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rac-Ethyl (8a*R*,9a*S*)-8a-methyl-8-(4-nitrophenyl)-9a,10-diphenyl-12-(*p*-tolyl)-9,9a-dihydro-8a*H*-di-1,2,4-triazolo[4,3-*a*:3′,4′-*d*][1,5]benzodiazepine-6-carboxylate

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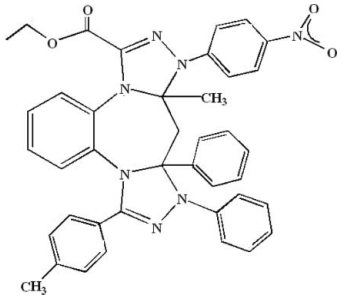
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.077; wR factor = 0.213; data-to-parameter ratio = 13.1.

The structure of the title compound, $C_{40}H_{35}N_7O_4$, is stabilized by weak C—H···N and C—H···O hydrogen bonds. There are also π–π interactions between triazole and 9a-phenyl rings [the distance between the pertinent centroids is 3.708 (2) Å], as well as C—H···π interactions. In the title molecule, the C8a-methyl and C9a-phenyl groups are present in *trans* positions. The structure analysis established the presence of the enantiomeric pair of the diastereoisomer *RS*/*SR* and excluded the presence of the enantiomers of the diastereoisomer *RR*/*SS*.

Related literature

For related literature, see: Baouid *et al.* (1994); Begtrup *et al.* (1988); Bellantuono *et al.* (1980); Benelbaghdadi *et al.* (1997); Boudina *et al.* (2006); Harrison *et al.* (2005); Sternbach (1978).



Experimental

Crystal data

$C_{40}H_{35}N_7O_4$
M_r = 677.75
Monoclinic, $P2_1/c$
a = 9.4951 (6) Å
b = 21.436 (1) Å
c = 18.885 (1) Å
β = 114.011 (5)°
V = 3511.2 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.47 × 0.36 × 0.13 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Absorption correction: none
59538 measured reflections
6080 independent reflections
4822 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.213
S = 1.14
6080 reflections
463 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

Values were calculated using *PLATON* (Version 200905; Spek, 2003). *Cg*1 and *Cg*2 are the centroids of the phenyl and 3-methylphenyl rings C35/C36/C39/C38/C37/C40 and C41–C46, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16A···O18	0.97	2.34	2.708 (6)	101
C20—H20···N7	0.93	2.42	2.751 (4)	101
C30—H30···N13	0.93	2.40	2.779 (4)	104
C46—H46···N13	0.93	2.61	2.938 (4)	101
C34—H34···$Cg1^{i}$	0.98	2.93	3.666 (5)	121
C19—H19···$Cg2^{ii}$	0.93	2.86	3.697 (5)	146

Symmetry codes: (i) x, y, z; (ii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Version 1.075; Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2049).

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supplementary materials

Acta Cryst. (2007). E**63**, o3301-o3302 [**doi:10.1107/S1600536807030103**]

rac-Ethyl (8a*R*,9a*S*)-8a-methyl-8-(4-nitrophenyl)-9a,10-diphenyl-12-(*p*-tolyl)-9,9a-dihydro-8a*H*-di-1,2,4-triazolo[4,3-*a*:3',4'-*d*][1,5]benzodiazepine-6-carboxylate

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Comment

Several benzodiazepine derivatives containing additional rings have proven to be of pharmacological interest (Sternbach, 1978; Bellantuono *et al.*, 1980). For years, our research team is interested in the synthesis of such compounds by cyclization reactions onto 1,4-benzodiazepines (Benelbaghdadi *et al.*, 1997) and 1,5-benzodiazepines (Baouid *et al.*, 1994; Boudina *et al.*, 2006). Within this context, we have studied the 1,3-dipolar cycloadditions of diarylnitrilimines with ethyl 3a-methyl-3-(4-nitrophenyl)-5-phenyl-3a,4-dihydro[1,2,4] triazolo[4,3-*a*][1,5]benzodiazepine-1-carboxylate **(1)** (Baouid *et al.*, 1994).

From the spectral data (mass; ^{1}H– ^{13}C– NMR) possible diastereoisomers **3X** or **3Y** of the cycloadduct were established. In particular, the chemical shifts of 86 and 90 p.p.m. observed for the quaternary carbon atoms C8a and C9a have ruled out the formation of the alternative regioisomer that would be formed by a reverse addition of the dipolar compound **(2)** on C=N of the ethyl 3a-methyl-3-(4-nitrophenyl)-5-phenyl-3a,4-dihydro[1,2,4]triazolo[4,3-*a*] [1,5]benzodiazepine-1-carboxylate, **(1)**. For the alternative regioisomer chemical shifts of about 50 p.p.m. would be expected (Begtrup *et al.* 1988). However, the NMR spectroscopic data (^{1}H and ^{13}C) did not allow to distinguish between the two diastereoisomers **3X** (*RS*/*SR*) and **3Y** (*RR*/*SS*).

On the other hand, the present crystallographic study has confirmed the formation of the (**3X**) *trans* diastereoisomer with its two asymmetric carbon atoms C8a and C9a displaying respective (*RS*,*SR*) absolute configurations. The 1,3-dipolar cycloaddition of diarylnitrilimine on ethyl 3a-methyl-3-(4-nitrophenyl)-5-phenyl-3a,4-dihydro[1,2,4]triazolo[4,3-*a*] [1,5]benzodiazepine-1-carboxylate, (**1**), is completely regio- and diastereoselective.

The molecule of the title compound (Scheme 1; Fig. 1) is composed of a tetracylic core formed by a benzodiazepine bicycle and two 5-membered rings (triazoles) that are differently substituted.

