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Synthesis and photochromic properties of 4-[2-(anthracen-9-yl)-5-methyloxazolyl] fulgide

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New photochromic fulgide, *viz.*, 4-{1-[2-(anthracen-9-yl)-5-methyloxazol-4-yl]ethylidene}-3-isopropylidenetetrahydrofuran-2,5-dione, with fluorescent properties was synthesized. Studies by electronic, IR, and ^{1}H NMR spectroscopy and X-ray diffraction demonstrated that this fulgide exists in the *Z* form. Light irradiation of its solutions at a wavelength of 365 nm causes *Z*/*E* isomerization giving rise to the thermally stable cyclic form. The latter is transformed into the starting *E* isomer under light irradiation at λ = 436 nm.

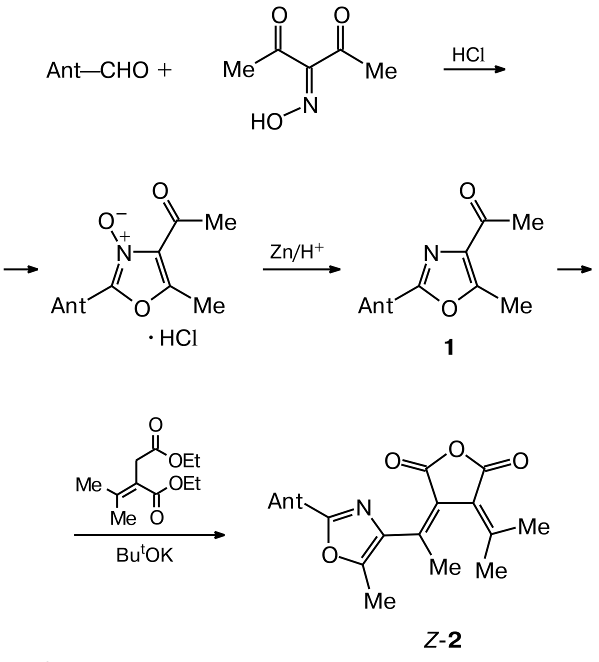
Key words: fulgide, synthesis, structure, photochromism.

Fulgides containing heterocyclic substituents can exhibit photochromic properties, which are important from the practical point of view, due to high thermal stability of the cyclic form and fatigue resistance.[1—3] Various oxazolyl fulgides are used for optical information recording.[4,5] Systems, which exhibit fluorescent properties in one or both forms that undergo a reversible rearrangement, offer particular advantages for nondestructive reading of optical information and construction of high-capacity 3D multilayer memory systems based on photochromic compounds.[1—3] With the aim of studying a new photochromic system with luminescent properties, we synthesized 4-oxazolyl fulgide containing the fluorophoric anthryl group at position 2 of the oxazole ring and investigated its spectral-luminescent and photochemical properties.

Results and Discussion

Previously unknown 4-[2-(anthracen-9-yl)-5-methyloxazolyl] fulgide (**2**) was synthesized by Stobbe condensation of diethyl isopropylidenesuccinate with 4-acetyl-2-(anthracen-9-yl)-5-methyloxazole (**1**), which was prepared from 9-anthraldehyde and 3-nitrosopentane-2,4-dione (Scheme 1).

Scheme 1



Ant is 9-anthryl

The IR spectrum of fulgide **2** shows characteristic bands at 1800 and 1750 cm^{-1} corresponding to two exocyclic carbonyl groups. The ^{1}H NMR spectra exhibit signals of four methyl groups, one of the signal being observed at δ 1.18, which corresponds to the *Z* configuration of fulgide **2**, as confirmed by X-ray diffraction data.[5]

