

Rotationally-hindered furyl fulgides

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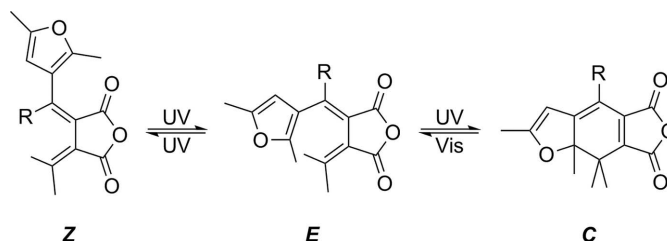
Fulgides are a representative class of photochromic organic molecules which exhibit several interesting properties for diverse applications in fields such as data storage or high-resolution spectroscopy. The crystal structures of three furyl fulgides with different steric constraints were determined and for two of the compounds both the *E* and *Z* isomer structures were defined. The compounds are 3-[(*E*)-1,3-dimethyl-4,5,6,7-tetrahydro-2-benzofuran-4-ylidene]-4-isopropylidenetetrahydrofuran-2,5-dione, C₁₇H₁₈O₄, (I-*E*), 3-[(*E*)-1,3-dimethyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*c*]furan-4-ylidene]-4-isopropylidenetetrahydrofuran-2,5-dione, C₁₈H₂₀O₄, (II-*E*), and the *Z* isomer, (II-*Z*), and 3-isopropylidene-4-[(*E*)-1-(5-methoxy-2-methyl-1-benzofuran-3-yl)ethylidene]tetrahydrofuran-2,5-dione, C₁₉H₁₈O₅, (III-*E*), with two molecules in the asymmetric unit, and the *Z* isomer, (III-*Z*). The structures of the *E* and *Z* isomers show only little differences in the bond lengths and angles inside the hexatriene unit. Because of the strained geometry there are deviations in the torsion angles. Furthermore, small differences in the distances between the bond-forming C atoms in the electrocyclization process give no explanation for the unequal photochromic behaviour.

Comment

Among photochromic compounds, furyl fulgides exhibit suitable properties with a high application potential (Yokoyama, 2000). Upon wavelength-specific illumination they undergo a remarkable reversible colour change, which can be followed by UV–visible spectroscopy. The photochromic reaction occurs by a photochemical ring-closing reaction of a hexatriene system and can be reversed by irradiation with light of a different wavelength. Concomitantly there is a photochemical equilibrium between the open *E* and *Z* forms. The photochromism of a furyl fulgide with variable substituents at the hexatriene moiety is illustrated in Scheme 1.

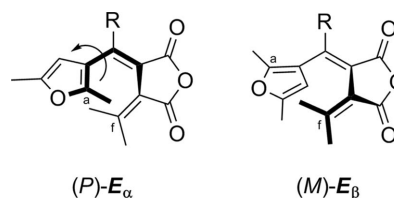
One great advantage of fulgides compared with other photochromic compounds is their high thermal stability, which is due to structural modifications at the hexatriene part. This

was intensively investigated by Heller *et al.* in the 1980s (Darcy *et al.*, 1981). Furthermore, electronic variations have a great influence on the UV–visible spectroscopic characteristics of a fulgide (Yokoyama *et al.*, 1991, 1996). Steric modifications at the hexatriene unit have strong effects on the quantum

