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An unexpected participation of oxygen in a novel synthesis of [2,2′-bi-1*H*-indene]-3,3′-dialkyl-3,3′-dihydroxy-1,1′-diones

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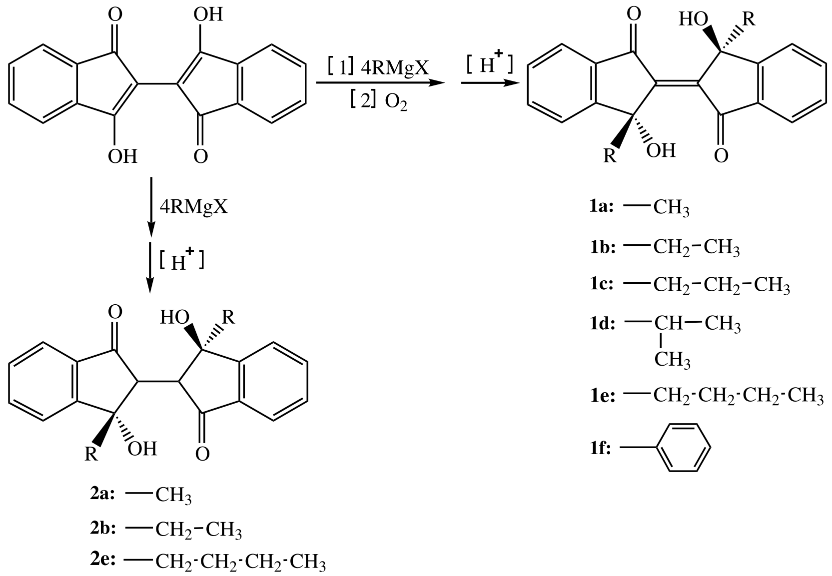
Abstract—This paper describes, for the first time, a short synthetic procedure for [2,2′-bi-1*H*-indene]-3,3′-dialkyl-3,3′-dihydroxy-1,1′-diones (**1a**–**f**). The key feature of this synthetic method lies in the participation of oxygen when the intermediate arises from the nucleophilic addition of alkylmagnesium bromide to 2,2′-biindanylidene-1,1′,3,3′-tetraone. The background leading to the development of this synthesis is discussed, together with the proposal of a novel reaction mechanism. The structures of all the new compounds have been determined by X-ray crystallography. © 2002 Elsevier Science Ltd. All rights reserved.

Organic solid-state photochromism has been an active area of research in organic photochemistry for a long time.[1–5] Among the various organic compounds exhibiting photochromic behaviour, [2,2′-bi-1*H*-indene]-3,3′-dialkyl-3,3′-dihydroxy-1,1′-diones (**1a**–**f**) have attracted our interest due to their unusual properties: they can undergo photochromism in a single crystalline phase with the generation of radical species. Comparable cases are rare.[6,7] More recently, we have reported our investigation on the photochromic and photomagnetic properties of [2,2′-bi-1*H*-indene]-3,3′-diethyl-3,3′-dihydroxy-1,1′-dione (**1b**).[8] Herein, we wish to report our recent synthesis of a series of this kind of compound (**1a**–**f**), and on a possible reaction mechanism.

The synthetic method is outlined in Scheme 1.



Scheme 1.

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Of all the compounds (**1a–f**), [2,2′-bi-1H-indene]-3,3′-diethyl-3,3′-dihydroxy-1,1′-dione (**1b**) was first obtained unexpectedly by the nucleophilic addition reaction of ethylmagnesium bromide with 2,2′-biindanylidene-1,1′,3,3′-tetraone (a dimer of 1,3-indandione), which exists in the di-enolic form.[9] The reaction had been anticipated to give bis-2,2′-(1-ethylindanone-3-ol-1) (**2b**) (Scheme 1). For two reasons this finding was deemed worthy of further investigation: firstly, compound **1b** can perform photochromism and photomagnetism in the single crystalline phase. Secondly, it was obtained through a controlled procedure in contrast to the synthesis of 3,3′-diaryl-2,2′-biindenylidene-1,1′-diones,[7] which possess similar photochemical properties.[7,9] Much effort has been invested into searching for the reason why the nucleophilic addition reaction gave **1b** as the major product.

