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Synthesis of novel photochromic methyl cyanoacetate-condensed fulgide derivatives

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Abstract

New thermally irreversible photochromic methyl cyanoacetate-condensed fulgide derivatives were prepared and their photochromic properties were investigated. Coloured form of methyl cyanoacetate-condensed derivatives **C**-**4**(**a**–**d**) show large bathochromic shifts of their long wavelength absorption bands compared to the coloured form of corresponding fulgides **Z**-**1**(**a**–**d**). Solvent effects on the compound **ZZ**-**4a** and its ring-closed form **C**-**4a** were investigated. The polarity of the solvent caused a bathochromic shift of both coloured and uncoloured forms.

Keywords: Photochromism; Fulgides; Methyl cyanoacetate; Quantum efficiency

1. Introduction

Photochromism [1] is defined as a reversible change of a single chemical species between two states whose absorption spectra are distinguishably different, the colour change being induced in one direction or both directions by light. Reversibility and a change in at least one direction induced by electromagnetic radiation ($h\nu$) are important criteria for this definition.

$$\mathrm{A} \underset{h\nu_B}{\overset{h\nu_A}{\rightleftarrows}} \mathrm{B}$$

Organic photochromic compounds have attracted a significant amount of attention because of their possible application in optical devices such as optical memorise and switches [2]. Fulgides [3,4] and diarylethylenes [5,6] are well known photochromic compound that show completely reversible photochromism. From the viewpoint of practical applications, it is desired to develop photochromic compounds that have high sensitivities in the long wavelength region [5].

Substantial changes to the photochromic properties of fulgide can be made by modifying the anhydride ring. Heller et al. [7] and Asiri [8] reported that replacement of one of the carbonyl groups in fulgides by a dicyanomethylene group (=C(CN)$_2$) gave a new class of thermally stable photochromic compounds which were near infrared active. Near infrared active photochromic compounds were also prepared either by base catalysed rearrangement of E$_\beta$-dicyanomethylene derivatives of fulgides or condensation of acetophenone and appropriate derivatives with E-fulgide [9].

In this paper, we report the syntheses of new methyl cyanoacetate-condensed fulgide derivatives, obtained by condensation of Z-fulgides **Z**-**1**(**a**–**d**) with methyl cyanoacetate.

2. Results and discussion

When Z-fulgide is reacted with methyl cyanoacetate, two regioisomer are expected, depending on which carbonyl group of the anhydride ring was involved in the reaction.

However, recent studies have established that the condensation of pure Z-fulgides with malononitrile (NC–CH$_2$–CN) gives only Z$_\alpha$-dicyanomethylene compounds (Scheme 1) [9]. Since the methyl cyanoacetate (NC-CH$_2$-CO$_2$Me) closely related to the malononitrile (NC-CH$_2$-CN), the condensation product of methyl cyanoacetate (NC-CH$_2$-CO$_2$Me) with pure Z-fulgide was expected to be only α-isomers.

On the other hand, two α-isomers (**ZZ**-**4** and **ZE**-**5**) are possible because of geometrical isomers of new double bond formed from the condensation. In the **ZZ**-**4** isomers cyano group is located next to the 3-methylcyclohexanylidene **ZZ**-**4a**

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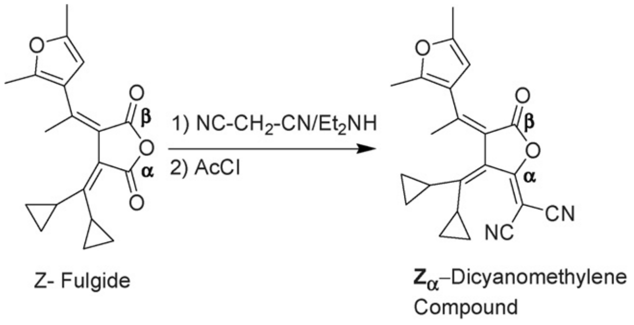

Scheme 1. Reaction of Z-fulgide with malononitrile.

or 4-*tert*-butylcyclohexanylidene **ZZ-4b** or isopropylidene **ZZ-4c** or adamantylidene **ZZ-4d** moieties, whereas in the **ZE-5** isomers sterically crowded methyl ester moiety is located next to the 3-methylcyclohexanylidene **ZE-5a** or 4-*tert*-butylcyclohexanylidene **ZE-5b** or related structural elements (Scheme 2).

