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Ethyl 3-[4-(ethoxycarbonyl)phenyl]-3,4-dihydroquinazoline-6-carboxylate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.008 Å
R factor = 0.045
wR factor = 0.095
Data-to-parameter ratio = 9.0

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

The crystal structure of the title compound, $C_{20}H_{20}N_2O_4$, contains two molecules in the asymmetric unit. The crystal packing involves π–π, C—H···O and C—H···N interactions.

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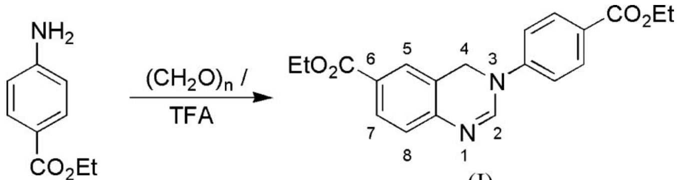
Comment

A 3,4-dihydroquinazoline with methyl substituents *para* to the N atoms was first reported in 1906 (von Walther & Bamberg, 1906) and was later shown to be one of the by-products formed in a synthesis of Tröger's base (Eisner & Wagner, 1934). Maffei established that analogous compounds with nitro and ethoxy substituents *para* to the N atoms were formed from condensation reactions of 4-nitroaniline (Maffei, 1928) and 4-ethoxyaniline (Maffei, 1929), respectively, with formaldehyde in the presence of an acid catalyst. Subsequently, bromo and chloro (Wagner & Eisener, 1937) analogues were also reported, together with highly substituted systems derived from 4-methoxy-2,3,5-trimethylaniline (Smith & Schubert, 1948) and methyl 4-amino-3-chloro-2-methoxybenzoate (Becker *et al.*, 1993) as side-products in the formation of Tröger's base analogues. Spielman showed that 1,2,3,4-tetrahydroquinazolines were intermediates in the synthesis of Tröger's base systems by condensing a tetrahydroquinazoline with formaldehyde to afford Tröger's base (Spielman, 1935). Other researchers confirmed the role of tetrahydroquinazolines by using them as intermediates in the synthesis of Tröger's base analogues (Miller & Wagner, 1941; Abonia *et al.*, 2002). A possible pathway for the oxidation of tetrahydroquinazolines to 3,4-dihydroquinazolines has been proposed (Simons, 1937). In the present case, the title compound, (I), was obtained as a by-product in the formation of a 2,8-diester-substituted Tröger's base.



(I)

Crystals of (I) suitable for X-ray analysis were grown by the slow evaporation of an ethyl acetate solution. Despite appearing (at least visually) to be single, they proved to be a two-component twin, which was resolved using the program *GEMINI* (Siemens, 1995). The asymmetric unit contains two independent molecules, which interact *via* offset face-to-face π–π interactions to form infinite one-dimensional columns (Fig. 2), with $Csp^2\cdots Csp^2$ distances in the range 3.25–3.75 Å.

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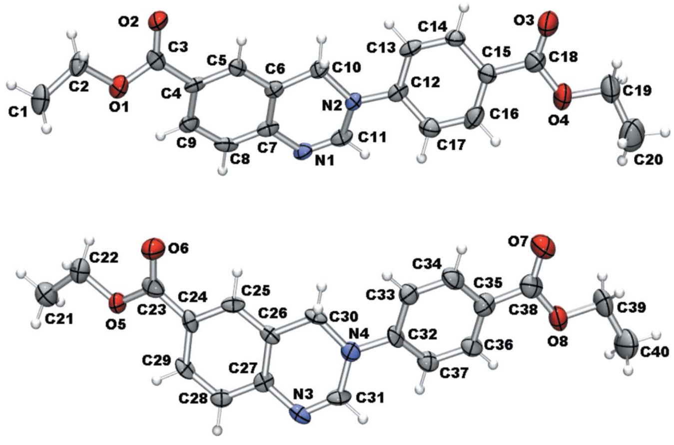

Figure 1
The structures of the two crystallographically independent molecules of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

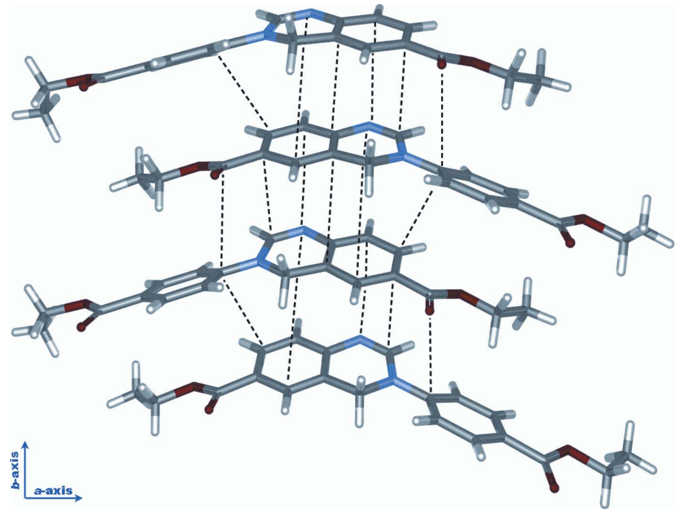

Figure 2
A schematic representation of part of the column formed *via* π–π interactions (dashed lines) present in (I).

