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ORIGINAL PAPER

Monitoring Structural Transformations in Crystals. Part 15. Structural Changes in Crystals Caused by UV Radiation Despite the Lack of a Photochemical Reaction

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Abstract Crystals of 3-benzoylbicyclo[2.2.1]heptane-2-carboxylic acid ($C_{15}H_{16}O_3$) do not undergo the photochemical reaction, namely the Yang photocyclization, but they undergo UV radiation damage. The initial stages of this process were monitored by X-ray diffraction and structure analysis. The results show that the process is smooth and accompanied by the decrease of the overall scale factor, the certain increase of width of reflections, the increase of the cell parameters, intermolecular distances, atomic displacement parameters and the small changes in orientation of molecular fragments.

Keywords X-ray structure analysis · Photochemical reaction · Monitoring photo-induced structural changes · UV radiation damage

Introduction

In the recent decade the papers on monitoring photochemical reactions in crystals by means of X-ray structure analysis have started to appear in the scientific literature [1–12]. Those papers have provided the knowledge on structural changes brought about by photochemical reactions, in particular in a reaction center and positions of molecules in crystals.

X-ray structure analysis has also helped to monitor the decrease of crystal diffracting power caused by X-rays [13–20] (crystal damage by bright X-ray beams is a serious problem in crystallographic studies of macromolecules

[14–20]). However, monitoring crystal damages caused by UV radiation has been extremely rare [21].

In this paper, we present results of monitoring structural changes induced by UV radiation in crystals of 3-benzoylbicyclo[2.2.1]heptane-2-carboxylic acid, compound (1). See Scheme 1a for the chemical formula. Compound (1) does not undergo a photochemical reaction. Nevertheless, we discovered and monitored interesting UV radiation damage in its crystals.

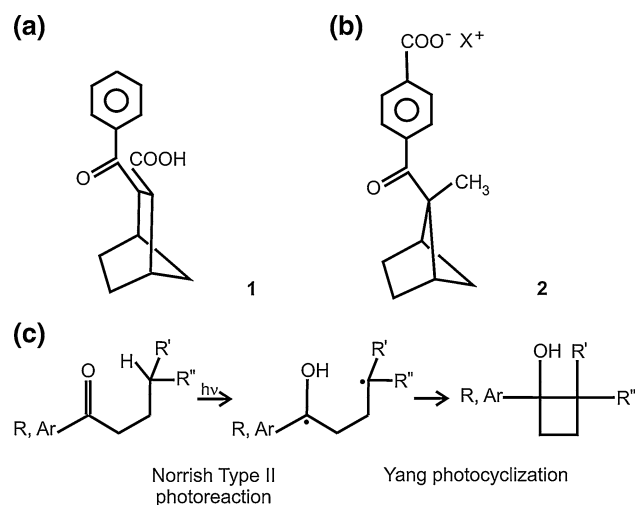
Materials and Methods

Crystallographic Studies

Compound (1) was purchased from Acros Organics. The main crystallographic experiment was carried out for one crystal at ambient temperature and in the dark (however, we also examined two other crystals but not in detail). The crystal was irradiated in steps by an Hg 100 W lamp. The lamp was equipped with a water filter to protect the sample from heating. The beam was directed perpendicularly to the longest crystal edge and the crystal was rotated during irradiation. The exposure times were as follows: 0, 60, 120, 240, 360, 480, and 660 min in total. During the whole irradiation the crystal did not change its size, shape, transparency and color. However, after 120 min a few (five) very small cracks appeared.

After each UV exposure of the crystal, the X-ray data were collected by means of a CCD diffractometer. The general strategy for data collection using area-detector diffractometer was described by Scheidt and Turowska-Tyrk [22]. The cell constants were determined on the basis of the 1,000 strongest reflections by the CrysAlis software

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Scheme 1 The formula of (a) compound (1) and (b) compound (2). c The Norrish-Yang reaction scheme

[23]. The data reductions were also carried out with the same software.

The structure of a non-irradiated crystal of compound (1) was published previously [24]. We redetermined it in order to have all data coming from the same sample. The structures were solved by means of SHELXS97 and refined using SHELXL97 [25]. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were found in difference Fourier maps and refined without constraints for the irradiated structures except those for 480 and 660 min of irradiation. For these two cases positions of H atoms were

calculated geometrically and refined with constraints and the H atom in the carboxylic group was omitted.