When pure Z-fulgides **Z-1**(**a–d**) were reacted with methyl cyanoacetate in the presence of excess diisopropylamine followed by cyclisation with acetyl chloride two new photochromic spots were observed on TLC.[1] The upper spot was larger than the lower one. The first major spot was separated by column chromatography, and then further purification was done by recrystallization using ethyl acetate and hexane. The lower minor photochromic spot could not be isolated pure enough for proper identification.

The major photochromic spot was tentatively assigned as the less sterically crowded structures **ZZ-4** (rather than the **ZE-5**). The assignment was also conformed by X-ray structure (Fig. 1) of the **ZZ-4a**, which was isolated from the first major fraction.

Synthesis of new photochromic methyl cyanoacetate-condensed fulgide derivatives are shown in Scheme 2.

When Z-fulgides (and their derivatives) are irradiated with UV light, they isomerize to the E-form, which in turn photocyclises to the C-form. This is the general behavior of Z-fulgides and it has been well documented [10–12]. For example, the X-ray structure of C-form which was isolated from the photoreaction of **Z-1c** was succeeded by Kaftory [13]. It was an indubitable proof for the photoreactions mechanism of Z-fulgides and their closely related derivatives.

Upon irradiation at 365 nm, the **ZZ-4** in toluene isomerised to the **EZ-4**, which cyclised to the thermally stable coloured photochromes **C-4**. On exposure to white light, coloured photochromes ring opened to the **EZ-4** forms. Photoreactions of methyl cyanoacetate-condensed fulgide derivatives are shown in Scheme 3.

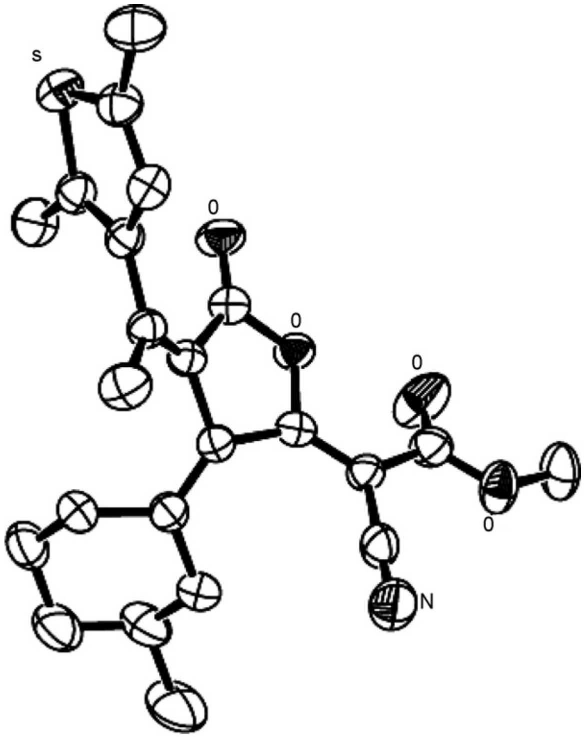

Fig. 1. The X-ray structure of methyl cyanoacetate-condensed fulgide **ZZ-4a**.

The UV–vis spectrum of compound **ZZ-4a** and its ring-closed form **C-4a** in toluene (1×10^{-4} M) are shown in Fig. 2.

Replacement of the carbonyl group in the fulgide **Z-1**(**a–d**) by the methoxycarbonyl(cyano)methylene group caused 57–83 nm bathochromic shift in the coloured form of compound **ZZ-4**(**a–d**) compared to the coloured form of fulgides. Ultraviolet and visible spectral data of Z-fulgides **Z-1**(**a–d**) and their methoxycarbonyl(cyano)methylene derivatives **ZZ-4**(**a–d**) before and after irradiation at 365 nm are listed in Table 1.

Replacement of the methyl group on the thiophene ring with a phenyl group (Scheme 2) resulted in a shift of the absorption toward longer wavelength. This was attributed to the powerful π-donor phenyl group extends the conjugation in the C-form.