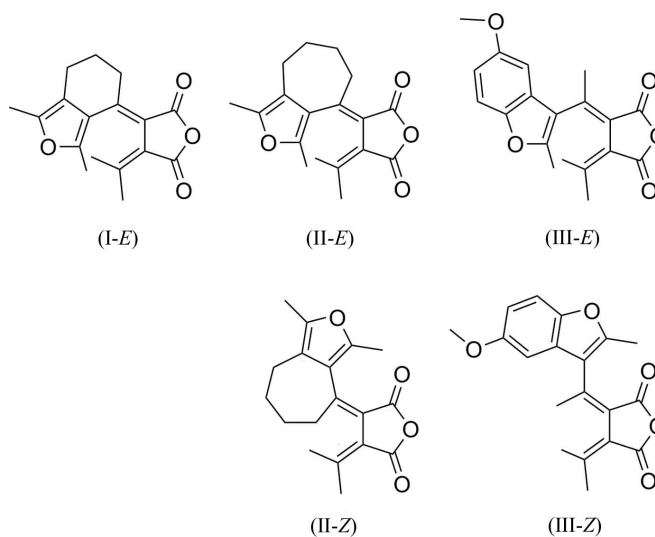


Scheme 1

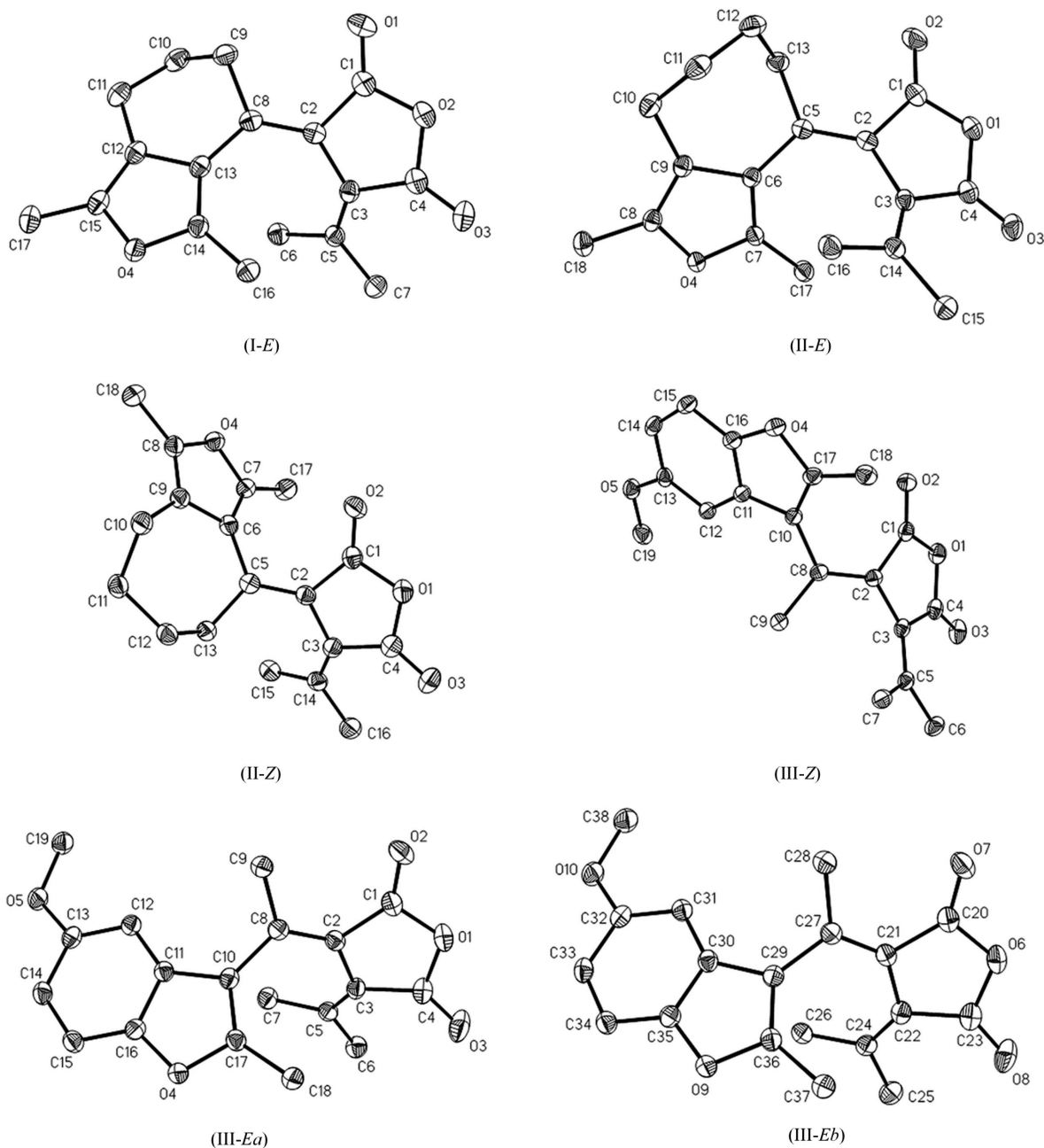
yields, which correspond with the effectiveness of the photochromic reaction. Bulky substituents reduce the *E*–*Z* isomerization in favour of the *E*–*C* ring closure and increase the quantum yield of the latter (Yokoyama *et al.*, 1988; Kiji *et al.*, 1995). Because of the single bond connection between the heterocyclic part and the anhydride moiety, a rotation process is possible. This process of diastereotopomerization results in an equilibrium of the (*P*)-*E*_α and (*M*)-*E*_β conformations (Scheme 2). With the synthesis of a series of rotationally-



Scheme 2



hindered fulgides, we improved the efficiency of the photochromic reaction. This was achieved by limiting unfavourable reactions, which compete with the ring closure from the *E* to the *C* isomer. In a comparative study, we analysed three furyl fulgides with different steric constraints to their furyl back-


Figure 1

The molecular structures of fulgides (I)–(III). H atoms have been omitted for clarity. The unit cell of (III-E) contains two independent molecules of similar conformation, *viz.* (III-Ea) and (III-Eb). For each structure, the displacement ellipsoids are drawn at the 50% probability level.

bone. Fulgides (I) and (II) contain a bridging alkyl chain between the hexatriene and furyl moieties. Therefore, the rotation around the C_b-C_c bond is unfeasible and no $E_\alpha-E_\beta$ diastereotopomerization occurs. For fulgide (III), the rotation should be limited to a minimal amount because of benzoannulation to the furyl part. By limiting the rotation all or at least most of the photochromic molecules are available in the correct geometric conformation for cyclization. The effects of the structural modifications were investigated by UV–visible and femtosecond time-resolved transient absorption spectroscopy (Siewertsen *et al.*, 2011; Strübe *et al.*, 2011).

