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Crystal structure of diethyl 3,9-bis(4-fluorophenyl)-6,12-diphenyl-3,9-diazapentacyclo[6.4.0.0^{2,7}.0^{4,11}]dodecane-1,5-dicarboxylate, C₄₀H₃₆F₂N₂O₄

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.25 × 0.23 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8118, 2856, 0.018
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2380
$N(\text{param})_{\text{refined}}$:	218
Programs:	Bruker [1], SHELX [2, 3]

Source of material

Preparation of 1,4-diaryl-1,4-dihydropyridine-3-carboxylic acid photoreactive raw materials was performed by a literature method [4]. Starting with 4-fluoroaniline (0.5 mmol) ethyl propiolate (0.5 mmol) and 4-fluorocinnamaldehyde (0.5 mmol) as starting materials; piperazine (0.25 mmol) and *p*-toluenesulfonic (0.02 mmol) acid were used as catalysts, and 1,2-dichloroethane (20 mL) was used as a solvent. The mixture was heated under reflux for 12 h to obtain 1,4-(4-fluorodiaryl)-1,4-dihydrogen ethyl pyridine-3-carboxylate. The product of 1,4-(4-fluorodiaryl)-1,4-dihydrogen ethyl pyridine-3-carboxylate (0.5 mmol) obtained in the first step of the reaction was placed on a blue LED (365 nm) for a photoreaction for 3 h [5]. The product was obtained by column chromatography eluting with petroleum ether and *n*-hexane 9:1. The resulting solution was evaporated to dryness to get some purple crystals.

Experimental details

All hydrogen atoms were placed in the calculated positions and all the non-hydrogen atoms were refined anisotropically.

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Abstract

C₄₀H₃₆F₂N₂O₄, monoclinic, $P2_1/c$ (no. 14), $a = 8.0755(7)$ Å, $b = 19.7663(19)$ Å, $c = 10.1987(9)$ Å, $\beta = 95.940(2)^\circ$, $V = 1619.2(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0465$, $wR_{\text{ref}}(F^2) = 0.1188$, $T = 296$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
C1	0.2612 (3)	0.38980 (12)	−0.03214 (19)	0.0506 (5)
C2	0.2643 (3)	0.45774 (12)	−0.00638 (19)	0.0530 (6)
H2	0.219324	0.488426	−0.069413	0.064 [*]
C3	0.3360 (3)	0.48006 (10)	0.11581 (18)	0.0422 (5)
H3	0.337826	0.526057	0.135123	0.051 [*]
C4	0.4052 (2)	0.43413 (9)	0.20949 (16)	0.0307 (4)
C5	0.4004 (2)	0.36536 (9)	0.17786 (18)	0.0378 (4)
H5	0.446794	0.334099	0.239191	0.045 [*]
C6	0.3277 (3)	0.34296 (11)	0.05657 (19)	0.0460 (5)
H6	0.324367	0.297099	0.036091	0.055 [*]
C7	0.4232 (2)	0.42666 (8)	0.45182 (16)	0.0288 (4)
H7	0.370654	0.382327	0.435837	0.035 [*]
C8	0.5549 (2)	0.52102 (8)	0.35474 (16)	0.0280 (4)
H8	0.595585	0.539625	0.274982	0.034 [*]
C9	0.4453 (2)	0.57404 (8)	0.42579 (16)	0.0282 (4)
C10	0.4319 (2)	0.64193 (9)	0.35726 (18)	0.0327 (4)
C11	0.3314 (3)	0.69737 (10)	0.1559 (2)	0.0482 (5)
H11A	0.438531	0.716471	0.141242	0.058 [*]
H11B	0.269044	0.730918	0.199922	0.058 [*]
C12	0.2377 (3)	0.67694 (13)	0.0279 (2)	0.0602 (6)
H12A	0.299568	0.642987	−0.013490	0.090 [*]
H12B	0.222353	0.715676	−0.028880	0.090 [*]
H12C	0.131075	0.659058	0.043757	0.090 [*]
C13	0.6891 (2)	0.52386 (9)	0.47627 (16)	0.0291 (4)
H13	0.791449	0.545951	0.454644	0.035 [*]
C14	0.7257 (2)	0.45729 (8)	0.55052 (16)	0.0292 (4)
H14	0.780555	0.469473	0.637536	0.035 [*]
C15	0.8429 (2)	0.40882 (9)	0.48957 (17)	0.0326 (4)
C16	0.8627 (3)	0.40722 (13)	0.3565 (2)	0.0532 (6)
H16	0.801432	0.436618	0.299200	0.064 [*]
C17	0.9736 (3)	0.36201 (14)	0.3075 (2)	0.0635 (7)
H17	0.985820	0.361708	0.217783	0.076 [*]
C18	1.0646 (3)	0.31811 (12)	0.3898 (3)	0.0572 (6)
H18	1.136681	0.287426	0.356236	0.069 [*]
C19	1.0487 (3)	0.31978 (11)	0.5223 (3)	0.0562 (6)
H19	1.111280	0.290567	0.579180	0.067 [*]
C20	0.9397 (2)	0.36478 (10)	0.5714 (2)	0.0439 (5)
H20	0.930915	0.365630	0.661547	0.053 [*]
F1	0.1925 (2)	0.36817 (8)	−0.15360 (13)	0.0834 (5)
N1	0.48461 (17)	0.45403 (7)	0.33375 (13)	0.0296 (3)
O1	0.4868 (2)	0.69432 (7)	0.40243 (15)	0.0570 (4)
O2	0.35359 (17)	0.63626 (6)	0.23566 (12)	0.0407 (3)

Comment

Cage dimer 4-aryl-1,4-dihydropyridines have a wide range of biological activities, such as anti-HIV and as an anti-multidrug resistance modulator [6–8]. Two caged dimeric compounds similar to the title compound have also been reported [9, 10]. Dimerization to form cage compounds by photoreaction is an alternative to our previous synthetic protocol [11]. When the wavelength of the UV lamp is

adjusted to 365 nm, a complete [2 + 2] reaction occurs, and the title compound is completely cyclized (see picture). It is worth to note that compared to previous studies, it can be shown that the electronic effect has little or no effect on the cyclization, and the incident wavelength plays a decisive role in the cycloaddition reaction. In the crystal structure, several important bond angle data are involved: C4–N1–C8 = 121.38(13)°, C9–C10–O1 = 125.64(16)°, C8–C13–C14 = 116.39(13)°, C8–N1–C13 = 112.31(13)°. The bond lengths and angles are in the expected ranges [9–11].

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