{-1}] in 35% yield (see the Experimental section).[13c] Thus, these experimental findings further support the thesis that the protonated donor (*i.e.* protonated hexaethylbenzene **D**-H$^+$) acts as oxidant in the conversion of the fused homoadamantene to its cation radical (eqn. (4))—the role of DDQ being to intercept the resulting radical **D**-H$^\bullet$ by its ready oxidation to the carbocation **D**-H$^+$.[4]



(8)

FHA **FHA**$^{+\bullet}$

Thus all results consistently point to the protonated carbocations as the effective oxidant in the production of cation radicals from various electron-rich donors using Brønsted acids.

Experimental

Materials

The neutral donors octamethylbiphenylene[8] (**OMB**), adamantylideneadamantane[15] (**AA**), and **FHA**[15] were available from the standard literature procedures. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~20% by volume) until the acid layer remained colorless. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexane and toluene were distilled from P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH_2, the solvents were stored in the Schlenk flasks under an argon atmosphere.

Instrumentation

The UV-vis absorption spectra were recorded on HP 8453 diode array and Varian CARY 5 (UV-vis-NIR) spectrometers. The ^{1}H and ^{13}C NMR spectra were obtained on a General Electric QE-300 FT NMR spectrometer. Electrochemical apparatus and the procedures for the determination of oxidation potentials have been described elsewhere.[16]

Oxidation of octamethylbiphenylene (OMB) by Brønsted acids in dichloromethane. General procedure

To a solution of octamethylbiphenylene (26.4 mg, 0.10 mmol) in anhydrous dichloromethane (9 mL) was added methanesulfonic acid (1 mL) under an argon atmosphere with the aid of a hypodermic syringe. The color of the solution immediately turned bright blue and an aliquot of the highly colored solution was analyzed periodically by UV-vis spectroscopy, as shown in Fig. 1. For example within 1 min 66% of the **OMB**$^{+\bullet}$ had been formed and essentially no further absorbance change (at $\lambda_{mon} = 602$ nm) was observed during the course of 30 min. The blue solution was quenched by addition of solid sodium carbonate (5 g) and zinc dust (2 g). The resulting heterogeneous mixture was stirred for 10 min and it was filtered to afford a clear pale yellow solution. The GC and GC-MS analysis of the pale yellow solution (using an internal standard method) showed that octamethylbiphenylene was recovered quantitatively (98.5%). A similar procedure was employed for the oxidation of octamethylbiphenylene with different Brønsted acids (see earlier).

Reaction of adamantylideneadamantane (AA) with Brønsted acids. General procedure

To a cold (−10 °C) solution of **AA** (26.8 mg, 0.1 mmol) in dichloromethane (10 mL) was added trifluoromethanesulfonic acid (0.2 mL). The NMR spectrum of the resulting solution showed that a considerable amount of the **AA** was protonated. The colorless mixture was warmed to room temperature and stirred for 3 h. The resultant pale yellow reaction mixture was quenched with saturated aqueous sodium bicarbonate (10 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. The GC and GC-MS analysis of the crude product (using octadecane as an internal standard) indicated that the mixture contained reduced 2,2′-biadamantane **AA**-H$_2$ (32%), adamantylideneadamantane 2,2′-oxide (21%), the rearranged spiroketone (25%), together with several unidentified products. The crude product mixture (collected from four different runs under the same reaction conditions) upon chromatographic purification on silica gel with 25:75 ether–hexane mixture as eluent and recrystallization from methanol afforded pure 2,2′-biadamantane **AA**-H$_2$ (31%), mp 184–185 °C (lit.[17] 184–186 °C); ^{1}H NMR ($CDCl_3$) δ 1.38–1.88 (m, 30H); ^{13}C NMR ($CDCl_3$) δ 27.90, 28.06, 28.23, 31.63, 38.42, 39.61, 42.40; GC-MS *m*/*z* 270 (M$^+$), calcd for $C_{20}H_{30}$ *M* 270, together with the adamantylideneadamantane oxide[15] (17%) and the rearranged spiroketone[15] (27%). A similar procedure was employed for reduction of adamantylideneadamantane with different Brønsted acids (see earlier).