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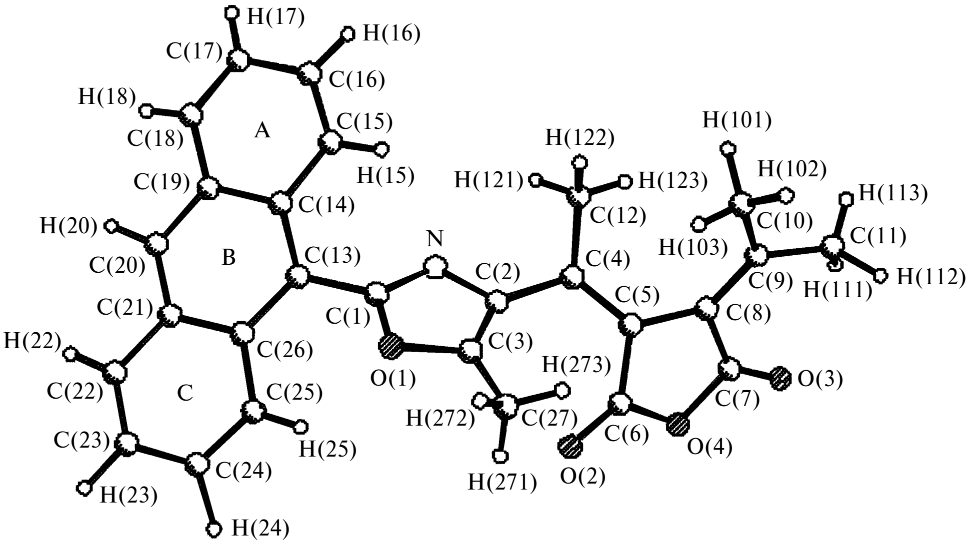


Fig. 1. Molecular structure of 4-[2-(anthracen-9-yl)-5-methyloxazolyl] fulgide (*Z*-**2**).

The anthryl substituent in molecule *Z*-**2** has a typical nonplanar structure (Fig. 1 and Table 1). The rings A and C of the anthracene fragment deviate upward from the plane of the ring B, whereas the C(1) atom deviates downward by 0.10 Å. The atoms of the oxazole fragment C(1)C(2)C(3)O(1)N lie in a plane with the C(13) atom to within 0.004 Å, whereas the C(4) and C(27) atoms deviate from this plane in the same direction by 0.16 and 0.05 Å, respectively. The furandione fragment C(5)C(6)C(7)C(8)O(4) is planar to within 0.05 Å, the O(2) and C(9) atoms deviate from this plane in the same direction by 0.13 and 0.52 Å, respectively, and the O(3) and C(4) atoms deviate in the opposite direction by 0.62 and 0.11 Å, respectively.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecule *Z*-**2**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Angle	ω/deg
O(1)—C(1)	1.372(4)	C(3)—C(2)—N	109.0(3)
O(1)—C(3)	1.368(4)	C(3)—C(2)—C(4)	130.4(3)
O(2)—C(6)	1.190(4)	N—C(2)—C(4)	119.9(3)
O(3)—C(7)	1.199(5)	C(2)—C(3)—O(1)	107.4(3)
O(4)—C(6)	1.392(5)	C(2)—C(3)—C(27)	137.0(4)
N—C(1)	1.286(4)	O(1)—C(3)—C(27)	115.6(3)
N—C(2)	1.394(4)	C(5)—C(4)—C(2)	123.2(3)
C(1)—C(13)	1.465(5)	C(2)—C(4)—C(12)	114.2(3)
C(2)—C(3)	1.349(5)	C(5)—C(4)—C(12)	122.5(3)
C(2)—C(4)	1.464(5)	C(4)—C(5)—C(6)	122.8(3)
C(3)—C(27)	1.467(5)	C(4)—C(5)—C(8)	129.0(3)
C(4)—C(5)	1.365(5)	C(8)—C(5)—C(6)	105.7(3)
C(4)—C(12)	1.490(5)	O(2)—C(6)—O(4)	118.7(3)
C(5)—C(6)	1.465(5)	O(2)—C(6)—C(5)	133.0(4)
C(5)—C(8)	1.458(5)	O(4)—C(6)—C(5)	108.1(3)
C(7)—C(8)	1.461(5)	O(3)—C(7)—O(4)	118.6(4)
C(8)—C(9)	1.362(5)	O(3)—C(7)—C(8)	133.6(4)
C(9)—C(10)	1.471(6)	O(4)—C(7)—C(8)	107.7(3)
C(9)—C(11)	1.489(6)	C(9)—C(8)—C(5)	129.9(3)
		C(9)—C(8)—C(7)	122.4(3)
Angle	ω/deg	C(5)—C(8)—C(7)	106.4(3)
C(3)—O(1)—C(1)	105.5(2)	C(8)—C(9)—C(10)	122.3(3)
C(6)—O(4)—C(7)	110.2(3)	C(8)—C(9)—C(11)	122.7(4)
C(1)—N—C(2)	105.6(2)	C(10)—C(9)—C(11)	114.8(4)
N—C(1)—O(1)	112.5(3)	C(14)—C(13)—C(1)	119.1(3)
N—C(1)—C(13)	127.7(3)	C(14)—C(13)—C(26)	120.3(3)
O(1)—C(1)—C(13)	119.7(3)	C(26)—C(13)—C(1)	120.6(3)

