

1,1,3,3-Tetraethyl-5-nitroisindoline

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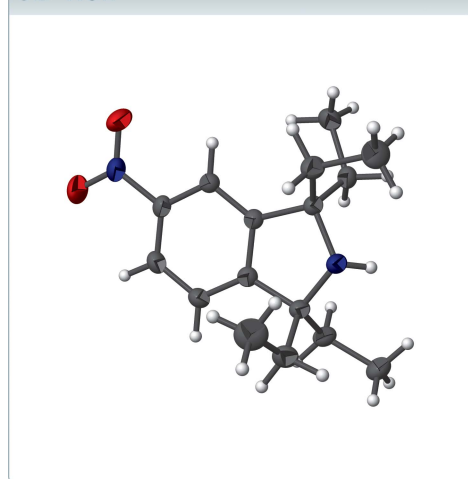
Keywords: crystal structure; structure–property relationship; organic synthesis.

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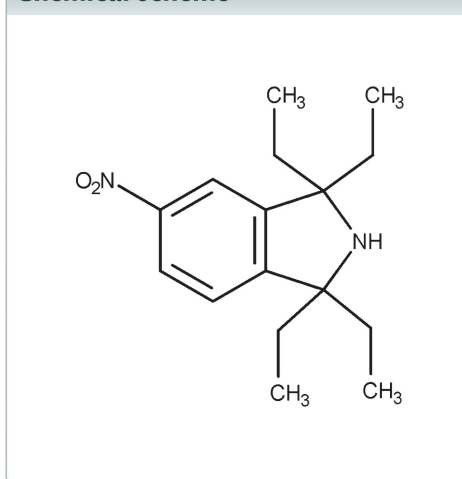
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₁₆H₂₄N₂O₂, previously obtained as a yellow oil, exhibits a rather low melting point close to room temperature 297–298 K). In the molecule, the isindoline ring system is approximately planar and coplanar to the nitro group, forming a dihedral angle of 5.63 (15)°. In the crystal, only weak N–H···O and C–H···π interactions are observed, linking molecules into chains parallel to the [101] direction.

3D view



Chemical scheme



Structure description

1,1,3,3-Tetraethyl-5-nitroisindoline is a precursor in the synthesis of 1,1,3,3-tetraethylisindolin-5-isothiocyanate-2-oxyl, which in turn is a versatile reduction-resistant spin label for RNA (Saha *et al.*, 2015). The atomic connectivity of the title compound has been established by NMR spectroscopy and confirmed by several analytical methods (Haugland *et al.*, 2016) but its crystal structure remained unknown, mainly due to its low melting point of 297–298 K (Tönjes *et al.*, 1964).

The title compound (Fig. 1) crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The isindoline ring system is approximately planar [r.m.s deviation of the nine fitted atoms = 0.0542 Å; maximum deviation 0.1005 (14) Å for atom N2] and forms a dihedral angle of 5.63 (15)° with the plane through the nitro group. In the crystal structure, each N–H group links *via* a weak hydrogen bond (Table 1) to the O–N group of an adjacent molecule. Centrosymmetrically related chains are further connected by weak C–H···π interactions (Table 1), forming chains parallel to [101]. Other interactions such as π–π stacking are not observed, which could be explained by the sterically demanding ethyl groups. This lack of strong intermolecular interactions may account for the low melting point of the substance.

A search of the Cambridge Structural Database (CSD, version 5.40, update August 2019; Groom *et al.*, 2016) for lengths of hydrogen bonds has been performed with a search

