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Structural properties of a series of photochromic fluorinated indolylfulgides

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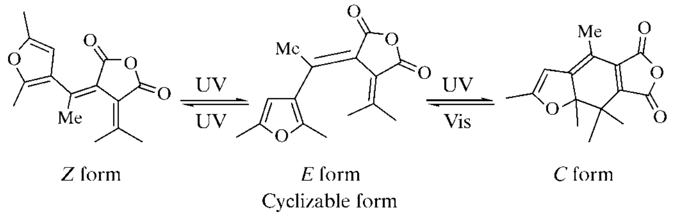
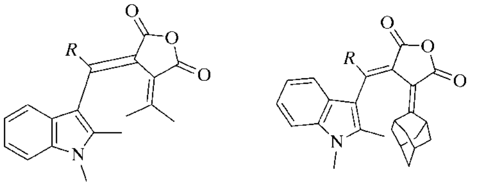
Fluorinated indolylfulgides are a class of photochromic organic compounds that meet many of the requirements for use as optical memory media and optical switches. The X-ray crystal structures of a series of five photochromic fluorinated indolylfulgides have been determined, namely (3*Z*)-3-[1-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,2-trifluoroethylidene]-4-(1-methylethylidene)dihydrofuran-2,5-dione (trifluoromethylisopropylideneindolylfulgide), $C_{19}H_{16}F_3NO_3$, (I), (3*Z*)-3-[1-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,3,3,3-pentafluoropropylidene]-4-(1-methylethylidene)dihydrofuran-2,5-dione (pentafluoroethylisopropylideneindolylfulgide), $C_{20}H_{16}F_5NO_3$, (II), (3*Z*)-3-[1-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,3,3,4,4,4-heptafluorobutylidene]-4-(1-methylethylidene)dihydrofuran-2,5-dione (heptafluoropropylisopropylideneindolylfulgide), $C_{21}H_{16}F_7NO_3$, (III), (3*Z*)-3-[1-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,2-trifluoroethylidene]-4-(tricyclo[3.3.1.1^{3,7}]decylidene)dihydrofuran-2,5-dione (trifluoromethyladamantylideneindolylfulgide), $C_{26}H_{24}F_3NO_3$, (IV), and (3*Z*)-3-[1-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,3,3,4,4,4-heptafluorobutylidene]-4-(tricyclo[3.3.1.1^{3,7}]decylidene)dihydrofuran-2,5-dione (heptafluoropropyladamantylideneindolylfulgide), $C_{28}H_{24}F_7NO_3$, (V). The photochromic property of fulgides is based on the photochemically allowed electrocyclic ring closure of a hexatriene system to form a cyclohexadiene. For each fulgide examined, the bond lengths within the hexatriene system alternate between short and long, as expected. Comparing the structures of the five fulgides with each other demonstrates no significant difference in bond lengths, bond angles or dihedral angles within the hexatriene systems. The distance between the bond-forming C atoms at each end of the hexatriene system does vary. Correlations of structural properties with optical properties are addressed.

Comment

Fulgides are an important class of organic photochromic compounds that undergo reversible color changes upon wavelength-specific illumination (Crano & Guglielmetti, 1999; Durr & Bousas-Laurent, 1990). Widely used in specialty inks and dyes, they are of particular interest for incorporation in high-density optical memory devices (Yokoyama, 2000). In such devices, binary information is encoded using two differently colored forms which are interconverted by the photochemical transformations of coloration (ring closure of the cyclizable form) and bleaching (ring opening of the *C* form); this is illustrated in the reaction *Scheme* below for commercially available Aberchrome 540 (Heller, 1986). There are many stringent requirements for photochromic materials intended for use as optical memory, including readily distinguishable absorption spectra for the separate colored forms, efficient photoreactions, high extinction coefficients, and both thermal and photochemical stability.