The 7-membered diazepine ring displays a boat conformation; the atoms N5, N13, C8a and C9a form the "bottom" of the boat. The atoms (C8a, C9, C9a) form the "prow" while (N5, N13, C13*a*, C4a) form the "stern". The angles between the best planes of the "bottom" and the "prow" and between the "bottom" and the "stern" equal to 47.5 (3) and 53.2 (2)°, respectively.

The bonds within the triazole rings are comparable with those reported in the literature for related compounds, as for example in 1-(2-Bromo-5-methoxyphenyl)-8-chloro-6-(2-fluorophenyl)- 4*H*-1,2,4-triazolo[4,3-*a*][1,4]benzodiazepine (Harrison *et al.*, 2005).

Experimental

Preparation is depicted in Scheme 2. A solution of ethyl 3a-methyl-3-(4-nitrophenyl)-5-phenyl-3a,4-dihydro [1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine-1-carboxylate **(1)** (0.65 mmol) and 4-methyl-*N*-phenylbenzohydrazonoyl chloride **(2)** (0.65 mmol) in dichloromethane (20 ml) was prepared; triethylamine (0.9 mmol) dissolved in dichloromethane (5

ml) was added dropwise. The mixture was stirred for 7 days at room temperature, washed several times with water. The aqueous phase was then extracted with dichloromethane (3 *x* 20 ml). The organic layer was dried over anhydrous sodium sulfate and then concentrated under reduced pressure. Then it was purified by chromatography on silica gel column (eluent: hexane/ethyl acetate), the isolated product was recrystallized from ethanol and the diastereoisomer 3X (*RS*/*SR*) was obtained in 50% yield. The diatereoisomer 3Y (*RR*/*SS*) was not isolated.

Melting point: 479–481 K. ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 1.20 (*t*, 3H, CH_3CH_2O), 1.80 (*s*, 3H, CH_3—C3a), 2.35 (*s*, 3H, CH_3—Ar), 2.90, 3.70 (2 d, *J* = 15 Hz, 2H, CH_2–4), 4.29 (*m*, 2H, CH_3CH_2O), 6.65- 7.73 (*m*, 22H, H—Ar). ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 14.31 (CH_3CH_2O), 21.81 (CH_3—Ar), 26.92 (CH_3—C3a), 41.22 (CH_2–C4), 62.42 (CH_3CH_2O), 85.93, 90.05 (C3a, C4a), 158.06 (C=O). Mass spectrum: m/*z* 678 (M^+, 100%). Anal. calc. for $C_{40}H_{35}N_7O_4$: C, 70.90; H, 5.17; N, 14.48; found: C, 70.56; H, 5.47; N, 14.26%.

Refinement

All the H atoms were found in a difference Fourier map. Nevertheless, the H atoms were refined using a riding model with C_{aryl}—H = 0.93 Å, $C_{methylene}$—H = 0.97 Å and C_{methyl}—H = 0.96 Å. U_{iso}(H) = 1.2U_{eq}(C) except for U_{iso}(H_{methyl}) = 1.5U_{eq}(C_{methyl}).

Figures

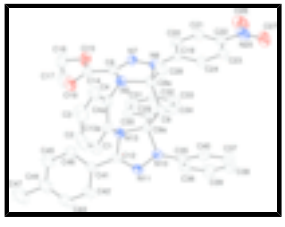

Fig. 1. Molecular view of the title molecule. The displacement ellipsoids are drawn at the 30% probability level (hydrogen atoms have been omitted for clarity).

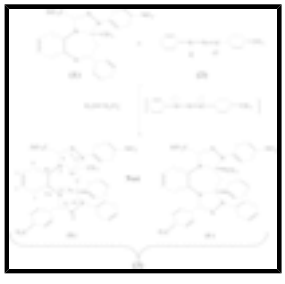

Fig. 2. Reaction scheme of the preparation of the title compound **3X** and the scheme of the hypothetic diastereoisomer **3Y** that was not found.

rac-Ethyl (8a*R*,9a*S*)-8a-methyl-8-(4-nitrophenyl)-9a,10- diphenyl-12-(*p*-tolyl)-9,9a-dihydro-8a*H*-di-1,2,4-triazolo[4,3 – a:3',4'-d][1,5]benzodiazepine-6-carboxylate

Crystal data

$C_{40}H_{35}N_7O_4$	F_{000} = 1424
M_r = 677.75	D_x = 1.282 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P2ybc	Cell parameters from 6080 reflections

a = 9.4951 (6) Å
b = 21.436 (1) Å
c = 18.885 (1) Å
β = 114.011 (5)º
V = 3511.2 (4) Å^3
Z = 4

θ = 3.1–25.0º
μ = 0.09 mm^{-1}
T = 293 (2) K
Parallelepiped, orange
0.47 × 0.36 × 0.13 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
T = 293(2) K
ω scans
Absorption correction: none
59538 measured reflections
6080 independent reflections

4822 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 32.4º
θ_{min} = 3.1º
h = −14→13
k = −31→31
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.213
S = 1.14
6080 reflections
463 parameters
136 constraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 1.8217P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: none

Special details

Experimental. A reference frame was measured every 25 frames. No significant intensity decay was observed.