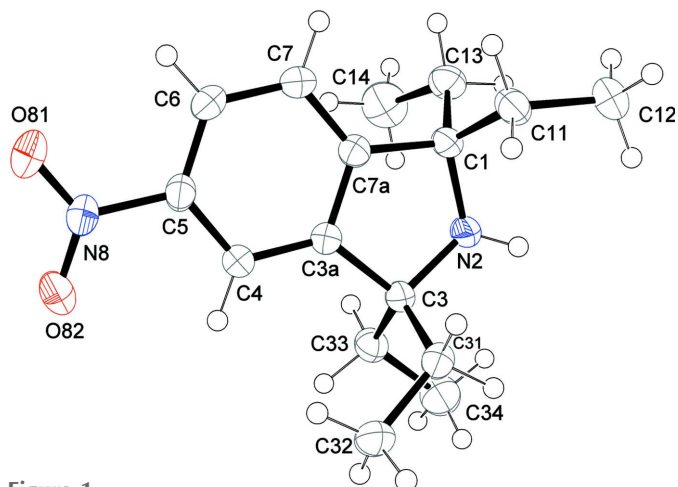


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

fragment of a twofold carbon-bound N–H donor to a carbon-bound NO₂ acceptor (Fig. 2). The mean length of (C–)₂N–H···O(–NOR) hydrogen bonds in deposited structures was found to be 2.28 (19) Å. This renders the H2···O81 length of 2.634 (16) Å found in the title compound a rather long but plausible peculiarity. Since the position of the H atom was freely refined against X-ray data, the H···O distance as well as the (still plausible) N–H distance is not fully trustworthy. The mean donor–acceptor distance for hydrogen bonds was found to be 2.96 (8) Å with a maximum of 3.07 Å. This confirms the value of 3.4860 (18) Å found for N2···O81 to be rather long.

Synthesis and crystallization

The title compound was synthesized in-house, using a modified literature procedure (Haugland *et al.*, 2016) as follows: to a solution of 1,1,3,3-tetraethylisoindoline (2.192 g, 9.47 mmol) in 21.9 ml sulfuric acid (95%), 21.9 ml of fuming nitric acid (100%) was added dropwise. During the addition, the reaction flask was cooled with ice/sodium chloride in order to hold the reaction temperature between –5 and 0°C (internal temperature control). The onset of the reaction was accompanied by a strong rise of temperature. After complete addition of nitric acid, the yellow solution was stirred at 0°C for 60 min. The cold reaction mixture was poured carefully into a cooled beaker containing 30 g of sodium hydroxide and 300 ml of ice/water. The pH of the resulting pale-yellow suspension

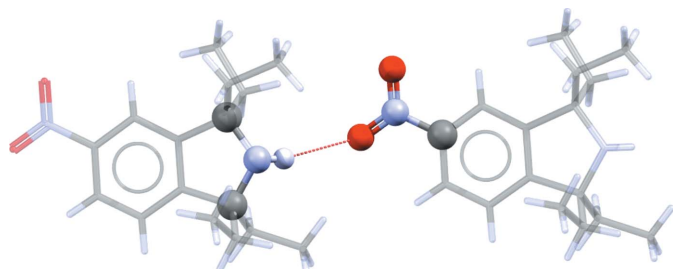


Figure 2
Search fragment for relevant hydrogen bonds in the CSD.

Table 1
Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C3A/C4/C5/C6/C7/C7A benzene ring.

D–H···A	D–H	H···A	D···A	D–H···A
N2–H2···O81 ⁱ	0.865 (15)	2.634 (16)	3.4860 (18)	168.4 (16)
C11–H11B···Cg1 ⁱⁱ	0.99	2.91	3.7552 (18)	144

Symmetry codes: (i) $x + 1, y, z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₂₄ N ₂ O ₂
<i>M_r</i>	276.37
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>n</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.0277 (6), 19.9356 (13), 9.4811 (7)
β (°)	116.169 (2)
<i>V</i> (Å ³)	1531.43 (18)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	0.63
Crystal size (mm)	1.20 × 0.60 × 0.60
Data collection	
Diffractometer	Siemens Bruker three circle
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.568, 0.753
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	32894, 2769, 2699
<i>R_{int}</i>	0.053
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.608
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.134, 1.09
No. of reflections	2769
No. of parameters	185
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.38, –0.25

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2006), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

was adjusted to 10 by the addition of more sodium hydroxide and the solution was stirred for 15 min. The aqueous solution was extracted four times with 100–150 ml of dichloromethane. The combined organic phases were washed with brine and dried over Na₂SO₄. After removing the solvent, the yellow residue was purified by means of column chromatography (alumina, 4% H₂O, 3 × 28 cm) with hexanes/ethyl acetate (95:5 v/v). The product was obtained as a yellow oil. Yield: 2.583 g (9.34 mmol, 98.7%). Crystals were obtained after storing the product at 277 K for 48 h. Several good-looking, yellow crystals could then be picked from the yellow oil. NMR analysis of the measured crystal confirmed its chemical identity with the yellow oil.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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References

- Bruker (2015). *APEX3*, *SAINT* and *SADABS*. Madison, Wisconsin: Bruker AXS Inc.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Haugland, M. M., El-Sagheer, A. H., Porter, R. J., Peña, J., Brown, T., Anderson, E. A. & Lovett, J. E. (2016). *J. Am. Chem. Soc.* **138**, 9069–9072.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Saha, S., Jagtap, A. P. & Sigurdsson, S. Th. (2015). *Chem. Commun.* **51**, 13142–13145.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Tönjes, H., Heidenbluth, K. & Scheffler, R. (1964). *J. Prakt. Chem.* **26**, 218–224.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2019). 4, x191629 [https://doi.org/10.1107/S2414314619016298]