The selected experimental data are given in Table 1 for three structures. The data for all refinements are given in the supplementary material.

In order to check if the studied process was not influenced by X-rays we compared diffraction patterns measured at the beginning and at the end of the each data collection. It occurred that they were the same. We also checked that visible radiation did not cause any changes in diffraction patterns.

Additionally, we collected reflections for two more crystals irradiated during 5 h at 50 and 100 °C, respectively and for two crystals obtained after recrystallization of powder irradiated during 12 h.

NMR and IR Studies

In order to check whether the Yang cyclization or any chemical reaction caused by radiation has occurred in objects which stopped being crystals, the ^1H NMR spectra of (1) and the irradiation product were also measured (Bruker Avance DRX spectrometer). (1) δ_{H} (300 MHz, CDCl_3 , Me_4Si): 1.34–1.51 (4H, m, CH_2), 1.59 (1H, d, J 9.9 Hz, CH), 1.94–2.02 (1H, m, CH), 2.60 (1H, br s, CH), 2.67 (1H, br s, CH), 3.00 (1H, dq, J 11.1, 1.8 Hz, CH), 4.04 (1H, ddd, J 11.1, 4.2, 1.2 Hz, CH), 7.41–7.55 (3H, m, ArH), 7.89 (2H, d, J 7.9 Hz, ArH). In comparison with (1), the ^1H NMR spectrum of the irradiated powder (10 h) was almost identical. The only changes which can be observed

Table 1 Experimental data for the crystal irradiated during 0, 4 and 11 h. The full data are available in the supplementary material

	0 min	240 min	660 min
Chemical formula	$\text{C}_{15}\text{H}_{16}\text{O}_3$	$\text{C}_{15}\text{H}_{16}\text{O}_3$	$\text{C}_{15}\text{H}_{16}\text{O}_3$
M_r	244.28	244.28	244.28
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
T (K)	299 (2)	299 (2)	299 (2)
a (Å)	9.809 (2)	9.8634 (19)	9.885 (2)
b (Å)	5.9731 (13)	6.0019 (11)	6.0267 (11)
c (Å)	21.608 (4)	21.625 (4)	21.646 (4)
β (°)	99.61 (2)	99.79 (2)	100.20 (2)
V (Å ³)	1248.2 (4)	1261.5 (4)	1269.2 (4)
Z	4	4	4
D_x (Mg m^{-3})	1.300	1.286	1.278
μ (mm^{-1})	0.09	0.09	0.09
No. of measured, independent and observed reflections	6,472, 2,162, 1,752	6,580, 2,186, 1,534	6,635, 2,199, 1,079
R_{int}	0.037	0.042	0.068
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.104, 1.06	0.049, 0.160, 1.09	0.068, 0.240, 1.01
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å^{-3})	0.15, -0.14	0.18, -0.20	0.21, -0.18

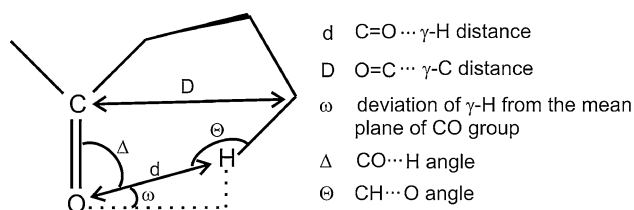
were disappearance of the smallest coupling constant in the signal at 4.04 ppm and distortion of the smaller coupling constant in the signal at 3.00 ppm. However, these changes disappeared completely in the spectrum of the same powder but measured after some time (3 months).

The solid state IR spectrum (KBr) of the irradiated powder was identical to the spectrum of (1) known from literature [24].

Results and Discussion

Compound (1) has a hydrogen atom in a γ -position from a carbonyl group, see Scheme 1a. Such compounds can potentially undergo the Yang photocyclization. Scheme 1b shows the formula of a similar compound (2), undergoing this photochemical reaction and studied by us in the past [9]. The Yang photocyclization is the second step of the Norrish-Yang reaction and involves formation of a cyclobutane ring from a 1,4-hydroxybiradical, see Scheme 1c [26]. The first step of the Norrish-Yang reaction can be reversible.