The molecule adopts a strained conformation, which is reflected in the following torsion angles:

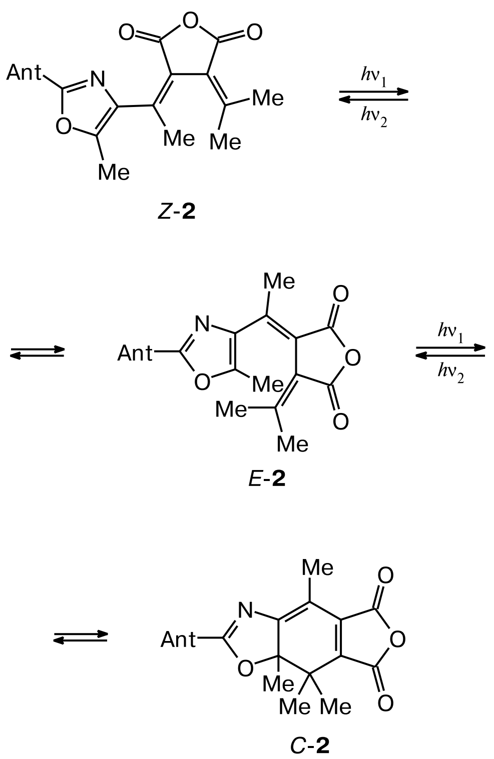
Angle	φ/deg
C(14)—C(13)—C(1)—N	−37.2(5)
N—C(2)—C(4)—C(12)	34.5(4)
C(3)—C(2)—C(4)—C(5)	49.7(6)
C(4)—C(5)—C(6)—O(2)	−24.7(6)
C(12)—C(4)—C(5)—C(8)	5.8(6)
C(4)—C(5)—C(8)—C(9)	45.6(6)
C(9)—C(8)—C(7)—O(3)	−20.0(7)
C(5)—C(8)—C(9)—C(10)	4.7(6)
C(5)—C(8)—C(9)—C(11)	179.7(4)

This fact can be attributed to steric strain in the fulgide. In particular, this is characterized by the following distances: N...H(15), 2.35 Å; O(1)...H(25), 2.17 Å; O(2)...H(271), 2.53 Å; and O(3)—H(111), 2.47 Å.

The photochromic behavior of fulgide **2** is determined by two successive *Z*→*E* isomerizations and conrotatory triene cyclization (Scheme 2).

Fulgide *Z*-**2** shows a broad structured absorption band at 330—380 nm (Table 2, Fig. 2) characteristic of anthracene derivatives,[6] the positions of individual maxima being virtually independent of the polarity of the solvent. Since the colored form *C* can be generated only from the

Scheme 2



E isomer,[1—3] we made an attempt to perform photochemical *Z*/*E* isomerization without further cyclization of the *E* form. However, the only process was observed upon light irradiation at wavelengths of 313 and 365 nm in solvents of different polarity: a decrease in the intensity of the absorption maximum at 330—380 nm and the appearance of a new band at 430—480 nm characteristic of the cyclic forms of oxazolyl fulgides.[4,5] In the absorption spectra, a clear isosbestic point persists, which is indicative of either the absence of isomer *E*-**2** or a virtually identical spectral patterns of the *E* and *Z* isomers in this region of absorption spectra (see Fig. 2). Analogous spectroscopic and photochemical data led to a conclusion[7] that the

