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The crystal structure of *tert*-butyl (*E*)-3-(2-(benzylideneamino)phenyl)-1*H*-indole-1-carboxylate, C₂₆H₂₄N₂O₂

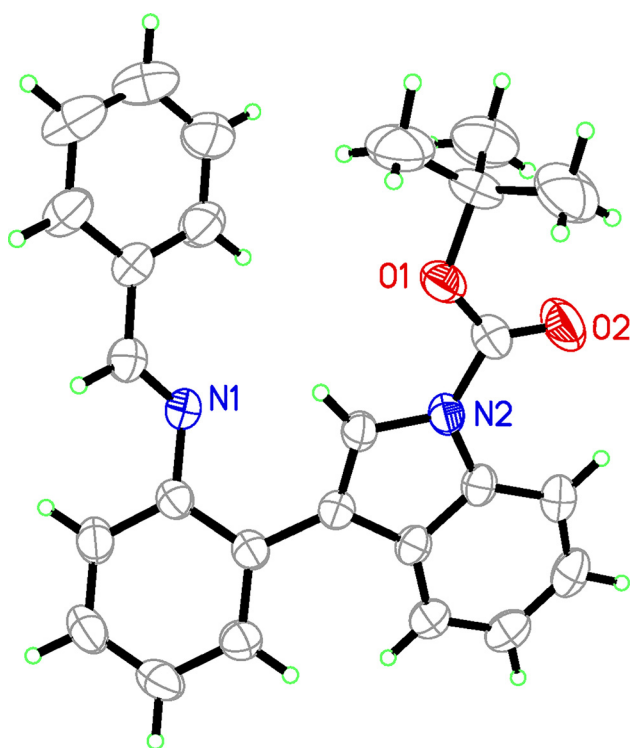


Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.30 × 0.25 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23,437, 4249, 0.048
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3131
$N(\text{param})_{\text{refined}}$:	274
Programs:	Bruker [1], SHELX [2, 3]

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.

1 Source of materials

The synthesis consists of two steps. In the first step, *tert*-butyl 3-bromo-1*H*-indole-1-carboxylate, 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, and Pd(PPh₃)₄ were mixed in a dioxane / K₂CO₃ mixture. The mixture was stirred at 100 °C under argon for 4 h. After cooling to room temperature, the mixture was extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane). The final product was obtained as maroon colored oil. In the second step, *tert*-butyl 3-(2-aminophenyl)-1*H*-indole-1-carboxylate was added to a mixture of chloroform and acetic acid in presence of molecular sieves. Benzaldehyde was then added dropwise into the mixture. The reaction was stirred at reflux under argon for 5 h. The yellow colored mixture was slowly poured into the NaOH solution. The organic layer was washed with water, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crystals were grown using a two solvent system (DCM/hexane) by slow diffusion at room temperature.