Recently discovered fluorinated isopropylidene indolylfulgides are promising candidates for optical memory that feature greatly enhanced photochemical fatigue resistance in comparison with other members of the fulgide family (Wolak *et al.*, 2001; Yokoyama & Takahashi, 1996). Additionally, they possess improved coloration quantum yields in solution relative to their non-fluorinated analogs. They are further characterized by a considerable bathochromic shift in absorption maxima for the cyclizable *Z* form. Adamantylidene-substituted fluorinated indolylfulgides possess many of the favorable properties of isopropylidene indolylfulgides, in addition to greater thermal stability for the cyclizable form (Wolak *et al.*, 2002).



(I) $R = CF_3$
(II) $R = C_2F_5$
(III) $R = C_3F_7$

(IV) $R = CF_3$
(V) $R = C_3F_7$

To aid in the preparation of further improved photochromic materials, we sought to identify relationships between crystal structure and optical properties. Herein, we examine in detail the structural attributes of a series of five cyclizable-form fluorinated indolylfulgides containing either isopropylidene or adamantylidene substitution, (I)–(V). Bond lengths, bond and dihedral angles, and distances between bond-forming C atoms are presented for each compound. Furthermore, we compare our findings with the reported photochemical yields for the coloration event, the optical property most likely to be asso-

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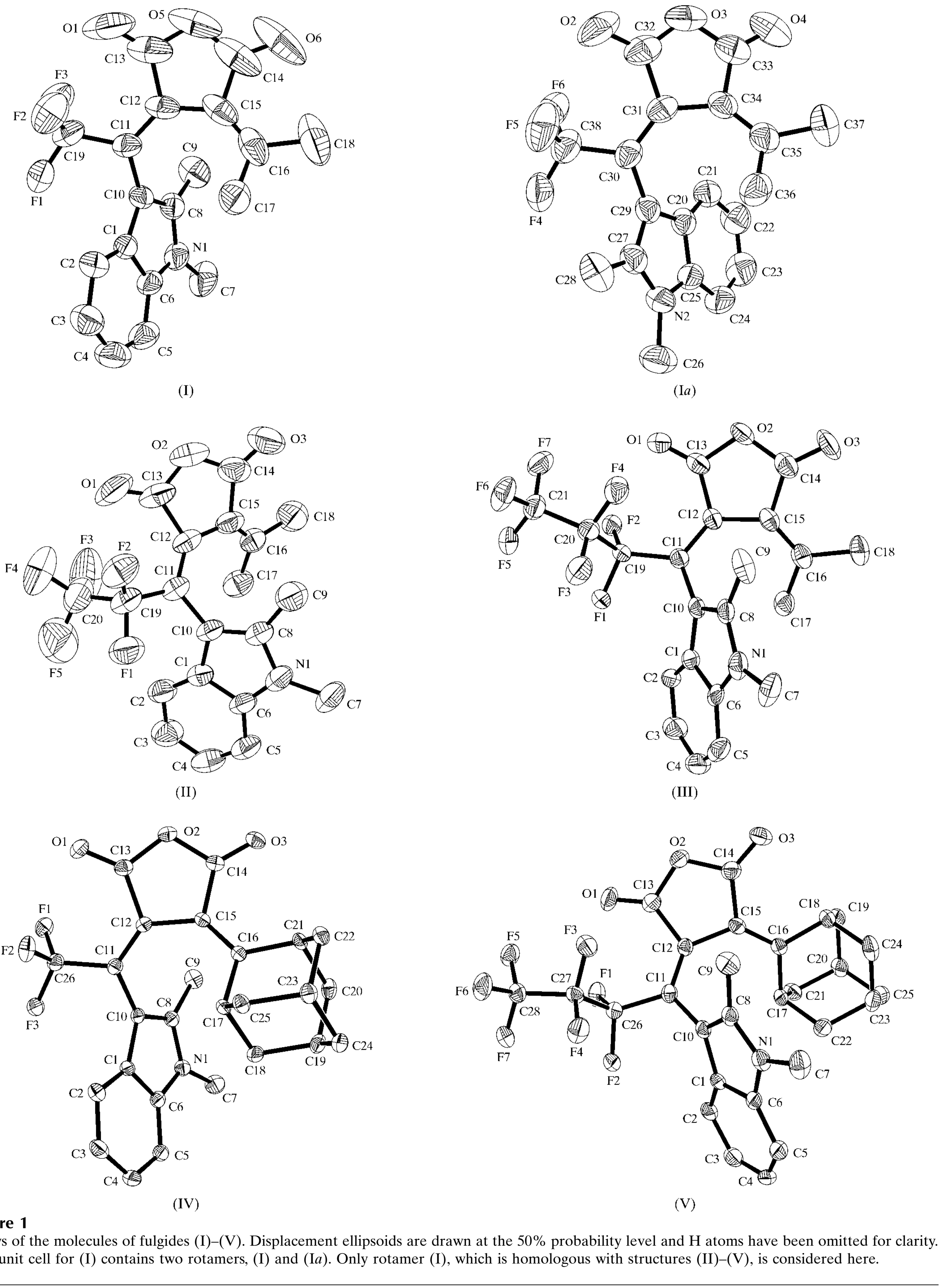