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Crystal data

$C_{16}H_{24}N_2O_2$

$M_r = 276.37$

Monoclinic, $P2_1/n$

$a = 9.0277$ (6) Å

$b = 19.9356$ (13) Å

$c = 9.4811$ (7) Å

$\beta = 116.169$ (2)°

$V = 1531.43$ (18) Å³

$Z = 4$

$F(000) = 600$

$D_x = 1.199$ Mg m⁻³

Melting point: 297 K

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 130 reflections

$\theta = 2.4$ – 67.7 °

$\mu = 0.63$ mm⁻¹

$T = 173$ K

Elongated block, pale yellow

$1.20 \times 0.60 \times 0.60$ mm

Data collection

Siemens Bruker three circle
diffractometer

Radiation source: Incoatec microfocus tube, X-
Ray microfocus tube

ω and Phi scans

Absorption correction: multi-scan
(SADABS; Bruker, 2015)

$T_{\min} = 0.568$, $T_{\max} = 0.753$

32894 measured reflections

2769 independent reflections

2699 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 69.7$ °, $\theta_{\min} = 4.4$ °

$h = -10 \rightarrow 10$

$k = -24 \rightarrow 24$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.134$

$S = 1.09$

2769 reflections

185 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.6801P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.38$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Extinction correction: SHELXL-2018/3

(Sheldrick, 2015b),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.034 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The H atom on nitrogen N2 was located in a difference Fourier map and refined freely with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$. All other H atoms were treated as riding, with C–H = 0.96–0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.52355 (17)	0.63396 (7)	0.61223 (17)	0.0270 (3)
N2	0.68275 (15)	0.65271 (7)	0.61351 (15)	0.0293 (3)
H2	0.763 (2)	0.6336 (10)	0.692 (2)	0.035*
C11	0.5343 (2)	0.57151 (8)	0.71234 (18)	0.0329 (4)
H11A	0.421439	0.559790	0.696521	0.039*
H11B	0.576055	0.533516	0.672895	0.039*
C12	0.6438 (2)	0.57893 (10)	0.8882 (2)	0.0420 (4)
H12A	0.642818	0.536966	0.941621	0.063*
H12B	0.756909	0.589122	0.906117	0.063*
H12C	0.601917	0.615460	0.929801	0.063*
C13	0.4529 (2)	0.69406 (8)	0.6662 (2)	0.0360 (4)
H13A	0.348788	0.679891	0.668267	0.043*
H13B	0.531851	0.706068	0.774917	0.043*
C14	0.4189 (3)	0.75591 (10)	0.5640 (3)	0.0530 (5)
H14A	0.374684	0.791465	0.605935	0.080*
H14B	0.521776	0.771261	0.563372	0.080*
H14C	0.338389	0.745038	0.456534	0.080*
C3	0.68746 (17)	0.63829 (7)	0.46225 (16)	0.0256 (3)
C31	0.79690 (18)	0.57636 (8)	0.47844 (18)	0.0311 (4)
H31A	0.907820	0.584989	0.564874	0.037*
H31B	0.749758	0.537598	0.510014	0.037*
C32	0.8174 (2)	0.55661 (9)	0.3331 (2)	0.0385 (4)
H32A	0.888629	0.517002	0.356522	0.058*
H32B	0.709085	0.546275	0.247067	0.058*
H32C	0.867657	0.593819	0.302103	0.058*
C33	0.74827 (19)	0.70079 (8)	0.40784 (19)	0.0326 (4)
H33A	0.739947	0.692250	0.301727	0.039*
H33B	0.674711	0.738960	0.399550	0.039*
C34	0.9256 (2)	0.72039 (10)	0.5175 (2)	0.0448 (5)
H34A	0.956411	0.760343	0.476221	0.067*
H34B	0.934523	0.730088	0.622251	0.067*
H34C	0.999824	0.683331	0.524330	0.067*
C3A	0.50770 (17)	0.62372 (7)	0.35502 (17)	0.0251 (3)
C4	0.43042 (18)	0.61567 (7)	0.19321 (17)	0.0277 (3)
H4	0.489482	0.620820	0.132134	0.033*
C5	0.26335 (18)	0.59978 (8)	0.12360 (17)	0.0300 (4)
C6	0.17277 (18)	0.59141 (8)	0.20808 (19)	0.0334 (4)
H6	0.059749	0.578847	0.156877	0.040*
C7A	0.41760 (17)	0.61856 (7)	0.44111 (17)	0.0263 (3)
C7	0.25063 (18)	0.60177 (8)	0.36886 (19)	0.0322 (4)
H7	0.190803	0.597473	0.429440	0.039*