Table 2. Electronic absorption spectra of photoisomers of fulgide **2**

Isomer	Solvent	EAS, λ_{max}/nm ($\varepsilon_{max} \cdot 10^{-4}$/L mol^{-1} cm^{-1})
Z-**2**	Toluene	333 (0.99), 352 (1.22), 369 (1.42), 387 (1.33)
E-**2**	Toluene	334 (0.83), 352 (1.02), 369 (1.20), 387 (1.13)
C-**2**	Toluene	333 (0.46), 350 (0.63), 367 (0.76), 386 (0.75), 458 (0.73)
Z-**2**	Acetonitrile	333 (1.12), 352 (1.30), 368 (1.47), 385 (1.36)
E-**2**	Acetonitrile	333 (0.92), 352 (1.08), 368 (1.25), 384 (1.15)
C-**2**	Acetonitrile	333 (0.49), 351 (0.66), 367 (0.80), 385 (0.82), 450 (0.78)

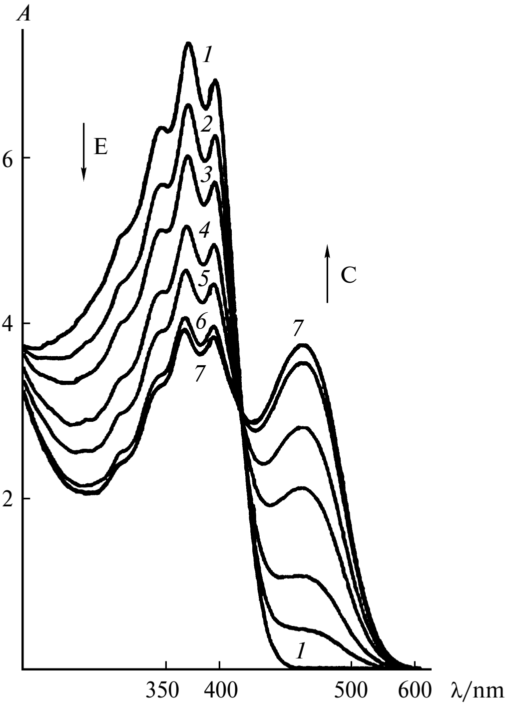


Fig. 2. Electronic absorption spectra of fulgide *Z*-**2** in toluene before irradiation (*1*) and after irradiation (λ = 436 nm, C = $2.5 \cdot 10^{-5}$ mol L^{-1}) for 10 s (*2*), 20 s (*3*), 40 s (*4*), 1 min (*5*), 2 min (*6*), and 5 min (*7*).

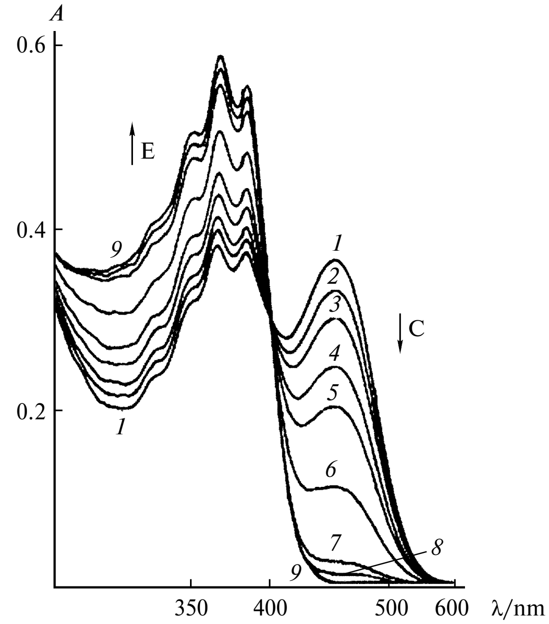


Fig. 3. Electronic absorption spectra of the cyclic form of fulgide *C*-**2** in toluene before irradiation (*1*) and after irradiation (λ = 436 nm, C = $2.5 \cdot 10^{-5}$ mol L^{-1}) for 5 s (*2*), 10 s (*3*), 20 s (*4*), 40 s (*5*), 1 min (*6*), and 2 min (*7*).

Z isomer in the excited state can be transformed into the cyclic isomer without the formation of the *E* isomer in the ground state. Upon light irradiation of the *C* form at λ = 436 nm (Fig. 3), the spectral pattern restores the original form with a slight decrease in the intensity of absorption bands.