(I) (I*a*)

(II) (III)

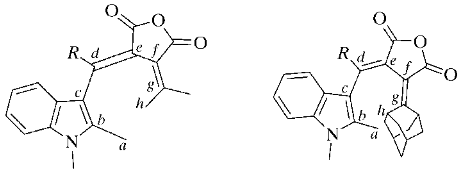
(IV) (V)

Figure 1

Views of the molecules of fulgides (I)–(V). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The unit cell for (I) contains two rotamers, (I) and (I*a*). Only rotamer (I), which is homologous with structures (II)–(V), is considered here.

ciated with the structure of the cyclizable form (Wolak *et al.*, 2001, 2002).

The structures of compounds (I)–(V) are depicted in Fig. 1. When fulgides are transformed from the cyclizable form to the cyclic form with light, the hexatriene system is converted to a cyclohexadiene system (see reaction *Scheme* above). Because the photochromic nature of fulgides is intimately associated with the hexatriene system (see *Scheme* below), we sought to examine how substituents alter the structure of the system, and to investigate whether structural trends are predictive of optical properties. The bond lengths and bond and dihedral angles for the hexatriene systems of the five indolylfulgides are shown in Table 1.



As expected, within the hexatriene system of the cyclizable form, the bond lengths alternate between short and long, corresponding to alternating double and single bonds. For a given bond, the bond lengths amongst the five compounds vary by no more than 0.02 Å. The minimal variations fall within expected experimental error owing to molecular motion and the use of spherical scattering factors for small-molecule carbon structures (Dunitz, 1999; Seiler *et al.*, 1984). Thus, although bond lengths appear to vary with the substitution pattern around the hexatriene system, it is difficult to say with certainty that observable trends exist. Similarly, the range of values for a given bond or dihedral angle corresponds approximately to the experimental error limits. Within the hexatriene system, the dihedral angles are observed to alternate between close to 0° and close to −50°. Bonds with dihedral angles of close to 0° correspond to double bonds, and those with values in the vicinity of −50° correspond to single bonds.

Previous reports have suggested that the *efgh* torsion angle or the distance between atoms *b* and *g* in the cyclizable form might be correlated with the quantum yield of coloration (Ilge & Colditz, 1990; Yokoyama *et al.*, 1996). The quantum yield of coloration, $\Phi_{\text{coloration}}$, is a measure of the efficiency of the photoreaction that forms a new bond between atoms *b* and *g*. One might imagine that the spatial proximity of atoms *b* and *g* in the cyclizable form would be a determining factor in the efficiency of the photocyclization reaction.

The distance between atoms *b* and *g* is always greater for the adamantylidene derivatives than for the corresponding isopropylidene derivatives (Table 2). Within the isopropylidene series, the $b-g$ distance decreases when the fluorinated substituent is changed from CF_3 in (I) to C_3F_7 in (III). In contrast, the data suggest that the opposite trend exists for the adamantylidene series. In Table 2, the $b-g$ distances are compared with the quantum yields measured in toluene at 427 nm. The quantum yields of the isopropylidene derivatives are greater than those of the adamantylidene derivatives and the $b-g$ distances are smaller, as expected. Within the isopropylidene series, the quantum yields remain relatively constant while the $b-g$ distance decreases, thus suggesting that other factors may be important.