The X-ray investigation on the single crystal of **1b** (Fig. 2) revealed that the bond joining the two loops of the 1,3-indanedione is definitely a double bond. Compared with the single bond product **2b**, **1b** ought to be formed through an oxygenation reaction. Considering the whole reaction carefully, we found that nothing but oxygen from the air had the opportunity to participate in the reaction system. We postulated that oxygen had acted as the oxidant at a certain stage during the reaction. In order to demonstrate the presumed involvement of oxygen, we performed the Grignard experiment once more and offered oxygen the chance to join in the reaction under the experimental procedure. The reaction of 2,2′-biindanylidene-1,1′,3,3′-tetraone with ethylmagnesium bromide having proceeded for 12 h, we exposed the reaction mixture to the air, stirring for another 3 h, and then hydrolyzed with saturated aqueous NH_4Cl solution. We obtained **1b** as the major product, in accordance with what we had expected.

Replacement of the air by an oxygen atmosphere before hydrolyzing afforded **1b** also. Following the same modified experimental procedure, we successfully obtained other biindenylidenedione derivatives such as **1a** and **1c–f**. Their structures have been unequivocally established by X-ray crystallography. The perspective drawings of compounds **1a–f** are shown in Figs. 1–6, respectively, with some selected crystal data and physical properties presented in Table 1.

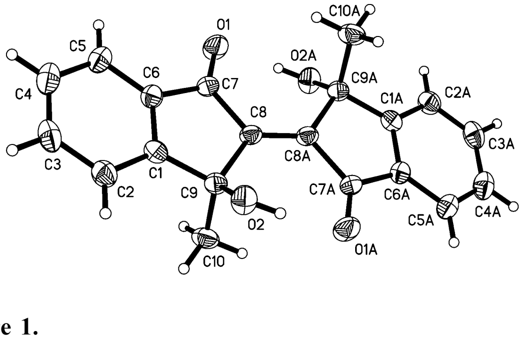


Figure 1.

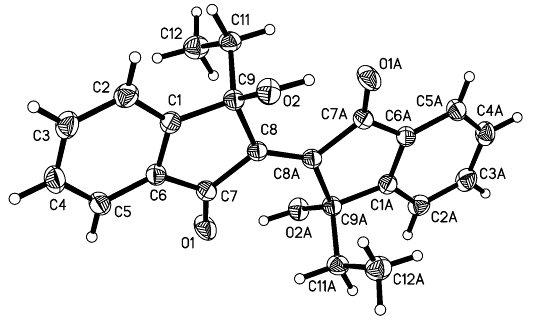


Figure 2.

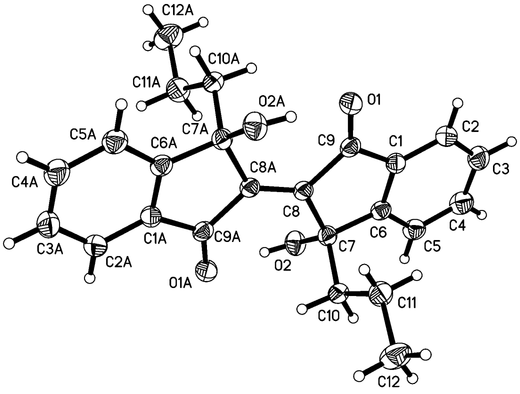


Figure 3.

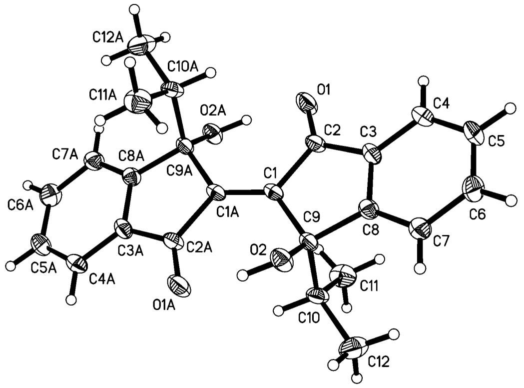


Figure 4.

