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Ethyl 4-(2,3,5,6-tetrahydro-3,3-dimethyl-5,6-dioxo-1,2-cycloheptapyrazol-2-yl)benzoate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.054
wR factor = 0.158
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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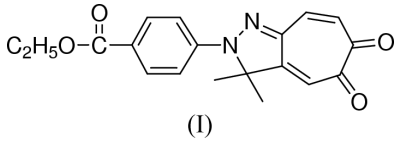
The title compound, $C_{19}H_{18}N_2O_4$, adopts an almost flattened conformation. The dihydropyrazole ring is almost coplanar with the seven-membered ring, the benzene ring, and the COO group. The plane defined by the α-dicarbonyl group intersects the seven-membered ring at an angle of 46.7 (1)°.

Comment

Hinopurpurins (2-aryl-2,3,5,6-tetrahydro-3,3-dimethyl-5,6-dioxo-1,2-cycloheptapyrazole) are known to be stable dyes (Mori *et al.*, 1989). The title compound, 4-ethoxycarbonylphenylhinopurpurin, (I), showed a remarkably large negative halochromism; 484 nm in ethyl acetate, 517, 566, and 600 (*sh*) nm in trifluoroacetic acid, and 455 nm in concentrated sulfuric acid. However, the crystal structures of hinopurpurins have never been elucidated. We now report the structure of (I) to elucidate its properties as a dye.



(I)

The C—C and C═C bond lengths of the seven-membered ring show apparent bond alternation. The C1═O1 [1.220 (4) Å] and C2═O2 [1.225 (4) Å] bond lengths are similar to that (1.259 Å) of tropone (Barrow *et al.*, 1973). The N1—N2 [1.332 (3) Å] and N1═C5 [1.328 (3) Å] bond lengths are close to those [1.343 Å for N—N and 1.322 Å for N═C] of pyrazole (la Cour & Rasmussen, 1973).

The deviations of each atom from the least-squares plane of the seven-membered ring are −0.134 (4) Å for C1, 0.097 (4) Å for C2, 0.025 (4) Å for C3, −0.041 (4) Å for C4, −0.014 (4) Å for C5, 0.064 (4) Å for C6, and 0.032 (4) Å for C7. The diketone structure (*A*) (least-squares plane defined by atoms C1, C2, O1 and O2) intersects the seven-membered ring (*B*) (defined by atoms C1–C7) at an angle of 15.5 (1)°. The dihydropyrazole ring (*C*) (defined by atoms N1, N2, C4, C5 and C8) is almost coplanar with the seven-membered ring (*B*), the benzene ring (*D*), and the carboxy group (*E*) (defined by atoms C17, O3 and O4). The dihedral angles between planes *B* and *C*, between *C* and *D*, and between *C* and *E* are 4.1 (1), 5.3 (1) and 4.3 (4)°, respectively.

Experimental

To a pyridine solution (2 ml) of 4-isopropyltropolone (164 mg, 1.0 mmol) was added drop by drop an aqueous solution of diazotized 4-ethoxycarbonylaniline (248 mg, 1.5 mmol) at 273 to 278 K with stirring for 2 h. After the solution was diluted with water (10 ml), the

precipitate was filtered and dried. An ethanol solution of the precipitate was refluxed for 4 h and cooled to yield the title compound (I) (142 mg, 42%) by filtration (Mori *et al.*, 1989). The single crystals of (I) were obtained by recrystallization from chloroform.

Crystal data

$C_{19}H_{18}N_2O_4$
M_r = 338.35
Orthorhombic, *Pbca*
a = 19.028 (3) Å
b = 19.166 (3) Å
c = 9.4466 (5) Å
V = 3445.1 (7) Å^3
Z = 8
D_x = 1.305 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 reflections
θ = 9.2–17.9°
μ = 0.09 mm^{-1}
T = 296 (2) K
Prism, red
0.33 × 0.27 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.969, T_{max} = 0.998
4149 measured reflections
4149 independent reflections
1280 reflections with $I > 2\sigma(I)$
θ_{max} = 28.0°
$h = 0 \rightarrow 25$
$k = -25 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.158
S = 0.89
4149 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

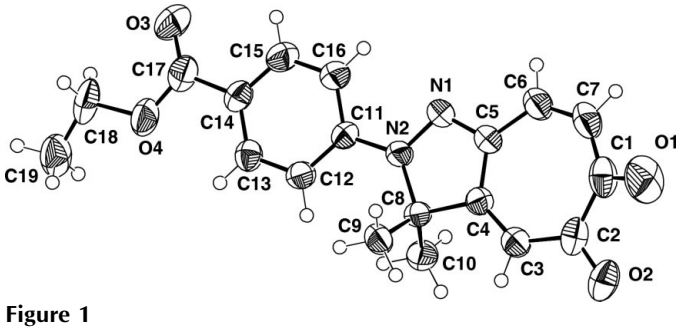


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.328 (3)	C2—C3	1.439 (4)
N1—N2	1.332 (3)	C3—C4	1.340 (4)
N2—C8	1.486 (4)	C4—C5	1.426 (4)
N2—C11	1.406 (3)	C4—C8	1.520 (4)
O1—C1	1.220 (4)	C5—C6	1.428 (4)
O2—C2	1.225 (4)	C6—C7	1.339 (4)
C1—C2	1.533 (5)	C8—C9	1.536 (4)
C1—C7	1.455 (5)	C8—C10	1.533 (4)
O1—C1—C2—O2	−19.3 (5)	C18—O4—C17—C14	175.6 (3)
N1—N2—C8—C9	117.7 (3)	C13—C14—C17—O3	−178.4 (3)
N1—N2—C8—C10	−114.9 (3)	C13—C14—C17—O4	1.6 (5)
N1—N2—C11—C12	175.4 (3)	C17—O4—C18—C19	169.5 (3)
N1—N2—C11—C16	−4.8 (4)		

All H atoms were located at ideal positions and restrained with U_{iso} held fixed to 1.2U_{eq} of the parent atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL*97.

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