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Abstract

C₂₆H₂₄N₂O₂, monoclinic, $P2_1/n$ (no. 14), $a = 10.949(6)$ Å, $b = 9.930(5)$ Å, $c = 20.125(13)$ Å, $\beta = 98.51(3)^\circ$, $V = 2164(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0465$, $wR_{\text{ref}}(F^2) = 0.1260$, $T = 296(2)$ K.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.59035 (13)	0.16789 (12)	0.31150 (6)	0.0497 (3)
O2	0.50419 (16)	0.19822 (15)	0.20392 (7)	0.0714 (5)
N1	0.69809 (13)	0.54819 (14)	0.44105 (7)	0.0409 (4)
N2	0.48904 (13)	0.35892 (14)	0.28235 (7)	0.0375 (3)
C1	1.0379 (2)	0.1985 (3)	0.47627 (15)	0.0773 (7)
H1A	1.095894	0.131131	0.473428	0.093*
C2	0.9761 (2)	0.2560 (3)	0.41880 (13)	0.0736 (7)
H2A	0.993781	0.229011	0.377009	0.088*
C3	0.88803 (19)	0.3538 (2)	0.42298 (10)	0.0593 (6)
H3A	0.846135	0.391699	0.383867	0.071*
C4	0.86142 (16)	0.39588 (19)	0.48468 (9)	0.0438 (4)
C5	0.76297 (17)	0.49321 (19)	0.49095 (9)	0.0437 (4)
H5A	0.747476	0.515623	0.533786	0.052*
C6	0.60100 (16)	0.63551 (16)	0.45176 (8)	0.0367 (4)
C7	0.48946 (16)	0.63197 (16)	0.40647 (8)	0.0356 (4)
C8	0.47230 (15)	0.53928 (16)	0.34880 (8)	0.0353 (4)
C9	0.52280 (16)	0.41520 (17)	0.34555 (8)	0.0369 (4)
H9A	0.573195	0.373478	0.380857	0.044*
C10	0.52764 (18)	0.23438 (18)	0.26077 (9)	0.0446 (4)
C11	0.6464 (2)	0.03439 (19)	0.30093 (11)	0.0567 (5)
C12	0.7014 (3)	−0.0053 (3)	0.37129 (13)	0.0869 (9)
H12A	0.745192	−0.088796	0.370052	0.130*
H12B	0.636585	−0.015977	0.398217	0.130*
H12C	0.757348	0.063535	0.390427	0.130*
C13	0.7452 (3)	0.0522 (3)	0.25673 (15)	0.0895 (9)
H13A	0.785547	−0.032423	0.252186	0.134*
H13B	0.804713	0.116988	0.276688	0.134*
H13C	0.708310	0.083445	0.213220	0.134*
C14	0.5452 (3)	−0.0629 (2)	0.27220 (16)	0.0908 (9)
H14A	0.578626	−0.152156	0.271720	0.136*
H14B	0.512571	−0.036311	0.227190	0.136*
H14C	0.480349	−0.061583	0.299511	0.136*
C15	0.41353 (15)	0.45163 (17)	0.24304 (8)	0.0366 (4)
C16	0.35770 (17)	0.4439 (2)	0.17694 (9)	0.0453 (4)
H16A	0.367863	0.368996	0.150593	0.054*
C17	0.28633 (18)	0.5518 (2)	0.15161 (10)	0.0519 (5)
H17A	0.246130	0.548182	0.107580	0.062*
C18	0.27263 (18)	0.6658 (2)	0.18993 (10)	0.0511 (5)
H18A	0.224833	0.737425	0.171046	0.061*
C19	0.32921 (16)	0.67355 (19)	0.25551 (9)	0.0433 (4)
H19A	0.320253	0.750071	0.280996	0.052*
C20	0.40043 (15)	0.56494 (17)	0.28347 (8)	0.0352 (4)
C21	1.0137 (2)	0.2408 (3)	0.53745 (14)	0.0757 (7)
H21A	1.056324	0.203107	0.576419	0.091*
C22	0.92624 (18)	0.3393 (2)	0.54186 (11)	0.0572 (5)
H22A	0.910882	0.367831	0.583862	0.069*
C23	0.61276 (18)	0.72731 (19)	0.50465 (9)	0.0467 (5)
H23A	0.686965	0.732066	0.533767	0.056*
C24	0.5172 (2)	0.81110 (19)	0.51482 (9)	0.0524 (5)
H24A	0.527179	0.871415	0.550569	0.063*
C25	0.4069 (2)	0.80566 (19)	0.47210 (10)	0.0511 (5)
H25A	0.341629	0.861028	0.479280	0.061*
C26	0.39393 (18)	0.71765 (18)	0.41864 (9)	0.0438 (4)
H26A	0.319345	0.715148	0.389756	0.053*

2 Experimental details

A crystal was mounted on a glass fiber with epoxy glue. Data collection was performed on a Bruker D8 VENTURE Photon II diffractometer. Data were processed using the Bruker AXS Crystal Structure Analysis Package [1]. Data collection: Bruker APEX2; cell refinement: Bruker SAINT; Data reduction: Bruker SAINT; Structure solution: SHELXS-97 [2]; Structure refinement: SHELXL-2016/6 [3]; Molecular graphics: Bruker SHELXTL [2]; Publication materials: Bruker SHELXTL [2]. All H-atoms were placed geometrically and refined using a riding model with common isotropic displacement factors $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (parent C-atom) or $1.5 U_{\text{eq}}$ (methyl C-atom).

3 Comment

The Pictet–Spengler condensation, firstly discovered more than 100 years ago, is a well-known reaction between arylethylamine and aldehyde (or ketone) to create nitrogen containing hetero aromatic compounds such as indole and isoquinoline alkaloids [4, 5]. It has been largely applied in the synthesis of bioactive compounds [6–8] and recently, it found its application in constructing aza-annulated organic semiconducting materials [9–12]. In the effort to prepare *tert*-butyl 6-phenyl-7*H*-indolo[2,3-*c*]quinoline-7-carboxylate, we isolated the intermediate *tert*-butyl (*E*)-3-(2-(benzylideneamino)phenyl)-1*H*-indole-1-carboxylate, the precursor for the cyclization.

The crystal structure shows that the compound adopts an *E* configuration for the imine unit. In the meantime, it's interesting to note that the *tert*-butyloxycarbonyl group remains intact in the presence of acetic acid. The angles of C(5)–N(1)–C(6) and N(1)–C(5)–C(4) were measured at 119.39(15)° and 123.34(17)° respectively. The C–N bond lengths were around 1.4 Å in most cases. A slightly shorter value was determined for N(1)–C(5) at 1.265(2) Å, showing a double bond character which is consistent with the imine structure. The bond lengths of the aromatic rings were between 1.356(2) and 1.451(2) Å, while the one that connects the two rings were slightly longer, at 1.471(2) Å.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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