Herein we present the molecular structures of furyl fulgides (I)–(III) in the crystalline state and a detailed analysis of the

bond lengths, bond angles and selected torsion angles of the hexatriene unit of each fulgide. In addition, we analysed the distances between the two bond-forming carbon atoms C_a and C_f . The structures of compounds (I)–(III) are depicted in Fig. 1. In the crystalline state, the *E* isomers of (I)–(III) take the helical (*P*)- E_α conformation. This is due to the steric repulsion of the methyl groups at C_a and C_f . For (III-E), the asymmetric unit contains two forms [(III-Ea) and (III-Eb)] with slightly different parameters owing to packing effects. Table 1 shows selected bond lengths, bond angles and torsion angles for the hexatriene systems of each fulgide. As expected, for all structures the bond lengths inside the hexatriene unit alternate between short and long corresponding to the alternating

Table 1

Selected interatomic distances, angles and torsion angles of compounds (I)–(III) (Å, °).

	(I-E)	(II-E)	(III-E)	(II-Z)	(III-Z)
<i>a</i> – <i>b</i>	1.3725 (15)	1.3679 (15)	1.3654 (17)	1.3632 (17)	1.3641 (14)
<i>b</i> – <i>c</i>	1.4507 (16)	1.4609 (15)	1.4669 (16)	1.4686 (16)	1.4712 (13)
<i>c</i> – <i>d</i>	1.3682 (15)	1.3661 (15)	1.3592 (17)	1.3614 (17)	1.3609 (14)
<i>d</i> – <i>e</i>	1.4721 (15)	1.4761 (15)	1.4768 (17)	1.4800 (17)	1.4722 (13)
<i>e</i> – <i>f</i>	1.3559 (15)	1.3552 (16)	1.3554 (18)	1.3564 (18)	1.3517 (14)
<i>f</i> – <i>a</i>	3.5482 (15)	3.5594 (15)	3.6629 (17)	3.5403 (17)	5.4409 (14)
<i>a</i> – <i>b</i> – <i>c</i>	131.14 (10)	128.62 (10)	124.95 (11)	126.72 (11)	126.51 (9)
<i>b</i> – <i>c</i> – <i>d</i>	126.50 (10)	125.58 (10)	121.83 (11)	122.25 (11)	122.59 (9)
<i>c</i> – <i>d</i> – <i>e</i>	132.48 (10)	132.98 (10)	132.19 (11)	133.53 (11)	128.33 (9)
<i>d</i> – <i>e</i> – <i>f</i>	129.11 (10)	129.41 (10)	129.69 (11)	130.98 (11)	130.30 (9)
<i>a</i> – <i>b</i> – <i>c</i> – <i>d</i>	28.51 (18)	–37.86 (17)	52.48 (18)	51.58 (19)	–55.72 (15)
<i>b</i> – <i>c</i> – <i>d</i> – <i>e</i>	16.47 (19)	–10.38 (19)	14.70 (2)	9.00 (2)	–178.29 (9)
<i>c</i> – <i>d</i> – <i>e</i> – <i>f</i>	41.06 (19)	–44.14 (19)	41.90 (2)	36.30 (2)	–49.02 (16)
<i>g</i> – <i>b</i> – <i>c</i> – <i>d</i>	–161.82 (10)	151.11 (11)	–136.83 (13)	–129.36 (13)	130.31 (11)
<i>h</i> – <i>d</i> – <i>e</i> – <i>f</i>	–147.93 (11)	144.83 (11)	–146.29 (13)	–152.36 (13)	151.31 (10)

single and double bonds. The fulgides (I)–(III) do not differ significantly with respect to bond distances and angles. These results are in agreement with previously published structures of indolyl fulgides (Wolak *et al.*, 2002). Furthermore, the atom distances between *C_a* and *C_f* are in the same range as for the indolyl fulgides. Hence, these values can give no explanation for the different photochromic properties. Because of the strained geometry, the torsion angles for fulgide (I-E) show deviations from the values found in the other compounds. At least no trend can be observed which correlates with the photochemical observations for the *E* forms. The *Z* isomers of (II) and (III) have almost equal properties with regard to the bond lengths and angles. Discrepancies up to 15° are observed for the torsion angles. As there is no possibility for direct *Z*–*C* cyclization it is not useful to make any suggestions for the correlation between the photochemical and structural properties. In summary, the small variations in the crystallographic structures give no explanation for the different photochromic behaviour.