When the isopropylidene groups in compound **ZZ-4c** was replaced with the adamantylidene group to give **ZZ-4d** resulted in a 32 nm bathochromic shift in the absorption band of the

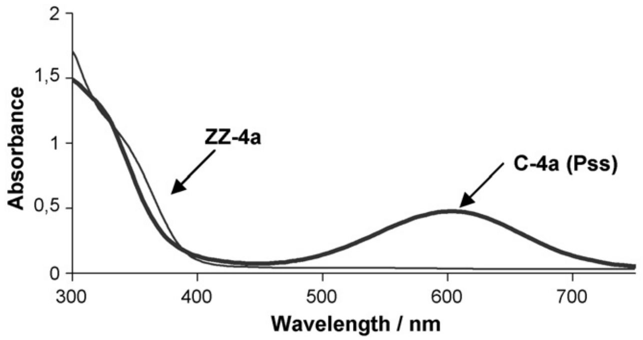

Fig. 2. Absorption spectral change of **ZZ-4a** in toluene (1×10^{-4} mol dm^{-3}) irradiated with 365 nm light.

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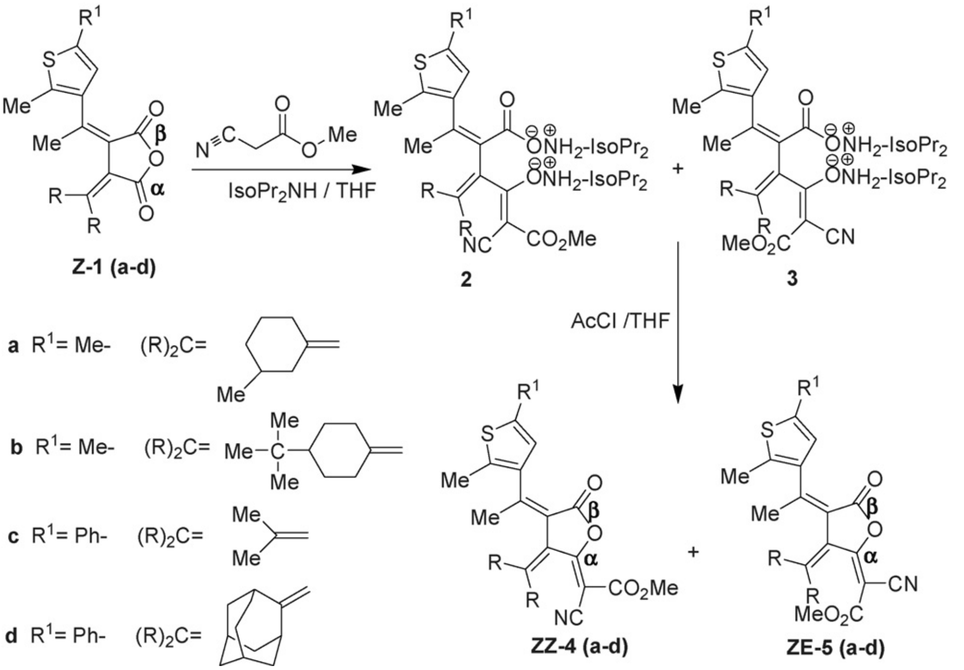
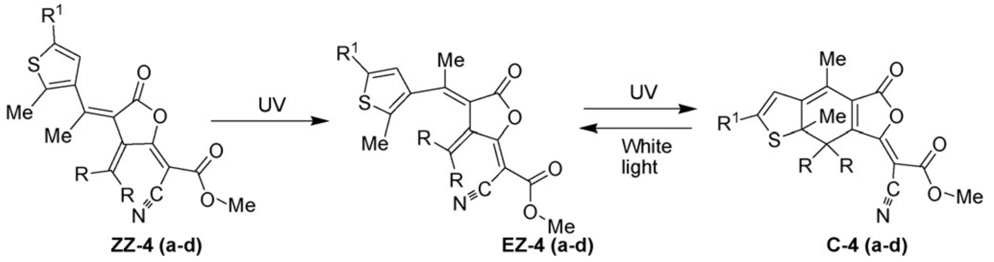
[1] The reaction of Z-fulgide **Z-1**(**a–d**) with methyl cyanoacetate gave two new photochromic spots on TLC (in ethyl acetate (50%) and hexane).The upper spots were major and the lower spots were minor. Rf of **ZZ-4a** 0.71 and Rf of unidentified photochromic spot (supposed to be **ZE-5a**) 0.65; Rf of **ZZ-4b** 0.75 and Rf of unidentified photochromic spot (supposed to be **ZE-5b**) 0.72; Rf of **ZZ-4c** 0.75 and Rf of unidentified photochromic spot (supposed to be **ZE-5c**) 0.70; Rf of **ZZ-4d** 0.64 and Rf of unidentified photochromic spot (supposed to be **ZE-5d**) 0.59.