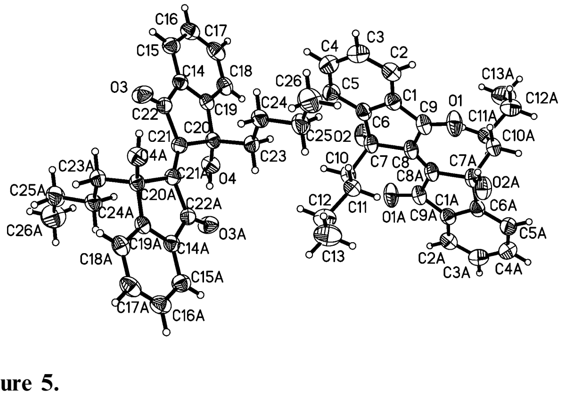


Figure 5.

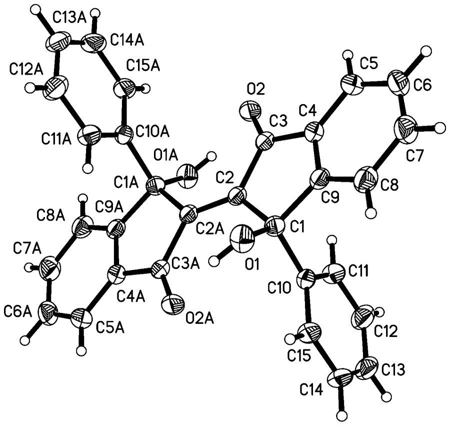


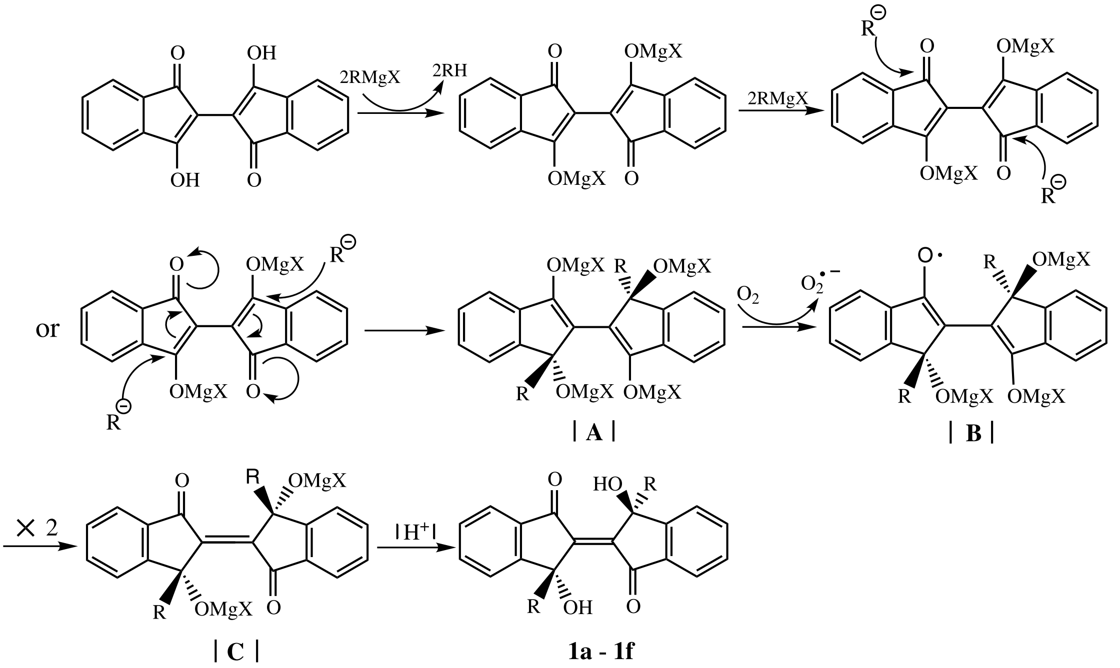
Figure 6.