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger. All H atoms were placed in geometrically idealized positions *via* HFIX instructions and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(C) for methyl groups and U_{iso}(H) = 1.2U_{eq} for others hydrogen atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N13	0.8798 (3)	0.64005 (11)	0.73679 (13)	0.0453 (6)
N10	0.9424 (3)	0.73291 (11)	0.70030 (13)	0.0480 (6)
N8	0.6017 (3)	0.59766 (11)	0.52064 (13)	0.0466 (6)
O15	0.7815 (3)	0.43645 (12)	0.63243 (16)	0.0766 (7)
C19	0.5837 (3)	0.61582 (14)	0.44793 (16)	0.0458 (7)
C9A	0.8549 (3)	0.67390 (12)	0.66433 (15)	0.0430 (6)
N11	1.0667 (3)	0.71352 (12)	0.76823 (14)	0.0535 (6)
N5	0.6045 (3)	0.58458 (12)	0.63816 (14)	0.0539 (6)
C12	1.0256 (3)	0.66285 (14)	0.79014 (16)	0.0483 (7)
C9	0.6868 (3)	0.68968 (13)	0.61452 (16)	0.0441 (6)
H9A	0.6840	0.7157	0.5720	0.053*
H9B	0.6482	0.7146	0.6457	0.053*
C30	1.0136 (3)	0.58390 (14)	0.64662 (19)	0.0534 (7)
H30	1.0219	0.5676	0.6938	0.064*
C6	0.6678 (3)	0.53484 (14)	0.61605 (17)	0.0496 (7)
C8A	0.5740 (3)	0.63483 (14)	0.57988 (16)	0.0487 (7)
C13A	0.7580 (3)	0.63447 (14)	0.76182 (16)	0.0492 (7)
N7	0.6638 (3)	0.53876 (11)	0.54741 (14)	0.0503 (6)
N25	0.5507 (4)	0.6741 (2)	0.22816 (19)	0.0823 (10)
C22	0.5580 (4)	0.65315 (18)	0.30281 (18)	0.0616 (9)
C1	0.7694 (4)	0.65645 (16)	0.83336 (18)	0.0610 (8)
H1	0.8577	0.6775	0.8660	0.073*
C29	0.9337 (3)	0.63911 (13)	0.61937 (16)	0.0449 (7)
O27	0.5059 (4)	0.72786 (19)	0.20691 (18)	0.1052 (11)
C35	0.9795 (4)	0.77661 (14)	0.65434 (17)	0.0518 (7)
C24	0.5323 (4)	0.67613 (15)	0.41974 (18)	0.0577 (8)
H24	0.5065	0.7040	0.4503	0.069*
C21	0.6053 (4)	0.59292 (18)	0.32795 (19)	0.0644 (9)
H21	0.6282	0.5652	0.2962	0.077*
C36	1.1210 (4)	0.77877 (17)	0.65089 (19)	0.0663 (9)
H36	1.1990	0.7518	0.6812	0.080*
O26	0.5892 (4)	0.6378 (2)	0.18951 (18)	0.1127 (12)
C23	0.5198 (4)	0.69428 (17)	0.34791 (19)	0.0639 (9)
H23	0.4856	0.7342	0.3298	0.077*
C14	0.7398 (4)	0.48117 (16)	0.6684 (2)	0.0594 (9)
C41	1.1213 (3)	0.62815 (15)	0.85988 (17)	0.0535 (7)
C32	1.0725 (4)	0.57616 (19)	0.5349 (2)	0.0715 (10)
H32	1.1172	0.5548	0.5064	0.086*
C20	0.6181 (3)	0.57443 (16)	0.39974 (18)	0.0548 (8)
H20	0.6499	0.5340	0.4167	0.066*
C46	1.0849 (5)	0.56743 (16)	0.8711 (2)	0.0724 (10)
H46	0.9982	0.5484	0.8341	0.087*
C28	0.4078 (3)	0.65696 (18)	0.5526 (2)	0.0638 (9)
H28A	0.3959	0.6960	0.5259	0.096*
H28B	0.3825	0.6622	0.5966	0.096*

H28C	0.3401	0.6265	0.5181	0.096*
O18	0.7576 (4)	0.48085 (13)	0.73454 (16)	0.0943 (9)
C34	0.9279 (3)	0.66300 (15)	0.54979 (17)	0.0523 (7)
H34	0.8772	0.7005	0.5310	0.063*
C4	0.5049 (4)	0.59495 (19)	0.7373 (2)	0.0729 (10)
H4	0.4151	0.5749	0.7045	0.087*
C37	0.8927 (6)	0.85982 (17)	0.5618 (2)	0.0833 (12)
H37	0.8159	0.8874	0.5318	0.100*
C40	0.8653 (4)	0.81866 (15)	0.61064 (19)	0.0628 (9)
H40	0.7707	0.8189	0.6145	0.075*
C33	0.9968 (4)	0.63152 (18)	0.5080 (2)	0.0670 (10)
H33	0.9916	0.6480	0.4614	0.080*
C2	0.6489 (5)	0.6469 (2)	0.8558 (2)	0.0775 (11)
H2	0.6571	0.6616	0.9037	0.093*
C31	1.0814 (4)	0.55270 (17)	0.6039 (2)	0.0680 (10)
H31	1.1335	0.5154	0.6225	0.082*
C43	1.3423 (4)	0.6215 (2)	0.9816 (2)	0.0785 (11)
H43	1.4301	0.6401	1.0184	0.094*
C42	1.2516 (4)	0.65532 (18)	0.91650 (19)	0.0635 (9)
H42	1.2777	0.6962	0.9106	0.076*
C4A	0.6243 (3)	0.60306 (14)	0.71428 (17)	0.0523 (7)
C3	0.5176 (5)	0.6162 (2)	0.8082 (2)	0.0849 (12)
H3	0.4377	0.6098	0.8239	0.102*
C45	1.1766 (6)	0.53514 (19)	0.9369 (2)	0.0909 (13)
H45	1.1502	0.4944	0.9435	0.109*
C44	1.3065 (6)	0.5615 (2)	0.9933 (2)	0.0891 (13)
C39	1.1476 (5)	0.8209 (2)	0.6026 (2)	0.0913 (13)
H39	1.2439	0.8225	0.6008	0.110*
C17	1.0267 (6)	0.3910 (3)	0.7055 (3)	0.1157 (18)
H17A	1.0771	0.3516	0.7231	0.174*
H17B	1.0629	0.4205	0.7473	0.174*
H17C	1.0494	0.4060	0.6634	0.174*
C38	1.0331 (6)	0.8603 (2)	0.5573 (3)	0.0998 (16)
H38	1.0506	0.8875	0.5233	0.120*
C16	0.8648 (5)	0.3833 (2)	0.6798 (3)	0.0949 (14)
H16A	0.8391	0.3794	0.7244	0.114*
H16B	0.8330	0.3452	0.6496	0.114*
C47	1.4031 (8)	0.5261 (3)	1.0664 (3)	0.144 (3)
H47A	1.4097	0.4831	1.0539	0.215*
H47B	1.3561	0.5289	1.1027	0.215*
H47C	1.5047	0.5437	1.0890	0.215*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N13	0.0399 (12)	0.0537 (14)	0.0384 (12)	−0.0037 (10)	0.0119 (10)	0.0001 (10)
N10	0.0520 (14)	0.0489 (14)	0.0373 (12)	−0.0058 (11)	0.0122 (11)	−0.0026 (10)
N8	0.0472 (13)	0.0500 (14)	0.0382 (12)	−0.0023 (11)	0.0129 (10)	−0.0002 (10)