Scheme 2. Synthesis of methyl cyanoacetate-condensed fulgide derivatives **ZZ-4** and **ZE-5**.



Scheme 3. Photoreactions of methyl cyanoacetate-condensed fulgide.

coloured form. The reason why the bulky and rigid adamantylidene group caused red shift is not clear.

The coloured photochrome **C-4d** has absorption maximum at 648 nm with an absorption tail going to the near infrared region. It is capable of responding to diode laser emitting in the region of $780 < \lambda < 840$ nm. This is required for optical memory systems [15].

Solvent effects on the compound **ZZ-4a** and its ring-closed form **C-4a** were investigated in five different solvents and the data are listed in Table 2. The polarity of the solvent caused a bathochromic shift of both coloured and uncoloured forms.

The quantum efficiency for colouring (ϕ_c) at 366 nm for **ZZ-4a** and bleaching (ϕ_b) at 546 nm of its coloured form **C-4a** were determined using the chemical actinometer Aberchrome 540 as described by Heller and Lagan [16].

The quantum efficiency for colouring (ϕ_c) and bleaching (ϕ_b) were found to be 24.37% and 7.4%, respectively. The actinometer (A540) shows (ϕ_c) 20% at 366 nm and (ϕ_b) 4.69% at 546 nm at 21 °C in toluene.

Table 1
Ultraviolet and visible spectral data of Z-fulgides **Z-1**(**a**–**d**) and their methoxycarbonyl(cyano)methylene derivatives **ZZ-4**(**a**–**d**) before and after irradiation at 365 nm

Compound	λ_{max}, nm (O-form)	ε_{max}, mol^{-1} dm^3 cm^{-1} (O-form)	λ_{max}, nm (at Pss)	Absorbance (at Pss)	Reference
Z-1a	346	8,595	535	0.569	[14]
Z-1b	345	6,853	535	0.400	[14]
Z-1c	–	–	545	1.190	[14]
Z-1d	318	14,000	565	1.080	[14]
ZZ-4a	257	38,000	605	0.699	
ZZ-4b	275	29,100	592	0.119	
ZZ-4c	278	35,400	616	0.383	
ZZ-4d	302	48,700	648	0.188	

Table 2
UV–VIS maximum absorption and extinction coefficients of **ZZ-4a** and its ring-closed form **C-4a** in various solvents

Solvent	**ZZ-4a**		**C-4a**	
	λ_{max} (nm)	ε_{max} ($mol^{-1}\,dm^3\,cm^{-1}$)	λ_{max} (nm)	Absorbance (at Pss)
Hexane	233	48,000	578	0.710
Toluene	–	–	605	0.699
Ethyl acetate	242	36,500	602	0.778
Ethanol	257	42,000	620	0.942
Acetonitrile	302	44,600	620	0.721

3. Conclusion

New class of thermally irreversible methyl cyanoacetate-condensed fulgides has been synthesized and their photochromic properties were investigated. The X-ray crystallographic analysis of **ZZ-4a** showed that the condensation of fulgides with the methyl cyanoacetate yielded to the less sterically hindered isomers. The absorption spectra, the quantum yields of photoreaction and the solvent polarity effects were determined. Replacement of the carbonyl group in fulgide **Z-1**(**a–d**) by the methoxycarbonyl(cyano)methylene group caused large bathochromic shift in the coloured form of compound **ZZ-4**(**a–d**) compared to the coloured form of fulgides.

The quantum yields of colouration and bleaching process for **ZZ-4a** were found to be 0.24 and 0.07, respectively. Polar solvents shift the absorption spectra to longer wavelength.

