Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction: none
10 118 measured reflections
3101 independent reflections
2485 reflections with
$I > 2\sigma(I)$

$R_{\rm int} = 0.0625$
$\theta_{\rm max} = 23.8°$
$h = -8 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R = 0.0367$
$wR = 0.0821$
$S = 1.075$
3101 reflections
240 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.023P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.10$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.11$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (V)

Crystal data

$C_{14}H_{18}O_5$
$M_r = 266.29$
Triclinic
$P\overline{1}$
$a = 7.7300$ (10) Å
$b = 9.4267$ (10) Å
$c = 9.9854$ (10) Å
$\alpha = 79.235$ (8)°
$\beta = 88.902$ (10)°
$\gamma = 75.125$ (9)°
$V = 690.54$ (14) Å^3
$Z = 2$
$D_x = 1.281$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 1736 reflections with $I/\sigma(I) > 12$
$\theta = 2.28$–$24.69°$
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Prism
0.46 × 0.40 × 0.15 mm
Colourless

Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction: none
4199 measured reflections
2159 independent reflections
1792 reflections with
$I > 2\sigma(I)$

$R_{\rm int} = 0.0273$
$\theta_{\rm max} = 24.69°$
$h = -8 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R = 0.0402$
$wR = 0.1130$
$S = 1.123$
2159 reflections
176 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.0961P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

For both compounds, data collection: *EXPOSE* (Stoe & Cie, 1996); cell refinement: *CELL* (Stoe & Cie, 1996); data reduction: *INTEGRATE* (Stoe & Cie, 1996); program(s) used to solve structures: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *PLATON* and *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-(9-Fluorenoxy)-2-phenylphthalazin-1(2*H*)-one

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Abstract

The title compound, $C_{27}H_{18}N_2O_2$, was prepared from the reaction of the ambidentate anion of 2-phenyl-1,2,3,4-tetrahydrophthalazine-1,4-dione with 9-bromo-

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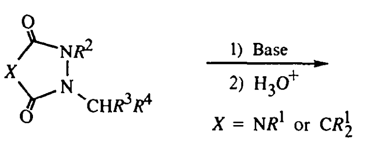
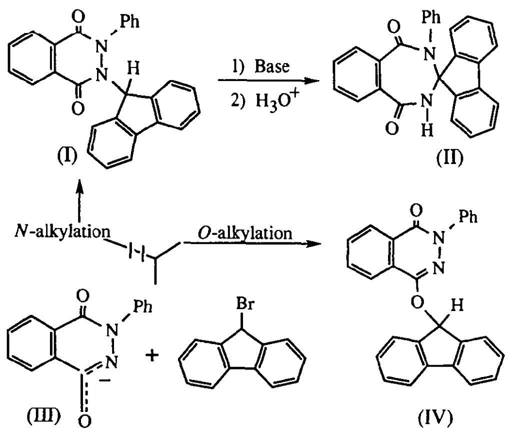
fluorene. The phthalazinone ring is nearly planar, edge-to-face aromatic–aromatic geometry is observed and the fluorenyl moiety is nearly perpendicular to the phenyl ring [88.15 (9)°].

Comment

Recently, we reported the ring-expansion reactions (equation 1) of certain pyrazolidinediones and urazoles, and the structures of the ring-expansion products hexahydropyrimidinedione (Gong, Robinson & Bausch, 1996) and dihydrotriazinedione (Robinson, Gong & Bausch, 1996). In trying to extend this new methodology to enable transformations of six-membered cyclic diacylhydrazines to the corresponding seven-membered ring systems, we attempted to prepare 2-(9-fluorenyl)-3-phenyl-1,2,3,4-tetrahydrophthalazine-1,4-dione, (I), in the hope that the same base-catalyzed N—N bond-cleavage ring-expansion chemistry depicted in equation 1 would result in the formation of dihydrobenzodiazepine-1,5-dione, (II) (equation 2).



(1)



(2)

(3)

One of the most direct methods for preparing (I) appeared to be *via* *N*-fluorenylation of the 2-phenyl-1,2,3,4-tetrahydrophthalazine-1,4-dione anion, (III). Previous findings showed that methylation of 5,8-dimethoxy-2-methylphthalazine-1,4-dione gave an *N*-methylated product (Parrick & Ragunathan, 1993). Conversely, *O*-alkylation prevailed in the chloroethylation of 1-hydroxy-3-methyl-3,4-dihydrophthalazin-4-one (Pring & Swahn, 1973). Finally, methylation of 2-methylphthalazine-1,4-dione (Elvidge & Redman, 1960) and aminoalkylation of 2-substituted 4-hydroxyphthalazin-1(2*H*)-one (Nagakura, Ota & Shimizu, 1974) gave a mixture of both the *N*- and *O*-alkylated isomers.