O15	0.0715 (16)	0.0647 (15)	0.0899 (18)	0.0106 (12)	0.0291 (14)	0.0220 (13)
C19	0.0350 (14)	0.0573 (17)	0.0407 (15)	−0.0116 (12)	0.0108 (12)	−0.0036 (13)
C9A	0.0445 (15)	0.0443 (15)	0.0387 (14)	−0.0038 (12)	0.0152 (12)	−0.0009 (11)
N11	0.0525 (15)	0.0591 (16)	0.0418 (13)	−0.0064 (12)	0.0119 (12)	−0.0063 (11)
N5	0.0505 (14)	0.0645 (16)	0.0422 (13)	−0.0104 (12)	0.0144 (11)	0.0058 (12)
C12	0.0461 (16)	0.0525 (17)	0.0422 (16)	−0.0015 (13)	0.0137 (13)	−0.0031 (13)
C9	0.0458 (15)	0.0493 (16)	0.0401 (14)	0.0010 (12)	0.0204 (12)	0.0007 (12)
C30	0.0425 (16)	0.0569 (18)	0.0592 (19)	−0.0051 (14)	0.0191 (14)	−0.0073 (14)
C6	0.0340 (14)	0.0551 (18)	0.0513 (18)	−0.0118 (12)	0.0088 (13)	−0.0012 (14)
C8A	0.0428 (15)	0.0590 (18)	0.0435 (15)	−0.0052 (13)	0.0169 (13)	0.0008 (13)
C13A	0.0512 (17)	0.0550 (17)	0.0423 (16)	0.0027 (13)	0.0200 (13)	0.0063 (13)
N7	0.0420 (13)	0.0521 (14)	0.0485 (15)	−0.0095 (11)	0.0098 (11)	0.0021 (11)
N25	0.0636 (19)	0.129 (3)	0.0521 (19)	−0.027 (2)	0.0212 (16)	0.006 (2)
C22	0.0478 (18)	0.091 (3)	0.0426 (17)	−0.0173 (17)	0.0153 (14)	0.0058 (17)
C1	0.064 (2)	0.072 (2)	0.0452 (17)	0.0077 (16)	0.0210 (16)	0.0023 (15)
C29	0.0354 (14)	0.0509 (16)	0.0479 (16)	−0.0096 (12)	0.0165 (12)	−0.0086 (12)
O27	0.107 (2)	0.132 (3)	0.076 (2)	−0.020 (2)	0.0358 (17)	0.0350 (19)
C35	0.0597 (19)	0.0485 (17)	0.0443 (16)	−0.0127 (14)	0.0182 (14)	−0.0082 (13)
C24	0.0613 (19)	0.0615 (19)	0.0462 (17)	−0.0011 (15)	0.0177 (15)	0.0029 (14)
C21	0.0565 (19)	0.088 (3)	0.0521 (19)	−0.0121 (18)	0.0253 (16)	−0.0100 (18)
C36	0.065 (2)	0.076 (2)	0.0543 (19)	−0.0186 (17)	0.0199 (17)	−0.0001 (16)
O26	0.114 (3)	0.175 (3)	0.0635 (18)	−0.018 (2)	0.0513 (19)	−0.006 (2)
C23	0.062 (2)	0.071 (2)	0.0493 (18)	−0.0096 (17)	0.0131 (16)	0.0110 (16)
C14	0.0499 (18)	0.059 (2)	0.057 (2)	−0.0162 (15)	0.0084 (15)	0.0109 (16)
C41	0.0475 (17)	0.0626 (19)	0.0445 (16)	0.0044 (14)	0.0126 (14)	−0.0033 (14)
C32	0.058 (2)	0.078 (2)	0.091 (3)	−0.0171 (18)	0.044 (2)	−0.034 (2)
C20	0.0450 (16)	0.0653 (19)	0.0524 (18)	−0.0071 (14)	0.0180 (14)	−0.0029 (15)
C46	0.080 (2)	0.058 (2)	0.057 (2)	0.0063 (17)	0.0053 (18)	−0.0025 (16)
C28	0.0415 (17)	0.088 (2)	0.060 (2)	0.0027 (16)	0.0188 (15)	0.0089 (17)
O18	0.125 (2)	0.0802 (19)	0.0605 (18)	−0.0032 (16)	0.0206 (16)	0.0145 (13)
C34	0.0443 (16)	0.0655 (19)	0.0481 (17)	−0.0104 (14)	0.0198 (14)	−0.0095 (14)
C4	0.061 (2)	0.102 (3)	0.060 (2)	−0.0136 (19)	0.0289 (18)	0.0178 (19)
C37	0.105 (3)	0.060 (2)	0.065 (2)	−0.012 (2)	0.014 (2)	0.0089 (18)
C40	0.076 (2)	0.0505 (18)	0.0559 (19)	−0.0041 (16)	0.0207 (17)	−0.0053 (15)
C33	0.0561 (19)	0.092 (3)	0.060 (2)	−0.0223 (19)	0.0308 (17)	−0.0215 (18)
C2	0.087 (3)	0.110 (3)	0.0479 (19)	0.021 (2)	0.040 (2)	0.0155 (19)
C31	0.0472 (18)	0.063 (2)	0.097 (3)	−0.0027 (15)	0.0322 (19)	−0.0198 (19)
C43	0.060 (2)	0.104 (3)	0.052 (2)	0.015 (2)	0.0030 (17)	−0.0076 (19)
C42	0.0533 (19)	0.079 (2)	0.0517 (19)	0.0007 (16)	0.0141 (16)	−0.0066 (16)
C4A	0.0506 (17)	0.0612 (19)	0.0450 (16)	−0.0048 (14)	0.0194 (14)	0.0089 (14)
C3	0.072 (3)	0.126 (4)	0.074 (3)	0.006 (2)	0.046 (2)	0.023 (2)
C45	0.118 (4)	0.062 (2)	0.066 (2)	0.020 (2)	0.011 (2)	0.0047 (19)
C44	0.107 (3)	0.077 (3)	0.058 (2)	0.035 (2)	0.008 (2)	0.000 (2)
C39	0.083 (3)	0.114 (3)	0.074 (3)	−0.033 (3)	0.029 (2)	0.009 (2)
C17	0.095 (4)	0.145 (5)	0.111 (4)	0.035 (3)	0.046 (3)	0.062 (3)
C38	0.113 (4)	0.105 (3)	0.071 (3)	−0.041 (3)	0.027 (3)	0.020 (2)
C16	0.078 (3)	0.078 (3)	0.120 (4)	0.008 (2)	0.031 (3)	0.047 (3)
C47	0.170 (6)	0.117 (4)	0.078 (3)	0.051 (4)	−0.017 (3)	0.013 (3)