There exist several parameters describing the geometrical conditions which must be fulfilled by a chemical compound undergoing the Norrish-Yang reaction in a crystalline state. The definition of these parameters is presented in Scheme 2. Table 2 gives their ideal values, the average literature values, the range for crystals where this reaction proceeds and the results for compound (1) before



Scheme 2 The definition of the intramolecular geometrical parameters

crystal irradiation. For comparison, the data for compound (2) were also included. As can be seen, the values of the parameters for (1) are in the ranges observed for the compounds undergoing the Yang photocyclization. We decided to irradiate crystals of (1) and found out that they are sensitive to UV radiation. Owing to this we monitored the photo-induced changes in the cell parameters and determined the photo-induced crystal structures. During the experiments we noticed disappearance of crystal diffracting power caused by UV radiation.

Monitoring the Cell Parameters

Figure 1 presents the variations in the cell parameters and the cell volume along with the time of crystal irradiation by a UV beam. As can be noticed, the cell parameters and the cell volume increase with the irradiation time. The size of the changes in a , b and c is similar.

Changes in cell constants are a typical symptom of chemical reactions proceeding in crystals. In the case of intra- and intermolecular chemical processes, a cell volume can change by several percent [4, 7–11]. It is interesting that even for one type of a chemical reaction, cell constants and a cell volume for different compounds can change in a different manner [34, 35].

It should be also said that a phenomenon of an increase of cell constants caused by electromagnetic radiation is known in the crystallographic literature concerning radiation damage, however, in the case of use of X-rays [13–20] and not for UV radiation. An increase of a cell volume resulting from X-rays damages was described in the last decade mainly for crystals of macromolecules. For such crystals this increase is linear in most cases [17, 18]. However, a non-linear dependence was also presented [14] and even a decrease of a cell volume was described [36]. In the case of X-rays and crystals of macromolecules, the reasons of such observations were explained as being a result of radiochemical reactions [17], electrostatic repulsions [18, 20] and internal pressure [20]. It was also said

Table 2 Values of the geometrical parameters describing a Yang photocyclization

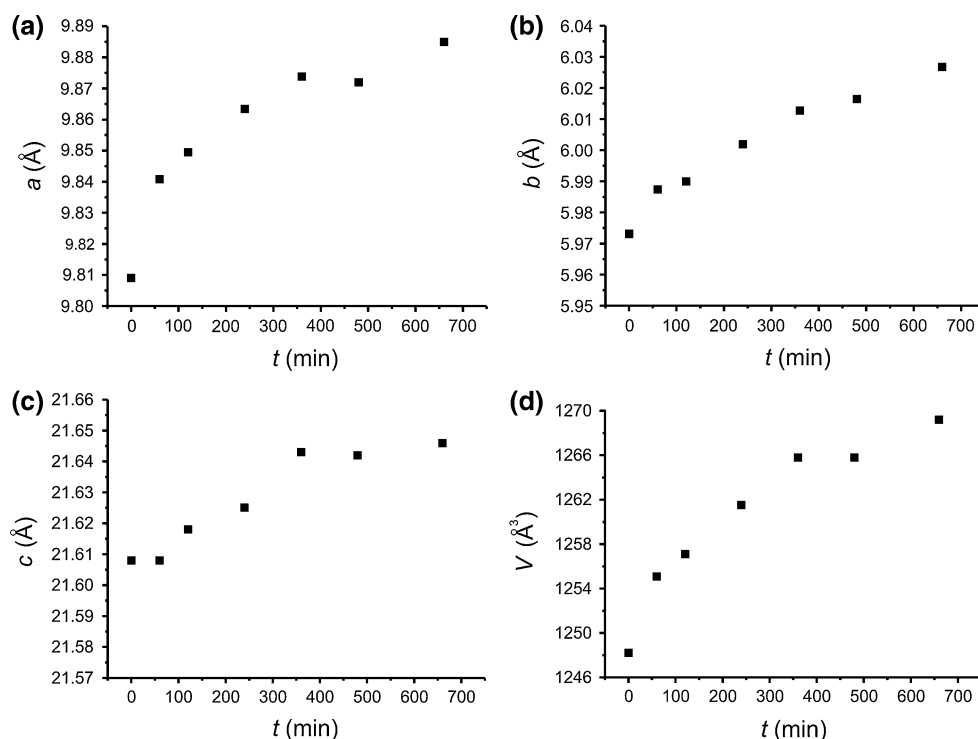
	d (Å)	D (Å)	ω (°)	Δ (°)	Θ (°)
Ideal value	<2.7		0	90–120	180
Average literature value ^a	2.64 (8)	3.00 (9)	54 (10)	82 (8)	116 (3)
Range ^b	2.49–2.95	2.82–3.12	50.8–83.1	52.9–88.0	112.0–128.0
(2) ^c	2.49	2.821 (8)	61.8	82.1	113.9
(1), This paper	2.59 (2)	2.901 (2)	71.6 (4)	73.7 (4)	113.4 (9)