N8	0.17901 (16)	0.59159 (8)	-0.04799 (16)	0.0380 (4)
O81	0.03459 (17)	0.57346 (10)	-0.10830 (17)	0.0695 (5)
O82	0.25620 (17)	0.60204 (9)	-0.12333 (14)	0.0549 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0263 (7)	0.0337 (8)	0.0227 (7)	-0.0013 (5)	0.0123 (6)	-0.0024 (6)
N2	0.0250 (6)	0.0415 (7)	0.0214 (6)	-0.0035 (5)	0.0102 (5)	-0.0032 (5)
C11	0.0368 (8)	0.0377 (8)	0.0269 (8)	-0.0023 (6)	0.0167 (7)	0.0001 (6)
C12	0.0455 (10)	0.0532 (10)	0.0280 (9)	0.0019 (8)	0.0168 (8)	0.0047 (7)
C13	0.0369 (8)	0.0407 (9)	0.0345 (9)	0.0017 (7)	0.0195 (7)	-0.0072 (7)
C14	0.0658 (13)	0.0385 (9)	0.0583 (12)	0.0112 (9)	0.0306 (11)	-0.0021 (8)
C3	0.0233 (7)	0.0316 (7)	0.0215 (7)	-0.0014 (5)	0.0095 (6)	-0.0014 (5)
C31	0.0264 (7)	0.0371 (8)	0.0264 (8)	0.0036 (6)	0.0085 (6)	0.0002 (6)
C32	0.0313 (8)	0.0490 (10)	0.0366 (9)	0.0061 (7)	0.0162 (7)	-0.0054 (7)
C33	0.0321 (8)	0.0369 (8)	0.0297 (8)	-0.0049 (6)	0.0144 (7)	0.0008 (6)
C34	0.0388 (9)	0.0504 (10)	0.0442 (10)	-0.0163 (8)	0.0173 (8)	-0.0043 (8)
C3A	0.0241 (7)	0.0269 (7)	0.0236 (7)	0.0010 (5)	0.0100 (6)	0.0007 (5)
C4	0.0257 (7)	0.0340 (7)	0.0240 (7)	0.0014 (5)	0.0114 (6)	0.0011 (6)
C5	0.0264 (7)	0.0365 (8)	0.0223 (8)	0.0037 (6)	0.0064 (6)	-0.0002 (6)
C6	0.0216 (7)	0.0442 (9)	0.0316 (8)	-0.0001 (6)	0.0091 (6)	-0.0018 (6)
C7A	0.0260 (7)	0.0281 (7)	0.0250 (8)	0.0012 (5)	0.0114 (6)	-0.0004 (5)
C7	0.0256 (7)	0.0427 (9)	0.0310 (8)	-0.0001 (6)	0.0149 (6)	-0.0009 (6)
N8	0.0282 (7)	0.0529 (9)	0.0256 (7)	0.0028 (6)	0.0053 (6)	-0.0014 (6)
O81	0.0307 (7)	0.1309 (15)	0.0340 (7)	-0.0130 (8)	0.0026 (6)	-0.0086 (8)
O82	0.0455 (8)	0.0941 (11)	0.0257 (6)	-0.0105 (7)	0.0161 (6)	-0.0053 (6)

Geometric parameters (Å, °)

C1—N2	1.4799 (18)	C31—H31B	0.9900
C1—C7A	1.5075 (19)	C32—H32A	0.9800
C1—C11	1.542 (2)	C32—H32B	0.9800
C1—C13	1.547 (2)	C32—H32C	0.9800
N2—C3	1.4815 (19)	C33—C34	1.526 (2)
N2—H2	0.86 (2)	C33—H33A	0.9900
C11—C12	1.525 (2)	C33—H33B	0.9900
C11—H11A	0.9900	C34—H34A	0.9800
C11—H11B	0.9900	C34—H34B	0.9800
C12—H12A	0.9800	C34—H34C	0.9800
C12—H12B	0.9800	C3A—C4	1.386 (2)
C12—H12C	0.9800	C3A—C7A	1.387 (2)
C13—C14	1.513 (3)	C4—C5	1.390 (2)
C13—H13A	0.9900	C4—H4	0.9500
C13—H13B	0.9900	C5—C6	1.384 (2)
C14—H14A	0.9800	C5—N8	1.470 (2)
C14—H14B	0.9800	C6—C7	1.384 (2)
C14—H14C	0.9800	C6—H6	0.9500