Geometric parameters (Å, °)

N13—C13A	1.421 (4)	C23—H23	0.9300
N13—C12	1.427 (4)	C14—O18	1.191 (4)
N13—C9A	1.480 (3)	C41—C46	1.385 (5)
N10—N11	1.407 (3)	C41—C42	1.391 (4)
N10—C35	1.416 (4)	C32—C31	1.367 (5)
N10—C9A	1.514 (3)	C32—C33	1.373 (5)
N8—C19	1.369 (4)	C32—H32	0.9300
N8—N7	1.398 (3)	C20—H20	0.9300
N8—C8A	1.482 (4)	C46—C45	1.378 (5)
O15—C14	1.325 (4)	C46—H46	0.9300
O15—C16	1.466 (4)	C28—H28A	0.9600
C19—C20	1.401 (4)	C28—H28B	0.9600
C19—C24	1.408 (4)	C28—H28C	0.9600
C9A—C9	1.525 (4)	C34—C33	1.388 (4)
C9A—C29	1.534 (4)	C34—H34	0.9300
N11—C12	1.278 (4)	C4—C3	1.373 (6)
N5—C6	1.370 (4)	C4—C4A	1.380 (4)
N5—C4A	1.428 (4)	C4—H4	0.9300
N5—C8A	1.482 (4)	C37—C38	1.370 (7)
C12—C41	1.463 (4)	C37—C40	1.376 (5)
C9—C8A	1.545 (4)	C37—H37	0.9300
C9—H9A	0.9700	C40—H40	0.9300
C9—H9B	0.9700	C33—H33	0.9300
C30—C29	1.387 (4)	C2—C3	1.373 (6)
C30—C31	1.392 (4)	C2—H2	0.9300
C30—H30	0.9300	C31—H31	0.9300
C6—N7	1.284 (4)	C43—C44	1.372 (6)
C6—C14	1.489 (4)	C43—C42	1.384 (5)
C8A—C28	1.523 (4)	C43—H43	0.9300
C13A—C1	1.393 (4)	C42—H42	0.9300
C13A—C4A	1.394 (4)	C3—H3	0.9300
N25—O26	1.220 (5)	C45—C44	1.381 (6)
N25—O27	1.238 (5)	C45—H45	0.9300
N25—C22	1.454 (4)	C44—C47	1.514 (6)
C22—C23	1.373 (5)	C39—C38	1.369 (7)
C22—C21	1.386 (5)	C39—H39	0.9300
C1—C2	1.387 (5)	C17—C16	1.421 (6)
C1—H1	0.9300	C17—H17A	0.9600
C29—C34	1.390 (4)	C17—H17B	0.9600
C35—C36	1.373 (5)	C17—H17C	0.9600
C35—C40	1.393 (5)	C38—H38	0.9300
C24—C23	1.369 (4)	C16—H16A	0.9700
C24—H24	0.9300	C16—H16B	0.9700
C21—C20	1.370 (4)	C47—H47A	0.9600
C21—H21	0.9300	C47—H47B	0.9600
C36—C39	1.377 (5)	C47—H47C	0.9600