4. Experimental

4.1. General

All commercially available materials were used without further purifications. The ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometers for samples in $CDCl_3$. The signals are expressed as parts per million down fields from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; m, multiplet. IR spectra were measured using a Jasco FT-IR-300E spectrometer. Mass spectra were taken with a Thermo Finnigan mass spectrometer. Melting points were not corrected. UV–vis spectra were recorded on a UNicam UV2-100 spectrophotometer or a Varian Cary 100 Bio UV–vis spectrophotometer. Photochemical reactions at 365 nm in toluene were carried out in a 10 mm path length quartz cell using 8 W Three-Way UV lamp (Cole–Parmer). During the photoreaction, solutions in the cell were stirred. Chemical reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and dichloromethane was distilled from CaH_2 immediately before use. Solutions were dried over anhydrous sodium sulphate. Flash column chromatographic separation was carried out on Merck Kieselgel 60 (230–400 mesh) using ethyl acetate and hexane as the eluent. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25 mm thick TLC plates.

4.2. Synthesis

Fulgides **Z-1**(**a–d**) were prepared according to reported method [10–18].

*4.2.1. General procedure for the preparation of methyl cyanoacetate-condensed fulgide derivatives **ZZ-4(a–d)** and **ZE-5(a–d)***

Excess diisopropylamine was added dropwise to a stirred solution of fulgide **Z-1**(**a–d**) (1 equiv.) and methyl cyanoacetate (1.2 equiv.) in THF under N_2 at room temperature. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure and the residue was dissolved in DCM. The reaction mixture was cooled in an ice bath to 0 °C and acetyl chloride (2 equiv.) was added dropwise. The reaction mixture stirred overnight at room temperature and solvent was removed. The crude product was purified by column chromatography on silica gel using hexane and ethyl acetate as eluent. Pure methoxycarbonyl(cyano)methylene compounds can be obtained by re-crystallization.

4.2.1.1. ZZ-4-(3-methylcyclohexanylidene)-3-[1-(2,5-dimethyl thienyl)ethylidene]-5-methoxycarbonyl(cyano)methylene-tetrahydrofuran-2-one, ***ZZ-4a***. Yield 0.48 g (32%), mp 161–164 °C (AcOEt/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 1.18–2.15, 2.46, 2.95 (9H, m, *cyclohexane*-**H**), 1.08 (3H, d, *cyclohexanylidene*-**Me**), 2.14 (3H, s, **Me**), 2.29 (3H, s, **Me**), 2.40 (3H, s, **Me**), 3.82 (3H, s, O–$\mathbf{CH_3}$), 6.53 (1H, s, *thienyl*-**H**). LRMS (EI, 70 eV) *m/z* (rel intensity), 411 (M^+, 90), 379 (100), 364 (98), 336 (40), 317 (48), 285 (44), 257 (34), 239 (30), 225 (18), 167 (26), 152 (36), 126 (94), 95 (58). Found: *m/z* 411.0837. Calculated: $C_{23}H_{25}NO_4S$ M, 411.1504. IR (KBr) υ_{max} (cm^{-1}) 2926, 2225 (CN), 1766 (C=O), 1720 (C=O), 1618, 1575, 1446, 1368, 1267, 1033, 925, 828. The crystals of **ZZ-4a** suitable for X-ray crystallographic analysis were obtained by re-crystallization from toluene. The crystallographic data for **ZZ-4a** are shown in Table 3.

4.2.1.2. ZZ-4-(4-tert-butylcyclohexanylidene)-3-[1-(2,5-dimethy thienyl)ethylidene]-5-methoxycarbonyl(cyano)methylene-tetrahydrofuran-2-one, ***ZZ-4b***. Yield 0.27 (33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.89 (9H, s, *tert-butyl*-**H**), 1.16–2.14, 2.55, 2.97 (9H, m, *cyclohexane*-**H**), 2.15 (3H, s, **Me**), 2.32 (3H, s, **Me**), 2.42 (3H, s, **Me**), 3.86 (3H, s, O–$\mathbf{CH_3}$), 6.44 (1H, s, *thienyl*-**H**). IR (KBr) υ_{max} (cm^{-1}) 2959,

Table 3
Crystallographic data of **ZZ-4a**

Empirical formula	$C_{23}H_{25}NO_4S$
Formula weight	411.51
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a (Å)	13.219(13)
b (Å)	7.8585(6)
c (Å)	20.784(2)
α (°)	90
β (°)	91.916(8)
γ (°)	90
Volume (Å^3)	2157.9(3)
Z	4
D(calc) (g cm^{-3})	1.267
Mu(Mo Kα) (mm^{-1})	0.178
F(0 0 0)	872
$T_{\min}$, $T_{\max}$	0.947, 0.982
Diffractometer/meas. meth.	STOE IPDS 2/ϖ-scan
θ range for data collection	1.80–27.12°
Unique reflections measured	19,306
Independent reflections	4695
Data/restraints/parameters	2355/0/262
Goodness of fit on F^2	0.930
R_1 [$I > 2\sigma(I)$]	0.0426
wR_1	0.0740

2219 (CN), 1769 (C=O), 1618, 1448, 1368, 1261, 1092, 922, 803.