We now review the mechanism outlined in Scheme 2. It is well known that alkaline solutions of quinol are easily oxidized in air to *p*-benzoquinone through a *p*-benzosemiquinone radical intermediate.[10,11] Also, it is accepted that when oxygen reacts with a Grignard reaction intermediate, a radical species is generated.[12] We propose the mechanism outlined in Scheme 2, involving successive nucleophilic attacks of 4 mol of the Grignard reagents on the substrate to result in the formation of the intermediate (**A**). This reacts with molecular oxygen undergoing electron transfer, as in the formation of the semiquinone radical from hydroquinone in alkaline solution, to give an anion radical (**B**). By means of intermolecular electron transfer, an analogous indigo structure (**C**) in possession of two carbonyl groups at the ends and one double bond

Table 1. Some selected crystal data, double bond lengths and physical properties for compounds **1a**–**f**

	1a	**1b**	**1c**	**1d**	**1e**	**1f**
Formula	$C_{20}H_{16}O_4$	$C_{22}H_{20}O_4$	$C_{24}H_{24}O_4$	$C_{24}H_{24}O_4$	$C_{26}H_{28}O_4$	$C_{30}H_{20}O_4$
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Final R indices $[I>2\sigma(I)]$	$R_1=0.0576$, $wR_2=0.1417$	$R_1=0.0373$, $wR_2=0.0828$	$R_1=0.0489$, $wR_2=0.1064$	$R_1=0.0637$, $wR_2=0.1312$	$R_1=0.0542$, $wR_2=0.1580$	$R_1=0.0613$, $wR_2=0.1505$
Double-bond length (Å)	1.3672	1.3496	1.3445	1.3702	1.3404, 1.3784	1.3452
Yield (%)	6	35	46	6	8	32
Photocolour development	Yes	Yes	Yes	Yes	Yes	Yes
Before irradiation	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
After irradiation	Brown	Green	Red	Reddish brown	Dark brown	Green
Photoinduced radical	Yes	Yes	Yes	Yes	Yes	Yes

The ^1H NMR data and elemental analysis data of **1a**–**f** are presented in Refs. 13–18.



Scheme 2.

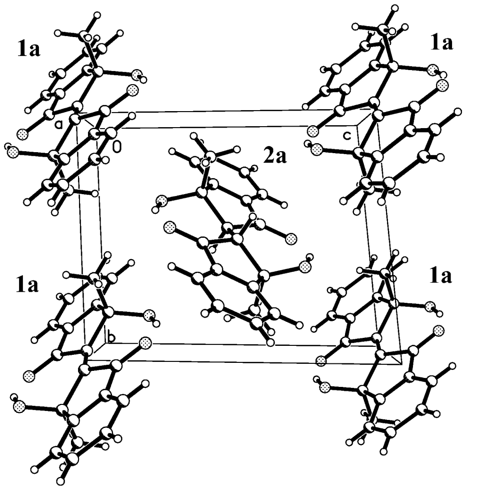


Figure 7. The 1:1 co-crystal of **1a** and **2a**, with a double bond length of 1.378 Å for **1a**, and with a single bond length of 1.481 Å for **2a**.

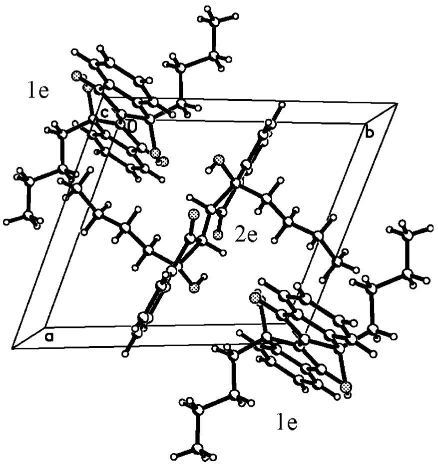


Figure 8. The 1:1 co-crystal of **1e** and **2e**, with a double bond length of 1.349 Å for **1e**, and with a single bond length of 1.483 Å for **2e**.

in the middle is generated. The subsequent hydrolysis with aqueous NH_4Cl solution leads to the formation of the observed products (**1a**–**f**). Regarding the whole reaction course, aerobic oxygen plays a key role in the synthetic course resulting in a double bond between the two loops of the 1,3-indanedione. In addition, the unexpected participation of oxygen gives a new sort of compound with extraordinary photochromic and photomagnetic properties, which will be discussed elsewhere.