To explain the observed phenomena, we measured ^{1}H NMR spectra of the following three samples in deuteriobenzene: the starting form *Z*-**2** before irradiation; a mixture obtained upon light irradiation of a solution of *Z*-**2** in an NMR tube at λ_{max} = 365 nm (it proved to be a mixture of isomers *Z*-**2**, *E*-**2**, and *C*-**2** in a ratio of 5 : 5 : 4), and a mixture of isomers formed upon light irradiation of this mixture at λ_{max} = 436 nm (a mixture of isomers *Z*-**2** and *E*-**2** in a ratio of 5 : 9). Therefore, irradiation of the starting isomer *Z*-**2** induces preliminary *Z*/*E* isomerization of fulgide, which is then followed by photocyclization of *E*-**2** to give a colored form (see Scheme 2). Upon photodecoloration, cyclic form *C*-**2** is cleaved to give *E*-fulgide. Isomers *Z*-**2**, *E*-**3**, and *C*-**2** are characterized by individual and clearly distinguished sets of signals of four methyl groups and aromatic protons in the ^{1}H NMR spectra.

In addition, the ^{1}H NMR spectrum, which was measured in the case when ~50% of isomer *C*-**2** was generated, showed also signals of both the *Z* and *E* isomers. The quantum yield of the transformation *C*-**2** → *E*-**2** is 0.46. The quantum yield of cyclization *E*-**2** → *C*-**2** is 0.47. The starting isomer *Z*-**2** shows low-intensity fluorescence at λ_{max}= 460 nm. The quantum yield of fluorescence is 0.003, which is, apparently, associated with an acoplanar structure of the anthryl fragment of the fulgide molecule, whereas cyclization giving rise to colored form *C*-**2** completely quenches this fluorescence and does not cause new longer-wavelength radiation.

To summarize, we established the mechanism of photocyclization of oxazolyl fulgide **2**, *Z*-**2** → *E*-**2** → *C*-**2**, and the mechanism of cleavage of the cyclic isomer, C-**3** → *E*-**2**. The fatigue resistance of the "working substance" opens up possibilities for the use of **2** for information recording.

Experimental

Electronic absorption spectra were measured on a Specord M-40 spectrophotometer. Solutions were irradiated using a DRSh-250 mercury lamp equipped with a kit of glass light filters. The quantum yields were determined with the use of potassium ferrioxalate.[8] The IR spectra were recorded on a Specord 75IR instrument in Nujol mulls. The ^{1}H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in deuteriobenzene with HMDS as the external standard.

4-Acetyl-2-(anthracen-9-yl)-5-methyloxazole (1). Dry HCl was passed with stirring through a solution of 9-anthraldehyde (10.3 g, 0.05 mol) and 3-nitrosopentane-2,4-dione (6.8 g, 0.05 mol) in glacial acetic acid (100 mL) cooled to 5—10 °C until saturation was achieved. Then the reaction mixture was kept in a refrigerator for 16 h. The precipitate that formed was filtered off and washed with methanol and diethyl ether. The resulting 4-acetyl-2-(9-anthryl)-5-methyloxazole *N*-oxide hydrochloride (12 g) was dissolved in glacial acetic acid (50 mL), after which zinc dust (1.3 g, 0.02 mol) was added portionwise with stirring. The solution was heated until it became colorless, cooled, and diluted with water to a volume of 200 mL. The precipitate that formed was filtered off and recrystallized from a 1 : 3 *n*-butanol—toluene mixture. The yield was 49.75%, m.p. 134—135 °C. Found (%): C, 79.49; H, 5.01; N, 4.62. $C_{20}H_{15}O_2N$. Calculated (%): C, 79.71; H, 5.03; N, 4.65. IR, ν/cm^{-1}: 1670, 1590. ^{1}H NMR (acetone-d$_6$), δ: 2.60 and 2.80 (both s, 3 H each, Me); 7.60 (m, 4 H, H arom.); 8.10 and 8.20 (both m, 2 H each, H arom.); 8.90 (s, 1 H, H arom.).

