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A sterically crowded triazene: 1,3-bis(3,5,3″,5″-tetramethyl-1,1′:3′;1″-terphenyl-2′-yl)triazene

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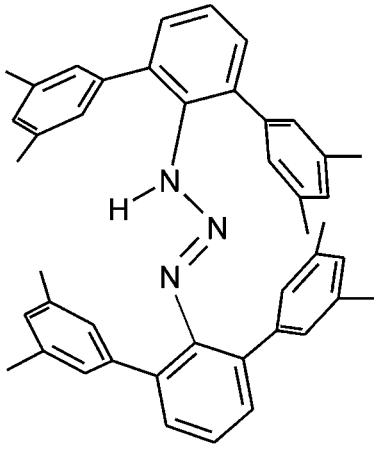
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.054; wR factor = 0.160; data-to-parameter ratio = 18.0.

The title compound, $[HN_3(Me_4Ter)_2]$ (Me_4Ter = 2,6-$Ar'_2C_6H_3$ with Ar′ = 3,5-$Me_2C_6H_3$) or $C_{44}H_{43}N_3$, crystallizes with a *trans* conformation of the central –N=N—N(H)– fragment. Steric crowding is manifested by a non-coplanar arrangement of the N=N—N and $C_6H_3(Ar'_2)$ planes and the distorted trigonal–pyramidal coordination of N(H), which is accompanied by a large displacement of one *ipso* C_{Ar} from the N_3 plane.

Related literature

For related work on sterically crowded triazenes and triazenides, see Hauber *et al.* (2005); Hauber & Niemeyer (2005); Lee & Niemeyer (2006). For examples of other structurally characterized diaryltriazenes, see Anulewicz (1997); Hörner *et al.* (2002); Hörner *et al.* (2003); Karadayı *et al.* (2005).



Experimental

Crystal data

$C_{44}H_{43}N_3$
M_r = 613.81
Triclinic, $P\overline{1}$
a = 9.0846 (17) Å
b = 12.0397 (18) Å
c = 17.667 (2) Å
α = 76.951 (9)°
β = 89.617 (10)°
γ = 75.534 (12)°
V = 1820.3 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 173 (2) K
0.60 × 0.50 × 0.45 mm

Data collection

Siemens $P4$ diffractometer
Absorption correction: none
8398 measured reflections
7892 independent reflections
6028 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
2 standard reflections
every 298 reflections
intensity decay: 0.1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.160
S = 1.06
7892 reflections
438 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1998).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2023).

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supplementary materials

Acta Cryst. (2007). E**63**, o3525 [**doi:10.1107/S1600536807031923**]

A sterically crowded triazene: 1,3-bis(3,5,3'',5''-tetramethyl-1,1':3';1''-terphenyl-2'-yl)triazene

S. Balireddi and M. Niemeyer

Comment

We recently succeeded in the preparation of metal derivatives of aryl-substituted, sterically crowded triazenes, *Ar*–N=N–N(H)–*Ar*'' (*Ar*, *Ar*'' - bulky biphenyl or terphenyl substituents), including the first examples of structurally characterized aryl compounds of the heavier alkaline earth metals Ca, Sr, and Ba (Hauber *et al.*, 2005) and unsolvated pentafluorophenylorganyls of the divalent lanthanides Yb and Eu (Hauber & Niemeyer, 2005). Due to the presence of additional metal-π-arene interactions, alkali metal salts of these ligands show *inverse aggregation* behavior in the solid-state (Lee & Niemeyer, 2006).

As continuation of this work we report here the synthesis and structural characterization of the title compound [HN_3(*Me*$_4$*Ter*)$_2$] (I). It crystallizes with strictly monomeric units (Fig. 1). Further aggregation by intermolecular N–H···A hydrogen bridges (A = N, O, Br) as normally observed in 1,3-disubstituted triazenes (*e.g.* Anulewicz, 1997; Hörner *et al.*, 2002; Hörner *et al.*, 2003; Karadayı *et al.*, 2005) is prevented by the bulky *Me*$_4$*Ter* substituents. Title compound adopts a typical *trans*-stereochemistry around the central N=N double bond as shown by the N1–N2=N3–C41 torsion angle of 179.29 (10)°. The N1–N2 and N2=N3 distances are in the expected range. However, in contrast to other structurally characterized diaryltriazenes the planes of the aryl groups defined by C11→C16 and C41→C46, respectively, are not coplanar with the central N_3-plane as indicated by the N2–N1–C11–C16 [53.75 (16)°] and N2=N3–C41–C46 [43.51 (16)°] torsion angles. This is undoubtly caused by steric crowding due to the presence of two *Ar*'' *ortho*-substituents. Within the *Me*$_4$*Ter*-groups, the Cn1→Cn6 (n = 2, 3, 5, 6) planes are tilted with respect to the C_6H_3 planes by 48.47 (19)°-61.70 (19)°.

In addition, steric crowding leads to a distortion from the expected planar to a pyramidal environment around N1 as shown by the angle sum of 348.4 (11)°. As a further consequence, C11 is displaced by 0.443 (2) Å from the N_3 plane, while C41 is almost coplanar [0.016 (2) Å]. Moreover, the N1–C11 bond is elongated to 1.4213 (16) Å, which is approximately 0.02–0.04 Å longer than the corresponding distances in other 1,3-disubstituted triazenes (*e.g.* Anulewicz, 1997; Hörner *et al.*, 2002; Hörner *et al.*, 2003; Karadayı *et al.*, 2005).