Each of these columns interacts with neighbouring columns through a combination of edge-to-face π–π interactions (C8—C5) and weak aryl H$\cdots$Nsp^2 and H$\cdots$Osp^2 interactions, indicated by distances of 2.82 [H25$\cdots$N1($x, 1-y, \frac{1}{2}+z$)] and 2.37 Å [H17$\cdots$O6($x, 1-y, -\frac{1}{2}+z$)], forming an infinite two-dimensional motif (Fig. 3). These distances are typical of interactions between phenyl H atoms and amine N atoms, which are well documented as playing a role in structure stabilization in other systems (Antonioli *et al.*, 2006; Lindoy & Atkinson, 2000; Jeffery, 2003; Alshahateet *et al.*, 2001; Rahman *et al.*, 2003).

Experimental

Ethyl 4-aminobenzoate (5.00 g, 30.26 mmol) and paraformaldehyde (1.46 g, 48.66 mmol) were dissolved in trifluoroacetic acid (75 ml) and the mixture was stirred under an argon atmosphere in the dark for 7 d. The reaction mixture was then neutralized by a solution of concentrated ammonia (80 ml) in water (120 ml). This mixture was then basified by the addition of a saturated sodium hydrogen carbonate solution (100 ml) and the crude material was extracted into ethyl acetate (3 × 75 ml). The combined organic layers were washed with brine (100 ml), dried over anhydrous sodium sulfate, filtered, and evaporated to dryness to yield an orange solid. The crude material was chromatographed (silica gel, ethyl acetate–dichloromethane 1:9) to afford ethyl 3-[4-(ethoxycarbonyl)phenyl]-3,4-dihydroquinazoline-6-carboxylate (722 mg, 14%), (I), as a white solid. This was the second major product eluted from the column.

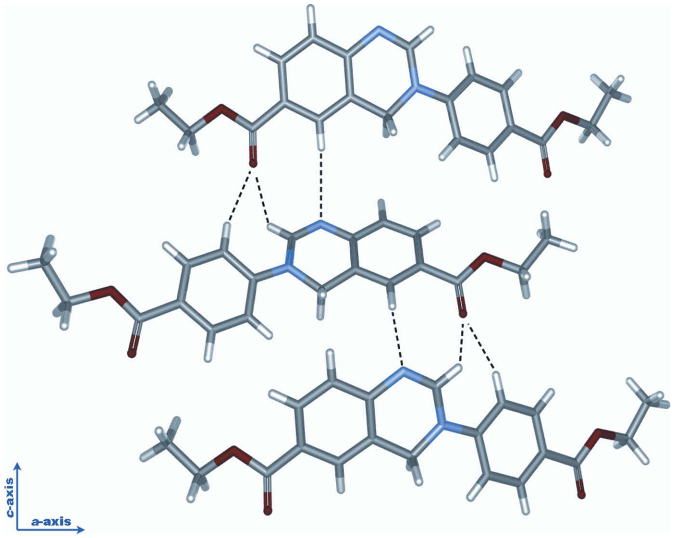

Figure 3
A schematic representation of the weak aryl$\cdots$N and aryl$\cdots$O interactions (dashed lines) present in (I) which, when combined with π–π interactions, form an infinite two-dimensional motif.

Crystal data

$C_{20}H_{20}N_2O_4$
$M_r = 352.38$
Monoclinic, Pc
$a = 19.875\ (9)$ Å
$b = 7.393\ (3)$ Å
$c = 11.529\ (5)$ Å
$\beta = 99.622\ (9)^\circ$
$V = 1670.2\ (13)$ Å^3
$Z = 4$
$D_x = 1.401$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 150\ (2)$ K
Plate, colourless
0.50 × 0.17 × 0.11 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*TWINABS*; Siemens, 1995)
$T_{\min} = 0.863$, $T_{\max} = 0.990$
7366 measured reflections
4288 independent reflections
3021 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 28.7^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.095$
$S = 0.94$
4288 reflections
474 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

C-bound H atoms were included in idealized positions and refined using a riding model. Methine, aromatic and methyl C—H bond lengths were fixed at 0.95, 0.95 and 0.98 Å, respectively. $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$(C) for methine and aromatic H atoms, and at $1.5U_{\rm eq}$(C) for methyl H atoms.

Data collection: *SMART* and *GEMINI* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997), *WinGX32* (Farrugia, 1999), *POV-RAY* (Cason, 2002) and *WebLab ViewerPro* (Molecular Simulations, 2000); software used to prepare material for publication: *enCIFer* (Version 1.0; Allen *et al.*, 2004).

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