^a The mean values of d , ω , Δ and Θ are given for 54 aromatic ketones undergoing a Yang photocyclization [27] and D for 53 structures [28]

^b The range of the parameters is given on the ground of 39 compounds for d , ω , Δ , Θ [7, 9, 11, 27, 29–33] and 16 compounds for D [7, 9, 11, 31, 33]

^c Ref. [9]

Fig. 1 Variations in the cell constants and the cell volume with time of crystal irradiation. For better comparison the range of axes for (a)–(c) parts of the figure was set to be the same. Standard uncertainties for a , b , c , and V are in the ranges 0.0016–0.002, 0.0009–0.0013, 0.003–0.004 Å and 0.3–0.4 Å³, respectively



that the complete explanation could not be given [19]. Literature on monitoring changes owing to UV radiation damage is very limited. Such studies were carried out for 1,5-diphenyl-1,4-pentadiene-3-one [21]. In that case the linear increase of c and V but linear decrease of a were observed; b was almost constant.

Monitoring the Decrease of Diffracting Power

The changes in the cell parameters brought about by UV radiation were accompanied by a decrease of diffracting power of the crystal of (1). It should be emphasized that during this process the crystal did not change its external appearance. Moreover, none signs of powder diffraction were observed. Any damage by X-rays was excluded (see [Crystallographic Studies](#)).

The decrease of the diffracting power of the crystal of (1) was monitored by means of the overall scale factor (OSF) (OSF was calculated during determination of the crystal structures). The results are presented in Fig. 2a. As can be seen, the values of OSF decrease linearly.

It should be added that after all experiments the crystal was irradiated by a UV beam once again until the full loss of its diffracting power. Also after this prolonged irradiation the studied object did not change its size, shape, transparency and color.

We also monitored the width of reflections. The relevant results were shown in Fig. 2b. As can be seen, long irradiation causes a certain increase of the width of reflections.

The above-described symptoms are accompanied by a gradual increase of atomic displacement parameters. The mean value, $\langle U_{eq} \rangle$, increases from 0.055 Å² for the unirradiated crystal to 0.087 Å² for 11 h of irradiation.

The reason that causes, among other things, the decrease of crystal diffracting power and the increase of the width of reflections of (1) is connected with an increase in crystal mosaicity, which in turn is connected with an increase in a number of crystal defects. The longer irradiation the more defects. After prolonged irradiation, the periodicity of crystal (1) is completely lost and consequently so are diffracted X-rays beams.

Monitoring the Intermolecular Distances and Molecular Orientation

Figure 3a shows the *ORTEP* view of (1) before irradiation. We also determined the structures for several steps of irradiation. The structures show absence of molecules of the product. This means that absorption of UV radiation by molecules in the crystal and their excitation do not lead to ring closure. Additionally, we determined structures for two crystals obtained after recrystallization of irradiated powder of (1). In both cases the crystal structures only showed existence of one type of molecules, namely molecules of (1). These facts can be a consequence of lack of a free space in the crystal, which can preclude necessary movements of molecular fragments and in this way the Yang photocyclization. Such a reason of chemical inertia was also given for