4.2.1.3. ZZ-2-[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]-3-isopropylidene-5-methoxycarbonyl(cyano)methylene-tetrahydrofuran-2-one, ***ZZ-4c***. Yield 0.19 g (22%), mp 164–166 °C (AcOEt/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 1.99 (3H, s, **CH_3**), 2.06 (3H, s, **CH_3**), 2.23 (3H, s, **CH_3**), 2.40 (3H, s, **CH_3**), 3.87 (3H, s, O–**CH_3**), 7.07 (1H, s, *thienyl*-**H**), 7.25–7.55 (5H, m, **Ar–H**), C-form **C-4c**: 1.62 (3H, s, **CH_3**), 1.70 (3H, s, **CH_3**), 1.93 (3H, s, **CH_3**), 2.22 (3H, s, **CH_3**), 3.90 (3H, s, O–**CH_3**), 6.73 (1H, s), 7.40–7.62 (5H, m, **Ar–H**). LRMS (EI, 70 eV) *m/z* (rel intensity), 419 (M^+, 100), 372 (63), 344 (32), 279 (42), 251 (20), 173 (12), 121 (5). Found: *m/z* 419.0323. Calculated: $C_{24}H_{21}NO_4S$, 419.1191. IR (KBr) $\upsilon_{\max}$ (cm^{-1}) 3081, 3036, 2920, 2853, 2230 (CN), 1737 (C=O), 1628, 1448, 1373, 1261, 1105, 1035, 927, 806, 757, 692.

4.2.1.4. ZZ-4-(2-adamantylidene)-3-[1-(2-methyl-5-phenyl-thienyl) ethylidene]-5-methoxycarbonyl(cyano)methylene-tetrahydrofuran-2-one, ***ZZ-4d***. Yield 0.23 (21%), mp 134–136 °C (AcOEt/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 1.73–2.18, 2.72, 4.18 (14H, m, *adamantylidene*-**H**), 2.17 (3H, s, **Me**), 2.30 (3H, s, **Me**), 3.76 (3H, s, O–**CH_3**), 6.98 (1H, s, *thienyl*-**H**), 7.18–7.46 (5H, m, Ar–H). LRMS (EI, 70 eV) *m/z* (rel intensity), 511 (M^+, 98), 479 (58), 430 (70), 368 (100), 313 (32), 255 (32), 237 (24), 185 (22), 225 (18), 160 (36), 81 (36). Found: *m/z* 511.2030. Calculated: $C_{31}H_{29}NO_4S$ M, 511.1817. IR (KBr) $\upsilon_{\max}$ (cm^{-1}) 2916, 2225 (CN), 1734 (C=O), 1625, 1447, 1260, 1186, 1105, 947, 886.

4.3. X-ray study

A suitable sample of size 0.44 mm × 0.23 mm × 0.13 mm was selected for the crystallographic study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo Kα radiation and an STOE IPDS 2 diffractometer. A total of 19,306 reflections with [$1.80° < \theta < 27.12°$] were collected in the rotation mode and cell parameters were determined by using X-AREA software [19]. Absorption correction ($\mu = 0.178\ \mathrm{mm}^{-1}$) was achieved by the integration method via X-RED software [19].

The structure was solved by direct methods using SHELXS-97 [20]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 262 crystallographic parameters. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms refined by using a riding model. The structure was refined to $R_1 = 0.0426$ for observed reflections which obeyed to the condition of $2355 I > 2\sigma(I)$. The maximum peaks and deepest hole observed in the final $\Delta\rho$ map were 0.33 and -0.15 eÅ^{-3}, respectively. The scattering factors were taken from SHELXL-97 [20]. The data collection conditions and parameters of refinement process are listed in Table 3.

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