Experimental

Fulgides (I)–(III) were synthesized following the principles of the Stobbe condensation (Strübe *et al.*, 2011). The condensation was performed using lithium diisopropylamide in tetrahydrofuran (THF) at 195 K followed by saponification with an aqueous solution of potassium hydroxide in ethanol at 343 K. For dehydration, *N,N'*-dicyclohexylcarbodiimide was used. Fulgides (I-E) and (III-E) were recrystallized from diethyl ether, fulgide (II) was recrystallized from cyclohexane and the (III-Z) isomer was recrystallized from ethanol. Full synthesis details and spectroscopic data for all compounds are available in the archived CIF.

Compound (I-E)

Crystal data

$C_{17}H_{18}O_4$
 $M_r = 286.31$
 Monoclinic, $P2_1/n$
 $a = 8.7142$ (2) Å
 $b = 12.0207$ (3) Å
 $c = 13.9102$ (4) Å
 $\beta = 100.9737$ (18)°

$V = 1430.46$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 100$ K
 $0.27 \times 0.12 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (DENZO and SCALEPACK;
 Otwinowski & Minor, 1997)
 $T_{\min} = 0.975$, $T_{\max} = 0.991$

33163 measured reflections
 3278 independent reflections
 2810 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.099$
 $S = 1.02$
 3278 reflections
 194 parameters

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³

Compound (II-E)

Crystal data

$C_{18}H_{20}O_4$
 $M_r = 300.34$
 Monoclinic, $P2_1/n$
 $a = 9.1881$ (2) Å
 $b = 12.0022$ (3) Å
 $c = 13.7215$ (3) Å
 $\beta = 100.4329$ (13)°

$V = 1488.16$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 100$ K
 $0.30 \times 0.30 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*DENZO* and *SCALEPACK*;
Otwinowski & Minor, 1997)
 $T_{\min} = 0.972$, $T_{\max} = 0.982$

28601 measured reflections
3402 independent reflections
2822 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.091$
 $S = 1.06$
3402 reflections

203 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

Compound (II-Z)

Crystal data

$\text{C}_{18}\text{H}_{20}\text{O}_4$
 $M_r = 300.34$
Orthorhombic, *Pbca*
 $a = 8.7024 (2) \text{ \AA}$
 $b = 12.8964 (4) \text{ \AA}$
 $c = 26.9492 (7) \text{ \AA}$

$V = 3024.50 (14) \text{ \AA}^3$
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 $0.30 \times 0.30 \times 0.26 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*DENZO* and *SCALEPACK*;
Otwinowski & Minor, 1997)
 $T_{\min} = 0.973$, $T_{\max} = 0.976$

29108 measured reflections
3444 independent reflections
2657 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.097$
 $S = 1.03$
3444 reflections

203 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

Compound (III-E)

Crystal data

$\text{C}_{19}\text{H}_{18}\text{O}_5$
 $M_r = 326.33$
Triclinic, $\bar{P}1$
 $a = 7.1750 (2) \text{ \AA}$
 $b = 12.0569 (2) \text{ \AA}$
 $c = 19.9592 (4) \text{ \AA}$
 $\alpha = 103.8136 (12)^\circ$
 $\beta = 91.1022 (13)^\circ$

$\gamma = 106.5927 (12)^\circ$
 $V = 1599.77 (6) \text{ \AA}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 $0.30 \times 0.25 \times 0.09 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*DENZO* and *SCALEPACK*;
Otwinowski & Minor, 1997)
 $T_{\min} = 0.971$, $T_{\max} = 0.991$

38746 measured reflections
7318 independent reflections
5802 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.107$
 $S = 1.03$
7318 reflections

443 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Compound (III-Z)

Crystal data

$\text{C}_{19}\text{H}_{18}\text{O}_5$
 $M_r = 326.33$
Monoclinic, *C2/c*
 $a = 26.5923 (4) \text{ \AA}$
 $b = 8.6140 (1) \text{ \AA}$
 $c = 15.3550 (2) \text{ \AA}$
 $\beta = 115.8482 (8)^\circ$

$V = 3165.41 (7) \text{ \AA}^3$
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 $0.30 \times 0.25 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*DENZO* and *SCALEPACK*;
Otwinowski & Minor, 1997)
 $T_{\min} = 0.971$, $T_{\max} = 0.990$

54136 measured reflections
3606 independent reflections
3205 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.091$
 $S = 1.06$
3606 reflections

222 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

For (I)–(III), H atoms were placed in geometric positions and refined as riding, with C–H = 0.95–0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *COLLECT* (Bruker, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3067). Services for accessing these data are described at the back of the journal.

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