We carried out the reaction of anion (III) with 9-bromofluorene and subjected the crystalline product to X-ray crystal structure analysis. The structure identified the main product as the *O*-fluorenylated isomer, 2-phenyl-4-(9-fluorenoxy)phthalazin-1(2*H*)-one, (IV) (equation 3). The X-ray structure with the atom-numbering scheme is shown in Fig. 1. The portion of the phthalazinone ring defined by atoms C14–C20 deviates from planarity by an average distance of only 0.007 (2) Å; however, atoms N1, N2 and C21 deviate from the plane by −0.257 (3), −0.134 (3) and −0.125 (3) Å, respectively, indicating that there is a minor twist in the heterocyclic part of the phthalazinone ring. As expected, the N2=C14 double bond of 1.286 (2) Å is significantly shorter than the N1—C21 bond [1.381 (2) Å]. The phenyl and fluorene rings in (IV) are arranged in a T-pattern, in which the edge of the fluorenyl moiety is oriented toward the face of the phenyl ring. The centroid–centroid distance between the phenyl ring and the closest aromatic ring of the fluorenyl moiety is 6.488 (2) Å. Edge-to-face aromatic interactions have been studied in other systems (Schladetzky, Haque & Gellman, 1995; Robinson, Gong & Bausch, 1996). The angle between the phthalazinone and phenyl rings is 45.99 (10)°, while the angle between the phthalazinone and fluorene rings is 79.28 (6)°. The fluorenyl moiety is nearly perpendicular to the phenyl ring [88.15 (9)°].

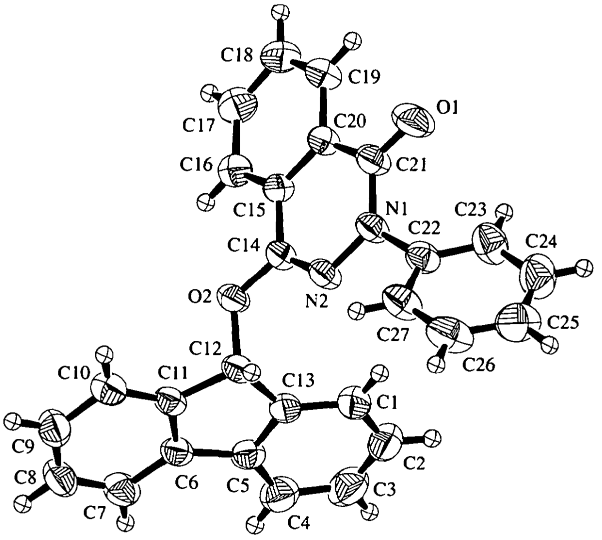


Fig. 1. The molecular configuration and atom-numbering scheme of (IV), with displacement ellipsoids at the 50% probability level. H atoms are shown as unlabeled isotropic spheres of arbitrary radii.

Experimental

A stirred solution of 2-phenyl-1,2,3,4-tetrahydrophthalazine-1,4-dione and potassium *tert*-butoxide in DMSO provided anion (III). To this solution, 9-bromofluorene was added and stirring was continued. The product obtained was recrystallized from chloroform to afford X-ray quality single crystals of (IV) (m.p. 482–483 K).

Crystal data

$C_{27}H_{18}N_2O_2$
$M_r = 402.43$
Triclinic
$P\overline{1}$
$a = 10.1662\,(16)$ Å
$b = 12.404\,(3)$ Å
$c = 9.0923\,(14)$ Å
$\alpha = 100.677\,(15)°$
$\beta = 102.334\,(12)°$
$\gamma = 111.728\,(14)°$
$V = 995.4\,(3)$ Å^3
$Z = 2$
$D_x = 1.3428\,(4)$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.3–11.9°$
$\mu = 0.086$ mm^{-1}
$T = 296$ K
Irregular fragment
0.41 × 0.38 × 0.30 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 8° min^{-1} in ω)
Absorption correction: none
3730 measured reflections
3511 independent reflections
2052 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0158$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 12$
$k = -14 \rightarrow 13$
$l = -10 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: −0.5%

Refinement

Refinement on F^2
$R(F) = 0.0350$
$wR(F^2) = 0.0863$
$S = 1.091$
3510 reflections
281 parameters
H atoms riding (C—H 0.93–0.98 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.129P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.151$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.145$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0109 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O2—C14	1.353 (2)	N1—N2	1.391 (2)
O2—C12	1.466 (2)	N1—C22	1.440 (2)
N1—C21	1.381 (2)	N2—C14	1.286 (2)
C14—O2—C12	117.98 (14)	O2—C12—C13	111.26 (15)
C21—N1—N2	124.9 (2)	N2—C14—O2	120.0 (2)
C21—N1—C22	122.7 (2)	N2—C14—C15	124.6 (2)
N2—N1—C22	112.38 (15)	O2—C14—C15	115.5 (2)
C14—N2—N1	118.0 (2)	N1—C21—C20	114.9 (2)
O2—C12—C11	107.28 (14)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*93 and *PLATON* (Spek, 1990).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1251). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-*N*-[1,8(10)-Menthadien-3-yl]toluenesulfonamide

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Abstract

In the cyclohexene ring of the title compound, $C_{17}H_{23}NO_2S$, four C atoms are planar and the other two atoms are on either side of the best plane. The toluenesulfonamide group is in an axial configuration. The molecules are linked in chains by N—H···O hydrogen bonds [N···O 2.948 (2) and H···O 2.14 (2) Å].