C36—H36	0.9300		
C13A—N13—C12	118.8 (2)	C42—C41—C12	120.8 (3)
C13A—N13—C9A	120.2 (2)	C31—C32—C33	119.4 (3)
C12—N13—C9A	103.2 (2)	C31—C32—H32	120.3
N11—N10—C35	115.4 (2)	C33—C32—H32	120.3
N11—N10—C9A	105.4 (2)	C21—C20—C19	120.6 (3)
C35—N10—C9A	120.4 (2)	C21—C20—H20	119.7
C19—N8—N7	118.8 (2)	C19—C20—H20	119.7
C19—N8—C8A	128.0 (2)	C45—C46—C41	120.3 (4)
N7—N8—C8A	113.0 (2)	C45—C46—H46	119.8
C14—O15—C16	116.7 (3)	C41—C46—H46	119.8
N8—C19—C20	120.3 (3)	C8A—C28—H28A	109.5
N8—C19—C24	121.5 (3)	C8A—C28—H28B	109.5
C20—C19—C24	118.2 (3)	H28A—C28—H28B	109.5
N13—C9A—N10	98.2 (2)	C8A—C28—H28C	109.5
N13—C9A—C9	114.3 (2)	H28A—C28—H28C	109.5
N10—C9A—C9	109.7 (2)	H28B—C28—H28C	109.5
N13—C9A—C29	110.1 (2)	C33—C34—C29	120.8 (3)
N10—C9A—C29	110.7 (2)	C33—C34—H34	119.6
C9—C9A—C29	113.0 (2)	C29—C34—H34	119.6
C12—N11—N10	107.1 (2)	C3—C4—C4A	120.5 (4)
C6—N5—C4A	128.9 (3)	C3—C4—H4	119.7
C6—N5—C8A	108.5 (2)	C4A—C4—H4	119.7
C4A—N5—C8A	116.9 (2)	C38—C37—C40	120.1 (4)
N11—C12—N13	113.5 (2)	C38—C37—H37	119.9
N11—C12—C41	124.3 (3)	C40—C37—H37	119.9
N13—C12—C41	122.0 (3)	C37—C40—C35	119.8 (4)
C9A—C9—C8A	117.6 (2)	C37—C40—H40	120.1
C9A—C9—H9A	107.9	C35—C40—H40	120.1
C8A—C9—H9A	107.9	C32—C33—C34	120.4 (3)
C9A—C9—H9B	107.9	C32—C33—H33	119.8
C8A—C9—H9B	107.9	C34—C33—H33	119.8
H9A—C9—H9B	107.2	C3—C2—C1	120.9 (3)
C29—C30—C31	120.5 (3)	C3—C2—H2	119.6
C29—C30—H30	119.8	C1—C2—H2	119.6
C31—C30—H30	119.8	C32—C31—C30	120.8 (3)
N7—C6—N5	114.9 (3)	C32—C31—H31	119.6
N7—C6—C14	122.5 (3)	C30—C31—H31	119.6
N5—C6—C14	122.6 (3)	C44—C43—C42	121.9 (4)
N8—C8A—N5	97.4 (2)	C44—C43—H43	119.0
N8—C8A—C28	112.9 (2)	C42—C43—H43	119.0
N5—C8A—C28	109.9 (2)	C43—C42—C41	120.1 (4)
N8—C8A—C9	115.0 (2)	C43—C42—H42	120.0
N5—C8A—C9	110.3 (2)	C41—C42—H42	120.0
C28—C8A—C9	110.5 (3)	C4—C4A—C13A	120.5 (3)
C1—C13A—C4A	118.6 (3)	C4—C4A—N5	119.5 (3)
C1—C13A—N13	122.8 (3)	C13A—C4A—N5	119.7 (3)
C4A—C13A—N13	118.5 (3)	C2—C3—C4	119.6 (3)
C6—N7—N8	105.0 (2)	C2—C3—H3	120.2