Moreover, it should be noted that besides the double bond products **1**, single bond compounds like **2b** were found to be major products, resulting from the unoxygenated intermediate (**A**). For example, we obtained a 1:1 co-crystal of **1a** and **2a** by purifying the organic phase by column chromatography (Fig. 7). They were eluted as one fraction and crystallized as reddish saffron prisms from dichloromethane. The double bond length of **1a** is 1.378 Å, and the single bond length of **2a** is 1.481 Å. Though it is very difficult to separate them from one another, we separated the absolutely pure products **1a**–**f** by precipitation from the hydrolyzed reaction mixture, while the single bond compounds **2** remained in the organic phase with a certain amount of dissolved double bond products **1**. A similar result was observed in the case of the synthesis of **1e**, which formed 1:1 co-crystals with **2e**. Its crystal structure is shown in Fig. 8, with a double bond length of 1.349 Å and a single bond length of 1.483 Å.

In conclusion, a novel synthesis has been achieved for [2,2′-bi-1*H*-indene]-3,3′-dialkyl-3,3′-dihydroxy-1,1′-diones **1a**–**f** by performing the reaction of an alkyl Grignard reagent and 2,2′-biindan-1,1′,3,3′-tetraone, with treatment by oxygen. The characteristic of this synthesis lies in an unusual procedure: oxygen is thought to be involved in the reaction process by oxygenating the Grignard intermediate, which leads to the formation of a double bond between the two loops of 1,3-indanedione. The structures of all the compounds synthesized by this method were determined by X-ray crystallography.

General procedure for the preparation of [2,2′-bi-1*H*-indene]-1,1′-dione-3,3′-dihydroxy-3,3′-dialkyls: To a solution of alkylmagnesium bromide prepared from 55 mmol bromoalkane and 50 mmol magnesium in 25 ml anhydrous ether, 10 mmol 2,2′-biindanylidene-1,1′,3,3′-tetraone suspended in 20 ml dry benzene was added portionwise over a period of 10 min. At room temperature, the dark green reaction mixture was stirred for 12 h under a nitrogen atmosphere, and then exposed to the air for another 3 h. Finally, the reaction mixture became a dark purple colour. Quenching the reaction with an excess of saturated aqueous NH_4Cl solution gave two immiscible liquid phases. The crude compounds **1a**–**f**, [2,2′-bi-1*H*-indene]-3,3′-dialkyl-3,3′-dihydroxy-1,1′-diones, precipitated as an insoluble yellow powder between the organic phase and aqueous phase. Upon filtration followed by crystallization from dichloromethane, the compound was obtained as bright yellow crystals, only stable in the dark.[13–18] Data for co-crystal **1a**·**2a** (1:1) and **1e**·**2e** (1:1) are given including X-ray crystal data.[19,20]