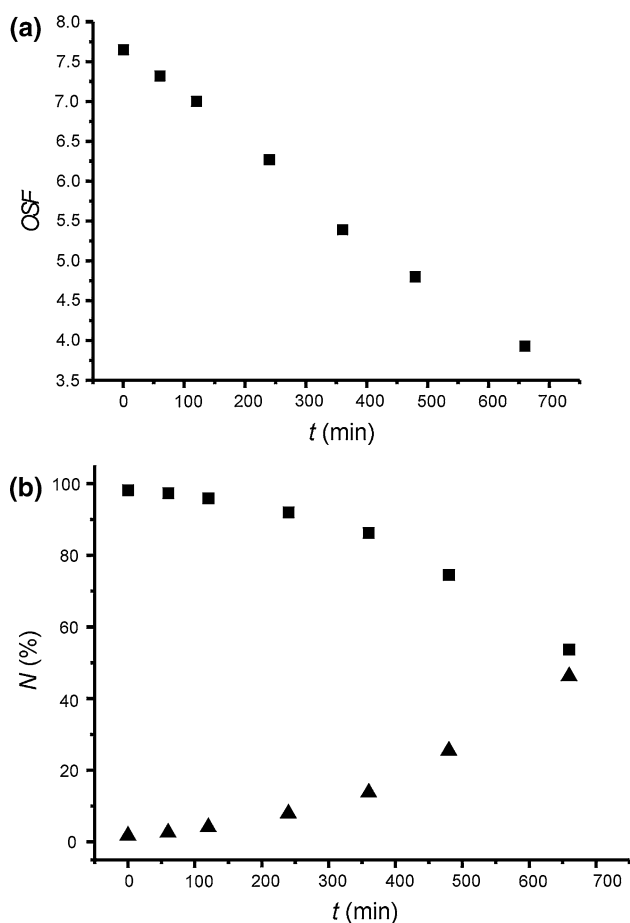


Fig. 2 **a** Variations in the OSF. **b** The change in the width of reflections; *squares* and *triangles* stand for reflections of width $<1.5^\circ$ and $>1.5^\circ$, respectively; *N* means the percentage of reflections in the above regions; 1,000 strongest reflections were taken into this analysis

other compounds which fulfill geometrical demands for reactions of photocyclization [38–40].

Since temperature influences packing of molecules, we irradiated two crystals at 50 and 100 °C, respectively. However, the X-ray structure analysis showed that the photochemical reaction did not proceed at the higher temperature.

Despite the absence of the photochemical reaction in the crystal of the studied compound, we observed the smooth changes in intermolecular and intramolecular geometrical parameters. The size of the changes was bigger for intermolecular distances than for non-bonding intramolecular ones. Figure 3b shows the variation in the $O1 \dots C7^i$ distance ($i = x, 1 + y, z$). Changes in other intermolecular distances are also smooth but smaller. Nevertheless, many of them are statistically significant. In the case of chemical reactions changes are usually bigger, namely even ca 0.25 Å [4, 5, 11]. The increase of intermolecular distances was also seen in the case of disappearance of diffracting properties of 1,5-diphenyl-1,4-pentadiene-3-one [21].