Experimental

The five title compounds were synthesized as reported previously by Thomas *et al.* (2001). The isopropylidene fulgides, (I)–(III), were recrystallized from propan-2-ol and the adamantylidene fulgides, (IV) and (V), were recrystallized from toluene–ligroin.

Compound (I)

Crystal data

$C_{19}H_{16}F_3NO_3$
$M_r = 363.33$
Monoclinic, $P2_1/n$
$a = 11.660$ (1) Å
$b = 17.164$ (2) Å
$c = 17.102$ (2) Å
$\beta = 92.75$ (2)°
$V = 3418.9$ (6) Å^3
$Z = 8$

$D_x = 1.412$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6045 reflections
$\theta = 1.7$–25.1°
$\mu = 0.12$ mm^{-1}
$T = 90$ (2) K
Plate, yellow
0.25 × 0.16 × 0.04 mm

Data collection

Bruker *P*4 diffractometer with CCD area-detector
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.971$, $T_{\max} = 0.995$
17 999 measured reflections
6045 independent reflections

2878 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.065$
$\theta_{\max} = 25.1°$
$h = -13 \rightarrow 13$
$k = -20 \rightarrow 19$
$l = -20 \rightarrow 18$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.160$
$S = 0.99$
6045 reflections
477 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.6437P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Compound (II)

Crystal data

$C_{20}H_{16}F_5NO_3$
$M_r = 413.34$
Monoclinic, $P2_1/c$
$a = 9.539$ (1) Å
$b = 16.716$ (1) Å
$c = 11.720$ (1) Å
$\beta = 92.90$ (1)°
$V = 1866.6$ (3) Å^3
$Z = 4$

$D_x = 1.471$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3291 reflections
$\theta = 2.1$–25.0°
$\mu = 0.13$ mm^{-1}
$T = 90$ (2) K
Plate, yellow
0.24 × 0.16 × 0.12 mm

Data collection

Bruker *P*4 diffractometer with CCD area-detector
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.970$, $T_{\max} = 0.982$
10 009 measured reflections
3291 independent reflections

1625 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.053$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 19$
$l = -12 \rightarrow 13$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.181$
$S = 1.01$
3291 reflections
267 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0903P)^2 + 0.1488P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.011 (2)

Compound (III)

Crystal data

$C_{21}H_{16}F_7NO_3$
$M_r = 463.35$
Triclinic, $P\overline{1}$
$a = 10.070$ (2) Å
$b = 11.003$ (2) Å
$c = 11.266$ (2) Å
$\alpha = 93.75$ (3)°
$\beta = 111.33$ (3)°
$\gamma = 115.80$ (2)°
$V = 1008.9$ (5) Å^3
$Z = 2$
$D_x = 1.526$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5487 reflections
$\theta = 2.0$–25.0°
$\mu = 0.15$ mm^{-1}
$T = 93$ (2) K
Rhomb, yellow
0.17 × 0.16 × 0.14 mm

Data collection

Bruker *P*4 diffractometer with CCD area-detector
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.975$, $T_{\max} = 0.980$
5487 measured reflections
3520 independent reflections
2421 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25°$
$h = -9 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -13 \rightarrow 10$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.152$
$S = 1.03$
3520 reflections
293 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0794P)^2 + 0.3462P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Compound (IV)

Crystal data

$C_{26}H_{24}F_3NO_3$
$M_r = 455.46$
Monoclinic, $P2_1/n$
$a = 7.721$ (1) Å
$b = 20.737$ (2) Å
$c = 13.496$ (1) Å
$\beta = 99.35$ (1)°
$V = 2132.1$ (4) Å^3
$Z = 4$
$D_x = 1.419$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5081 reflections
$\theta = 1.8$–28.3°
$\mu = 0.11$ mm^{-1}
$T = 90$ (2) K
Plate, yellow
0.27 × 0.15 × 0.06 mm