O26—N25—O27	123.2 (4)	C4—C3—H3	120.2
O26—N25—C22	118.4 (4)	C46—C45—C44	121.8 (4)
O27—N25—C22	118.4 (4)	C46—C45—H45	119.1
C23—C22—C21	121.1 (3)	C44—C45—H45	119.1
C23—C22—N25	118.9 (4)	C43—C44—C45	117.5 (4)
C21—C22—N25	120.0 (4)	C43—C44—C47	121.3 (4)
C2—C1—C13A	119.9 (3)	C45—C44—C47	121.1 (5)
C2—C1—H1	120.1	C38—C39—C36	120.4 (4)
C13A—C1—H1	120.1	C38—C39—H39	119.8
C30—C29—C34	118.1 (3)	C36—C39—H39	119.8
C30—C29—C9A	121.7 (3)	C16—C17—H17A	109.5
C34—C29—C9A	120.2 (3)	C16—C17—H17B	109.5
C36—C35—C40	119.4 (3)	H17A—C17—H17B	109.5
C36—C35—N10	123.0 (3)	C16—C17—H17C	109.5
C40—C35—N10	117.6 (3)	H17A—C17—H17C	109.5
C23—C24—C19	120.8 (3)	H17B—C17—H17C	109.5
C23—C24—H24	119.6	C39—C38—C37	120.1 (4)
C19—C24—H24	119.6	C39—C38—H38	120.0
C20—C21—C22	119.6 (3)	C37—C38—H38	120.0
C20—C21—H21	120.2	C17—C16—O15	110.9 (3)
C22—C21—H21	120.2	C17—C16—H16A	109.5
C35—C36—C39	120.0 (4)	O15—C16—H16A	109.5
C35—C36—H36	120.0	C17—C16—H16B	109.5
C39—C36—H36	120.0	O15—C16—H16B	109.5
C24—C23—C22	119.6 (3)	H16A—C16—H16B	108.0
C24—C23—H23	120.2	C44—C47—H47A	109.5
C22—C23—H23	120.2	C44—C47—H47B	109.5
O18—C14—O15	126.1 (3)	H47A—C47—H47B	109.5
O18—C14—C6	122.1 (4)	C44—C47—H47C	109.5
O15—C14—C6	111.8 (3)	H47A—C47—H47C	109.5
C46—C41—C42	118.3 (3)	H47B—C47—H47C	109.5
C46—C41—C12	120.9 (3)		
N7—N8—C19—C20	4.0 (4)	N13—C9A—C29—C34	−178.9 (2)
C8A—N8—C19—C20	178.9 (3)	N10—C9A—C29—C34	−71.4 (3)
N7—N8—C19—C24	−175.4 (2)	C9—C9A—C29—C34	52.0 (3)
C8A—N8—C19—C24	−0.4 (4)	N11—N10—C35—C36	30.3 (4)
C13A—N13—C9A—N10	105.0 (3)	C9A—N10—C35—C36	−98.0 (3)
C12—N13—C9A—N10	−30.1 (2)	N11—N10—C35—C40	−150.2 (3)
C13A—N13—C9A—C9	−11.0 (3)	C9A—N10—C35—C40	81.6 (3)
C12—N13—C9A—C9	−146.2 (2)	N8—C19—C24—C23	177.8 (3)
C13A—N13—C9A—C29	−139.4 (2)	C20—C19—C24—C23	−1.5 (4)
C12—N13—C9A—C29	85.5 (3)	C23—C22—C21—C20	−1.7 (5)
N11—N10—C9A—N13	34.7 (2)	N25—C22—C21—C20	177.3 (3)
C35—N10—C9A—N13	167.3 (2)	C40—C35—C36—C39	−2.1 (5)
N11—N10—C9A—C9	154.3 (2)	N10—C35—C36—C39	177.4 (3)
C35—N10—C9A—C9	−73.1 (3)	C19—C24—C23—C22	−0.1 (5)
N11—N10—C9A—C29	−80.5 (3)	C21—C22—C23—C24	1.7 (5)
C35—N10—C9A—C29	52.2 (3)	N25—C22—C23—C24	−177.3 (3)
C35—N10—N11—C12	−161.6 (2)	C16—O15—C14—O18	−3.5 (5)

C9A—N10—N11—C12	−26.3 (3)	C16—O15—C14—C6	175.3 (3)
N10—N11—C12—N13	5.7 (3)	N7—C6—C14—O18	171.9 (3)
N10—N11—C12—C41	−178.6 (3)	N5—C6—C14—O18	−6.3 (5)
C13A—N13—C12—N11	−118.5 (3)	N7—C6—C14—O15	−7.0 (4)
C9A—N13—C12—N11	17.4 (3)	N5—C6—C14—O15	174.8 (3)
C13A—N13—C12—C41	65.7 (4)	N11—C12—C41—C46	−165.7 (3)
C9A—N13—C12—C41	−158.4 (3)	N13—C12—C41—C46	9.7 (5)
N13—C9A—C9—C8A	−64.3 (3)	N11—C12—C41—C42	14.2 (5)
N10—C9A—C9—C8A	−173.4 (2)	N13—C12—C41—C42	−170.5 (3)
C29—C9A—C9—C8A	62.6 (3)	C22—C21—C20—C19	0.0 (5)
C4A—N5—C6—N7	−162.1 (3)	N8—C19—C20—C21	−177.8 (3)
C8A—N5—C6—N7	−10.2 (3)	C24—C19—C20—C21	1.5 (4)
C4A—N5—C6—C14	16.3 (4)	C42—C41—C46—C45	−0.2 (6)
C8A—N5—C6—C14	168.2 (2)	C12—C41—C46—C45	179.6 (4)
C19—N8—C8A—N5	175.8 (2)	C30—C29—C34—C33	1.6 (4)
N7—N8—C8A—N5	−9.0 (3)	C9A—C29—C34—C33	−179.1 (3)
C19—N8—C8A—C28	60.5 (4)	C38—C37—C40—C35	−1.3 (5)
N7—N8—C8A—C28	−124.3 (3)	C36—C35—C40—C37	3.1 (5)
C19—N8—C8A—C9	−67.7 (3)	N10—C35—C40—C37	−176.5 (3)
N7—N8—C8A—C9	107.5 (3)	C31—C32—C33—C34	−1.0 (5)
C6—N5—C8A—N8	10.7 (3)	C29—C34—C33—C32	−0.2 (5)
C4A—N5—C8A—N8	166.4 (2)	C13A—C1—C2—C3	−0.2 (6)
C6—N5—C8A—C28	128.5 (3)	C33—C32—C31—C30	0.7 (5)
C4A—N5—C8A—C28	−75.8 (3)	C29—C30—C31—C32	0.8 (5)
C6—N5—C8A—C9	−109.5 (3)	C44—C43—C42—C41	−1.3 (6)
C4A—N5—C8A—C9	46.2 (3)	C46—C41—C42—C43	0.9 (5)
C9A—C9—C8A—N8	−67.1 (3)	C12—C41—C42—C43	−179.0 (3)
C9A—C9—C8A—N5	41.8 (3)	C3—C4—C4A—C13A	−1.8 (5)
C9A—C9—C8A—C28	163.5 (2)	C3—C4—C4A—N5	−175.6 (3)
C12—N13—C13A—C1	7.0 (4)	C1—C13A—C4A—C4	1.1 (5)
C9A—N13—C13A—C1	−121.4 (3)	N13—C13A—C4A—C4	178.1 (3)
C12—N13—C13A—C4A	−169.8 (3)	C1—C13A—C4A—N5	174.9 (3)
C9A—N13—C13A—C4A	61.7 (4)	N13—C13A—C4A—N5	−8.1 (4)
N5—C6—N7—N8	4.0 (3)	C6—N5—C4A—C4	−107.8 (4)
C14—C6—N7—N8	−174.4 (2)	C8A—N5—C4A—C4	102.3 (3)
C19—N8—N7—C6	179.6 (2)	C6—N5—C4A—C13A	78.3 (4)
C8A—N8—N7—C6	3.9 (3)	C8A—N5—C4A—C13A	−71.6 (4)
O26—N25—C22—C23	177.9 (3)	C1—C2—C3—C4	−0.5 (6)
O27—N25—C22—C23	−2.0 (5)	C4A—C4—C3—C2	1.4 (6)
O26—N25—C22—C21	−1.1 (5)	C41—C46—C45—C44	−0.1 (7)
O27—N25—C22—C21	179.0 (3)	C42—C43—C44—C45	1.0 (7)
C4A—C13A—C1—C2	−0.1 (5)	C42—C43—C44—C47	−177.4 (5)
N13—C13A—C1—C2	−177.0 (3)	C46—C45—C44—C43	−0.3 (7)
C31—C30—C29—C34	−2.0 (4)	C46—C45—C44—C47	178.1 (5)
C31—C30—C29—C9A	178.8 (3)	C35—C36—C39—C38	−0.7 (6)
N13—C9A—C29—C30	0.4 (3)	C36—C39—C38—C37	2.5 (7)
N10—C9A—C29—C30	107.8 (3)	C40—C37—C38—C39	−1.5 (7)
C9—C9A—C29—C30	−128.8 (3)	C14—O15—C16—C17	−96.1 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16A···O18	0.97	2.34	2.708 (6)	101
C20—H20···N7	0.93	2.42	2.751 (4)	101
C30—H30···N13	0.93	2.40	2.779 (4)	104
C46—H46···N13	0.93	2.61	2.938 (4)	101