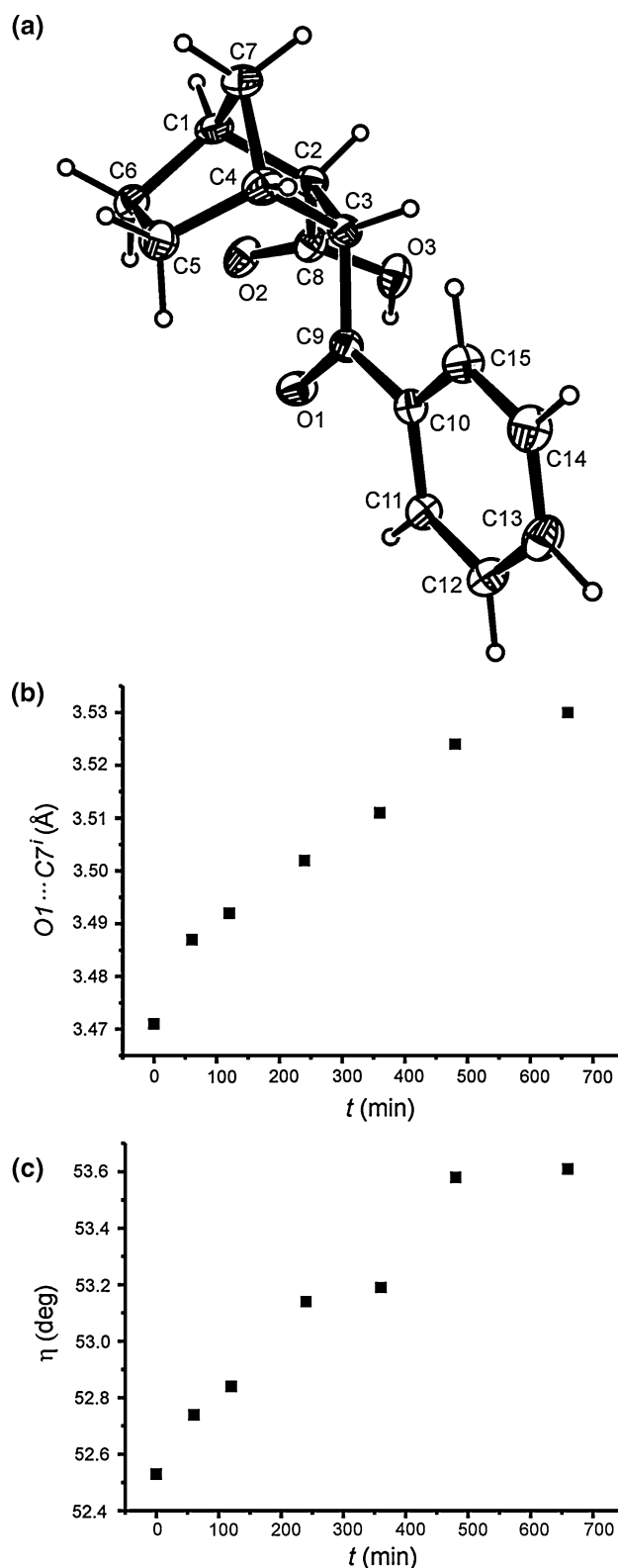


Fig. 3 **a** ORTEP [37] view of the molecule of (1). Displacement ellipsoids are drawn at the 20% probability level. Hydrogen atoms are diminished for clarity. Variations in **(b)** the $O1 \dots C7^i$ intermolecular distance ($i = x, 1 + y, z$) and **(c)** the angle between the carboxyl group and the benzene ring. Standard uncertainties are in the ranges 0.002–0.006 Å and 0.07–0.17°, respectively

Additionally, we monitored orientation of molecular fragments in the crystal of (1). Figure 3c shows the variation in the mutual orientation of the carboxyl group and the benzene ring. Although, the changes are small, they are statistically significant at the 3σ level. For chemical reactions the changes in orientation of molecular fragments are usually much bigger, namely even ca 20° [5–7, 9–11].

The chemical inertia of compound (1) was found out by means of the X-ray structure analysis and also the NMR and IR studies. Nevertheless, we cannot completely exclude formation of small amounts of some products, however, this cannot be stated on the ground of the methods applied.

Conclusions

Compound (1) does not undergo the photochemical reaction in a crystal and a solid state. However, UV radiation causes defects and higher mosaicity of the crystal. The observed certain increase of width of reflections and the reduction of diffracting power of the crystal are their symptoms.

The photo-induced process is accompanied by the increase of the cell parameters and the cell volume, the changes in intermolecular distances and small variations in orientation of molecular fragments. All changes proceed in a smooth manner. The symptoms observed for the UV radiation damage are similar to those for X-rays damage. In the scientific literature there are known examples of monitoring such symptoms for X-rays damage, however, examples of monitoring them for UV radiation are extremely rare.

Changes in cell volumes and non-bonded distances are not symptoms of only photochemical reactions. Changes in such parameters are also observed in the case of photo-physical processes. It means that one should be careful when concludes on proceeding of photochemical reactions in crystals on the basis of changes in diffraction pictures.

Supplementary Data

CCDC 718905, 718909, 718911, 718913–718916 contain the supplementary crystallographic data for this paper. These data can be obtain free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033.

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