C3—C3A	1.5153 (19)	C7A—C7	1.394 (2)
C3—C33	1.540 (2)	C7—H7	0.9500
C3—C31	1.546 (2)	N8—O82	1.216 (2)
C31—C32	1.521 (2)	N8—O81	1.225 (2)
C31—H31A	0.9900		
N2—C1—C7A	102.31 (11)	C32—C31—H31B	108.2
N2—C1—C11	113.68 (12)	C3—C31—H31B	108.2
C7A—C1—C11	109.62 (12)	H31A—C31—H31B	107.3
N2—C1—C13	110.01 (12)	C31—C32—H32A	109.5
C7A—C1—C13	110.81 (12)	C31—C32—H32B	109.5
C11—C1—C13	110.18 (12)	H32A—C32—H32B	109.5
C1—N2—C3	112.66 (11)	C31—C32—H32C	109.5
C1—N2—H2	110.0 (13)	H32A—C32—H32C	109.5
C3—N2—H2	111.8 (13)	H32B—C32—H32C	109.5
C12—C11—C1	115.41 (13)	C34—C33—C3	113.65 (13)
C12—C11—H11A	108.4	C34—C33—H33A	108.8
C1—C11—H11A	108.4	C3—C33—H33A	108.8
C12—C11—H11B	108.4	C34—C33—H33B	108.8
C1—C11—H11B	108.4	C3—C33—H33B	108.8
H11A—C11—H11B	107.5	H33A—C33—H33B	107.7
C11—C12—H12A	109.5	C33—C34—H34A	109.5
C11—C12—H12B	109.5	C33—C34—H34B	109.5
H12A—C12—H12B	109.5	H34A—C34—H34B	109.5
C11—C12—H12C	109.5	C33—C34—H34C	109.5
H12A—C12—H12C	109.5	H34A—C34—H34C	109.5
H12B—C12—H12C	109.5	H34B—C34—H34C	109.5
C14—C13—C1	114.59 (14)	C4—C3A—C7A	120.20 (13)
C14—C13—H13A	108.6	C4—C3A—C3	129.19 (13)
C1—C13—H13A	108.6	C7A—C3A—C3	110.60 (12)
C14—C13—H13B	108.6	C3A—C4—C5	117.57 (14)
C1—C13—H13B	108.6	C3A—C4—H4	121.2
H13A—C13—H13B	107.6	C5—C4—H4	121.2
C13—C14—H14A	109.5	C6—C5—C4	123.15 (14)
C13—C14—H14B	109.5	C6—C5—N8	118.51 (13)
H14A—C14—H14B	109.5	C4—C5—N8	118.34 (14)
C13—C14—H14C	109.5	C7—C6—C5	118.47 (14)
H14A—C14—H14C	109.5	C7—C6—H6	120.8
H14B—C14—H14C	109.5	C5—C6—H6	120.8
N2—C3—C3A	101.96 (11)	C3A—C7A—C7	121.09 (14)
N2—C3—C33	109.51 (12)	C3A—C7A—C1	111.09 (12)
C3A—C3—C33	111.40 (12)	C7—C7A—C1	127.82 (14)
N2—C3—C31	110.41 (12)	C6—C7—C7A	119.41 (14)
C3A—C3—C31	111.23 (12)	C6—C7—H7	120.3
C33—C3—C31	111.90 (12)	C7A—C7—H7	120.3
C32—C31—C3	116.40 (13)	O82—N8—O81	122.97 (15)
C32—C31—H31A	108.2	O82—N8—C5	118.68 (13)
C3—C31—H31A	108.2	O81—N8—C5	118.34 (15)

Hydrogen-bond geometry (Å, °)

*Cg*1 is the centroid of the C3*A*/C4/C5/C6/C7/C7*A* benzene ring.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2···O81 ⁱ	0.865 (15)	2.634 (16)	3.4860 (18)	168.4 (16)
C11—H11 <i>B</i> ··· <i>Cg</i> 1 ⁱⁱ	0.99	2.91	3.7552 (18)	144

Symmetry codes: (i) $x+1, y, z+1$; (ii) $-x+1, -y+1, -z+1$.