***Z*-4-{1-[2-(Anthracen-9-yl)-5-methyloxazol-4-yl]ethylidene}-3-isopropylidenetetrahydrofuran-2,5-dione (*Z*-2).** A solution of potassium *tert*-butoxide was prepared from potassium (0.65 g, 0.017 mol) in *tert*-butanol (15 mL). Then a mixture of 4-acetyl-2-(9-anthryl)-5-methyloxazole (1.90 g, 0.0063 mol) and ethyl isopropylidenesuccinate (3.5 mL, 0.007 mol) in benzene was added with stirring to this solution. The reaction mixture was stirred at room temperature for 1 h and then refluxed for 1 h. The solvent was evaporated *in vacuo*. The residue was treated with water. The precipitate that formed was filtered off and transferred to a flask. Then a 10% KOH solution in aqueous methanol was added. The solution was refluxed for 2 h, diluted with water, and filtered. The filtrate was acidified with 10% HCl. The precipitate that formed was filtered off and dried in air. The product was dissolved in acetic anhydride with heating. Yellow crystals that precipitated from the solution upon cooling were filtered off and recrystallized from *n*-butanol. The yield was 30%, m.p. 223—224 °C. Found (%): C, 76.42; H, 5.05; N, 3.24. $C_{27}H_{21}O_4N$. Calculated (%): C, 76.58; H, 5.01; N, 3.30. IR, ν/cm^{-1}: 1800, 1750. ^{1}H NMR, δ: 1.18, 1.95, 2.06, and 2.21 (all s, 3 H each, Me); 7.15—7.30 (m, 4 H, H arom.); 7.75 (m, 2 H, H arom.); 8.18—8.35 (m, 3 H, H arom.).

2-(Anthracen-9-yl)-4,8,8,8a-tetramethyl-8,8a-dihydrofuro[3,4-*f*][1,3]benzoxazole-5,7-dione (*C*-2) was prepared in an NMR tube as a mixture with isomers *Z*-**2** and *E*-**2** under light irradiation of a solution of fulgide (*Z*-**2**) in deuteriobenzene (C 2.4 • 10^{-2} mol L^{-1}) at λ = 365 nm for 6 h. ^{1}H NMR, δ: 1.05, 1.08, 1.09, and 2.35 (all s, 3 H each, Me); 7.14—7.36 (m, 4 H, H arom.); 7.67—7.78 (m, 2 H, H arom.); 8.11—8.41 (m, 3 H, H arom.).

***E*-4-{1-[2-(Anthracen-9-yl)-5-methyloxazol-4-yl]ethylidene}-3-isopropylidenetetrahydrofuran-2,5-dione (*E*-2)** was prepared analogously to *C*-**2** as a mixture with *Z*-**2** under light irradiation of fulgide *C*-**2** at λ = 436 nm for 5 h. ^{1}H NMR, δ: 1.35, 1.48, 2.00, and 2.89 (all s, 3 H each, Me); 7.14—7.36 (m, 4 H, H arom.); 7.73 (m, 2 H, H arom.); 8.17—8.36 (m, 3 H, H arom.).

X-ray diffraction study. The unit cell parameters were measured and a three-dimensional X-ray diffraction data set was collected on a KUMA-DIFFRACTION KM-4 diffractometer (Mo-Kα radiation, graphite monochromator) from an isometric single crystal of **2** of an arbitrary shape ~0.35 mm in radius. Compound **2** crystallizes in the monoclinic system, $C_{27}H_{21}NO_4$, M = 423.48, a = 20.610(4), b = 8.086(2), c = 12.907(3) Å, V = 2151.0(7) Å^3, space group $Pca2_1$, Z = 4, ρ = 1.308 g cm^{-3}.

The intensities of 2200 reflections were measured within an independent region of reciprocal space ($2\theta \leq 52.12°$) using the $\omega/2\theta$ scanning technique. After exclusion of systematic absences, the data set contained 1385 measured reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms using the SHELXL-97 program package. In the crystal structure of **2**, all hydrogen atoms were located from difference Fourier maps and refined isotropically. The final R factor was 3.6% (10% for 2196 reflections); GOOF = 0.926. In the last cycle of the full-matrix refinement, the absolute shifts of all 373 variable parameters of the structure were smaller than 0.001 σ. In the final difference Fourier synthesis: $-0.14 < \Delta\rho < 0.14\ e$ Å^{-3}.

The complete X-ray diffraction data, including the atomic coordinates and displacement parameters, were deposited with the Cambridge Structural Database.

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