Data collection

Bruker *P*4 diffractometer with CCD area-detector
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.975$, $T_{\max} = 0.992$
13 914 measured reflections
5081 independent reflections
4050 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 28.3°$
$h = -9 \rightarrow 9$
$k = -27 \rightarrow 19$
$l = -17 \rightarrow 17$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.140$
$S = 1.09$
5081 reflections
300 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 1.9760P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Compound (V)

Crystal data

$C_{28}H_{24}F_7NO_3$
$M_r = 555.48$
Triclinic, $P\overline{1}$
$a = 10.313$ (1) Å
$b = 10.924$ (1) Å
$c = 11.729$ (1) Å
$\alpha = 87.67$ (1)°
$\beta = 82.65$ (1)°
$\gamma = 73.24$ (1)°
$V = 1254.8$ (2) Å^3
$Z = 2$
$D_x = 1.470$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4383 reflections
$\theta = 1.8$–25.0°
$\mu = 0.13$ mm^{-1}
$T = 90$ (2) K
Plate, yellow
0.21 × 0.15 × 0.08 mm

Data collection

Bruker *P*4 diffractometer with CCD area-detector
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.978$, $T_{\max} = 0.990$
6916 measured reflections
4383 independent reflections
3293 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 25°$
$h = -10 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.110$
$S = 1.03$
4383 reflections
354 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.2697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
A comparison of the geometry of compounds (I)–(V) (Å, °).

See *Scheme* in *Comment* for atom labeling.

	(I)	(II)	(III)	(IV)	(V)
b—*c*	1.381 (4)	1.384 (5)	1.389 (4)	1.388 (3)	1.395 (3)
c—*d*	1.457 (4)	1.469 (4)	1.477 (4)	1.469 (3)	1.468 (3)
d—*e*	1.354 (4)	1.359 (4)	1.373 (4)	1.352 (3)	1.359 (3)
e—*f*	1.465 (5)	1.463 (5)	1.483 (4)	1.481 (3)	1.484 (3)
f—*g*	1.357 (5)	1.351 (5)	1.356 (5)	1.359 (3)	1.355 (3)
b—*c*—*d*	125.0 (3)	125.6 (3)	123.4 (3)	124.80 (19)	122.89 (19)
c—*d*—*e*	123.4 (3)	123.6 (3)	121.7 (3)	124.12 (18)	122.26 (19)
d—*e*—*f*	130.2 (3)	130.3 (3)	127.8 (3)	129.65 (18)	128.52 (19)
e—*f*—*g*	130.5 (3)	130.7 (3)	130.8 (3)	130.11 (18)	129.95 (19)
a—*b*—*c*—*d*	−4.5 (5)	0.3 (6)	−3.4 (5)	2.3 (3)	−2.7 (3)
b—*c*—*d*—*e*	−51.5 (5)	−54.5 (5)	−52.8 (4)	−57.6 (3)	−54.4 (3)
c—*d*—*e*—*f*	−9.9 (6)	−4.2 (6)	−12.3 (5)	−6.0 (3)	−11.6 (3)
d—*e*—*f*—*g*	−41.1 (6)	−43.8 (6)	−39.1 (5)	−45.9 (3)	−49.8 (3)
e—*f*—*g*—*h*	3.2 (6)	−1.0 (6)	−3.9 (5)	−1.3 (3)	3.1 (3)

Table 2
Distances between bond-forming atoms (Å) and coloration quantum yields.

	(I)	(II)	(III)	(IV)	(V)
$b-g$	3.517 (5)	3.517 (5)	3.459 (4)	3.625 (3)	3.644 (3)
$\Phi_{\rm coloration}$	0.20	0.15	0.18	0.051	0.040

H atoms were placed in geometric positions and refined as riding, with C—H = 0.93–0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The largest peak in the final difference map of structure (III) is located 1.3 Å from atom H9*A*, 1.4 Å from atom H9*C* and 1.6 Å from atom H7*A*.

For all compounds, data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1655). Services for accessing these data are described at the back of the journal.

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