D—H···π ring interactions

D—H···*Cg*	D—H	H···*Cg*	D···*Cg*	D—H···*Cg*
C34—H34···*Cg*1^{i}	0.98	2.93	3.666 (5)	121
C19—H19···*Cg*2^{ii}	0.93	2.86	3.697 (5)	146

Symmetry codes: (i) *x*, *y*, *z*; (ii) *x*, 3/2 − *y*, *z* − 1/2. Values were calculated using *PLATON* (Version 200905; Spek, 2003). *Cg*1 and *Cg*2 are the centroids of the phenyl and 3-methylphenyl rings C35/C36/C39/C38/C37/C40 and C41/C42/C43/C44/C45/C46, respectively.

Fig. 1

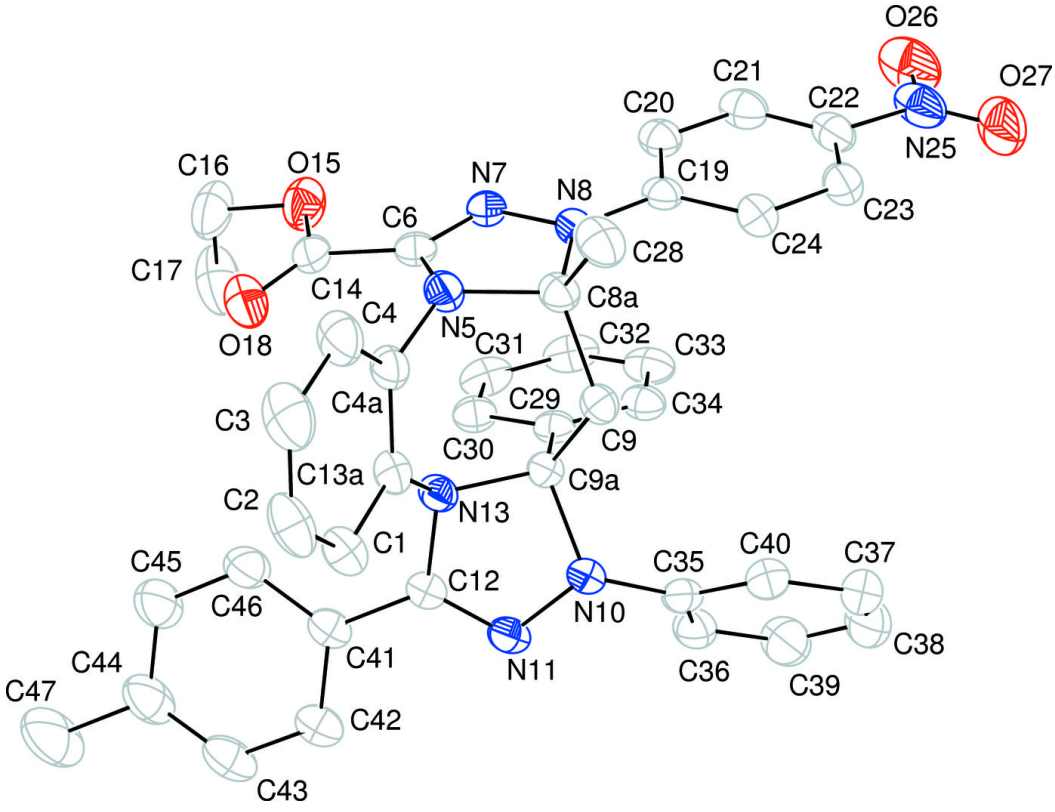
O26
C21
O27
C20
C22
N25
C16
O15
N7
N8
C19
C23
C6
C28
C24
C17
C14
C4
N5
C8a
O18
C31
C32
C33
C4a
C29
C34
C3
C30
C9
C13a
C9a
C2
N13
C1
C45
C40
C37
C12
C35
C46
N10
C38
C44
C41
N11
C36
C39
C47
C42
C43

Fig. 2