Acknowledgements

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13. Data for **1a**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.87–7.53 (m, 8H, 8×-Ar-H), 6.52 (s, 2H, 2×-OH), 1.78 (s, 6H, 2×-CH_3). Anal. calcd (found) for $C_{20}H_{16}O_4$: C, 74.99 (74.73); H, 5.03 (5.25).
14. Data for **1b**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.87–7.55 (m, 8H, 8×-Ar-H), 6.65 (s, 2H, 2×-OH), 2.27–2.17 (m, 4H, 2×-CH_2-), 0.57–0.50 (m, 6H, 2×-CH_3). Anal. calcd (found) for $C_{22}H_{20}O_4$: C, 75.84 (75.65); H, 5.79 (5.53).
15. Data for **1c**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.87–7.54 (m, 8H, 8×-Ar-H), 6.66 (s, 2H, 2×-OH), 2.22–2.07 (m, 4H, 2×-CH_2-), 0.74–0.64 (m, 10H, 2×-CH_2CH_3). Anal. calcd (found) for $C_{24}H_{24}O_4$: C, 76.57 (76.25); H, 6.43 (6.68).
16. Data for **1d**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.88–7.54 (m, 8H, 8×-Ar-H), 6.84 (s, 2H, 2×-OH), 2.59 (m, 2H, 2×-CH-), 1.25–1.22 (d, $J=6.4$ Hz, 6H, 2×-CH_3), 0.39–0.36 (d, $J=6.3$ Hz, 6H, 2×-CH_3). Anal. calcd (found) for $C_{24}H_{24}O_4$: C, 76.57 (76.35); H, 6.43 (6.65).
17. Data for **1e**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.87–7.54 (m, 8H, 8×-Ar-H), 6.66 (s, 2H, 2×-OH), 2.15 (m, 4H, 2×-CH_2-), 1.10–1.03 (m, 4H, 2×-CH_2-), 0.82–0.62 (m, 10H, 2×-CH_2CH_3). Anal. calcd (found) for $C_{26}H_{28}O_4$: C, 77.20 (76.99); H, 6.98 (7.19).
18. Data for **1f**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.71–7.51 (m, 8H, 8×-Ar-H), 7.27–7.17 (m, 10H, 10×-Ar-H), 6.95 (s, 2H, 2×-OH). Anal. calcd (found) for $C_{30}H_{20}O_4$: C, 81.07 (80.79); H, 4.54 (4.79).
19. Data for co-crystal **1a**·**2a** (1:1) including X-ray crystal data: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.89–7.50 (m, 16H, 16×-Ar-H), 6.54 (s, 2H, 2×-OH(**1a**)), 5.95 (s, 2H, 2×-OH(**2a**)), 3.42 (s, 2H, 2×-CH-(**2a**)), 1.80 (s, 6H, 2×-CH_3(**1a**)), 1.54 (s, 6H, 2×-CH_3(**2a**)). Anal. calcd (found) for $C_{20}H_{16}O_4$, $C_{20}H_{18}O_4$: C, 74.75 (74.42); H, 5.33 (5.58). Crystal data: $C_{20}H_{16}O_4$, $C_{20}H_{18}O_4$, $M=642.68$, triclinic, space group $P\bar{1}$, $a=8.624(3)$, $b=9.098(3)$, $c=10.705(3)$ Å, $\alpha=83.159(5)$, $\beta=80.186(5)$, $\gamma=71.448(5)°$, $V=782.7(4)$ Å^3, $Z=2$, $D_{calcd}=1.363$ g cm^{-3}, $T=293(2)$ K, μ (Mo Kα)$=0.095$ mm^{-1}, 3275 reflections measured, 2747 unique ($R_{int}=0.0160$) which were used in all calculations. The final $R_1=0.0474$, $wR_2=0.1206$ and for all data $R_1=0.0809$, $wR_2=0.1365$.
20. Data for co-crystal **1e**·**2e** (1:1) including X-ray crystal data: δ 7.87–7.48 (m, 16H, 16×-Ar-H), 6.66 (s, 2H, 2×-OH(**1e**)), 6.02 (s, 2H, 2×-OH(**2e**)), 3.45 (s, 2H, 2×-CH-(**2e**)), 2.15–1.59 (m, 8H, 4×-CH_2-), 1.13–0.61 (m, 28H, 4×-$CH_2CH_2CH_3$). Anal. calcd (found) for $C_{26}H_{28}O_4$, $C_{26}H_{30}O_4$: C, 77.01 (77.28); H, 7.21 (7.01). Crystal data: $C_{26}H_{28}O_4$, $C_{26}H_{30}O_4$, $M=810.98$, triclinic, space group $P\bar{1}$, $a=9.707(3)$, $b=10.999(4)$, $c=11.944(4)$ Å, $\alpha=105.597(5)$, $\beta=101.362(5)$, $\gamma=106.433(5)°$, $V=1125.5(6)$ Å^3, $Z=1$, $D_{calcd}=1.197$ g cm^{-3}, $T=293(2)$ K, μ (Mo Kα)$=0.079$ mm^{-1}, 4610 reflections measured, 3913 unique ($R_{int}=0.0197$) which were used in all calculations. The final $R_1=0.0505$, $wR_2=0.1227$ and for all data $R_1=0.0997$, $wR_2=0.1434$.