Reaction of adamantylideneadamantane (AA) with CF_3SO_3D

To a cold (−10 °C) solution of **AA** (26.8 mg, 0.1 mmol) in dichloromethane (10 mL) was added CF_3SO_3D (0.2 mL) and the resulting mixture was stirred for 3 h at 25 °C. The resultant pale yellow solution was quenched with saturated aqueous sodium bicarbonate (10 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. The GC and GC-MS analysis of the crude product (using octadecane as an internal standard) indicated that the mixture contained reduced 2,2′-biadamantane **AA**-D_2 [29%, ^{13}C NMR ($CDCl_3$) δ 27.90, 28.06, 28.23, 31.63, 38.42, 39.61, 42.40 (m); GC-MS *m*/*z* 272 (M^+), calcd for $C_{20}H_{28}D_2$ *M* 272] together with the adamantylideneadamantane oxide[15] (22%) and the rearranged spiroketone[15] (26%).

Oxidation of FHA

To a cold (−30 °C) solution of the fused homoadamantene (6 mg, 0.02 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (2.3 mg, 0.01 mmol) in dichloromethane (4.5 mL) was added trifluoroacetic acid (0.5 mL) in one portion. The resulting pale yellow mixture was stirred for 1 hour at −30 °C without any color change as monitored by UV-vis spectroscopy. [Moreover, a small aliquot (1 mL) of the reaction mixture was quenched (rapidly) with saturated aqueous sodium bicarbonate (10 mL) and the organic layer was separated and dried with anhydrous magnesium sulfate. The GC, GC-MS analysis of the pale yellow solution (using an internal standard method) showed that it contained only the fused homoadamantene **FHA** (98%).] To the stable pale yellow solution containing **FHA**, DDQ and trifluoroacetic acid at −30 °C was added a catalytic amount of hexaethylbenzene (1.5 mg, 0.006 mmol). The resulting mixture immediately turned reddish brown and the color intensified during the course of 30 min. A quantitative UV-vis spectral analysis of the red solution confirmed the formation of the cation radical **FHA**$^{+\bullet}$ [$\lambda_{max} = 360$ and 485(sh) nm, $\varepsilon_{360} = 4000$ M^{-1} cm^{-1}][13] in 35% yield. Quenching of the reaction mixture with solid sodium carbonate followed by zinc dust (as above) recovered the neutral **FHA** quantitatively (96%) together with traces of the isomeric adamantylideneadamantane (**AA**).[13]

X-Ray crystallography

The intensity data were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using Mo-Kα radiation ($\lambda = 0.71073$ Å), at −150 °C. The structure was solved by direct methods[18] and refined by full matrix least-squares procedure with IBM Pentium and SGI O_2 computers.

Crystal data for 2,2′-biadamantane [AA-H_2]. X-Ray quality crystals of 2,2′-biadamantane (**AA**-H_2) were obtained from a carefully layered solution of **AA**-H_2 (30.6 mg) in dry dichloromethane (10 mL) with hexane (20 mL) at −30 °C. A single crystal of **AA**-H_2 with dimensions 0.42 × 0.20 × 0.15 mm was mounted for data collection. Brutto formula: [$C_{20}H_{30}$], $M = 270.44$, monoclinic $C2/c$, $a = 9.2428(5)$, $b = 9.0959(11)$, and $c = 18.4539(13)$ Å, $\beta = 103.634(1)°$, $D_c = 1.191$ g cm^{-3}, $V = 1507.7(2)$ Å^3, $Z = 4$. The total number of reflections measured was 10681, of which 3308 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0390$ and $wR2 = 0.1039$ for 2493 reflections with $I > 2\sigma(I)$.‡

Acknowledgements

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‡ CCDC reference number 188/259. See http://www.rsc.org/suppdata/p2/b0/b003860l/ for crystallographic files in .cif format.

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