Experimental

n-Butyllithium (25 mmol, 2.5*M* hexane solution) was added at 273 K to a solution of *Me*$_4$*Ter*I (10.0 g, 24.3 mmol) in 150 ml of diethylether and stirring was continued for 2 h. The obtained clear solution of the lithium aryl was then treated with small portions of a solution of *Me*$_4$*Ter*N_3 (7.95 g, 24.3 mmol) in 60 ml of diethylether. After warming to ambient temperature and stirring for an additional 12 h, the red-brown solution was quenched with water (200 ml). The aqueous phase was separated and extracted with diethyl ether (3 × 80 ml). The organic phases were combined, repeatedly washed with water, and dried over Na_2SO_4. Filtration followed by solvent removal in vacuum afforded (I) as a yellow solid. Analytically pure, pale-yellow crystals were obtained by recrystallization from acetone. Yield: 10.7 g (17.4 mmol, 72%); mp: 432–433 K (dec.); ^{1}H NMR (250.1 MHz, C_6D_6): d 2.09 (s, 24H, *CH*$_3$), 6.67 (s, 4H, *p*-$C_6H_3Me_2$), 6.90 (s, 8H, *o*-$C_6H_3Me_2$), 6.99 (t, $^3J_{HH}$ = 7.6 Hz,

2H,, *p*-C_6H_3), 7.23 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *o*-C_6H_3), 8.80 (s, 1H, NH). Anal. Calc. for $C_{44}H_{43}N_3$: C, 86.09; H, 7.06; N, 6.85. Found: C, 85.64; H, 7.42; N 6.64.

Refinement

The H atom attached to N1 was located in a difference map and freely refined with U_{iso}. All other H atoms were positioned geometrically at distances of 0.95 (Aryl-H) or 0.98 (CH_3) and refined in a riding model approximation, including free rotation for methyl groups and variable isotropic displacement parameters.

Figures

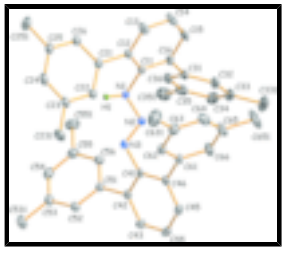


Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids. H atoms have been omitted for clarity, with exception of H1.

1,3-bis(3,5,3'',5''-tetramethyl-1,1':3';1''-terphenyl-2'-yl)triazene

Crystal data

$C_{44}H_{43}N_3$	$Z = 2$
$M_r = 613.81$	$F_{000} = 656$
Triclinic, $P\overline{1}$	$D_x = 1.120$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 432-433 K
$a = 9.0846$ (17) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 12.0397$ (18) Å	Cell parameters from 45 reflections
$c = 17.667$ (2) Å	$\theta = 5.0$–12.5º
$\alpha = 76.951$ (9)º	$\mu = 0.07$ mm^{-1}
$\beta = 89.617$ (10)º	$T = 173$ (2) K
$\gamma = 75.534$ (12)º	Prism, pale-yellow
$V = 1820.3$ (5) Å^3	0.60 × 0.50 × 0.45 mm

Data collection

Siemens P4 diffractometer	$R_{int} = 0.057$
Radiation source: fine-focus sealed tube	$\theta_{max} = 27.0$º
Monochromator: graphite	$\theta_{min} = 2.3$º
$T = 173(2)$ K	$h = 0 \rightarrow 11$
ω scans	$k = -14 \rightarrow 14$
Absorption correction: none	$l = -22 \rightarrow 22$
8398 measured reflections	2 standard reflections

7892 independent reflections	every 298 reflections
6028 reflections with $I > 2\sigma(I)$	intensity decay: 0.1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.054$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.160$	$w = 1/[\sigma^2(F_o^2) + (0.1052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
7892 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
438 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.19687 (13)	0.43828 (9)	0.23915 (6)	0.0256 (2)
H1	0.1630 (19)	0.4681 (15)	0.1896 (10)	0.038 (4)*
N2	0.33206 (12)	0.45578 (10)	0.25796 (6)	0.0268 (2)
N3	0.36612 (12)	0.53725 (9)	0.20773 (6)	0.0261 (2)
C11	0.17110 (14)	0.32721 (11)	0.27532 (7)	0.0260 (3)
C12	0.12638 (16)	0.26029 (12)	0.22803 (8)	0.0297 (3)
C13	0.0979 (2)	0.15227 (14)	0.26374 (9)	0.0453 (4)
H13A	0.0654	0.1069	0.2328	0.0493 (12)*
C14	0.1165 (3)	0.11037 (16)	0.34376 (10)	0.0562 (5)
H14A	0.0994	0.0358	0.3672	0.0493 (12)*
C15	0.1602 (2)	0.17746 (15)	0.38945 (9)	0.0467 (4)
H15A	0.1726	0.1479	0.4443	0.0493 (12)*
C16	0.18651 (16)	0.28720 (13)	0.35704 (8)	0.0323 (3)
C21	0.10876 (16)	0.29979 (11)	0.14118 (7)	0.0272 (3)
C22	0.22071 (16)	0.34079 (11)	0.09693 (8)	0.0280 (3)

H22A	0.3082	0.3480	0.1226	0.0493 (12)*
C23	0.20660 (17)	0.37138 (11)	0.01559 (8)	0.0306 (3)
C24	0.07696 (18)	0.35995 (12)	−0.02104 (8)	0.0343 (3)
H24A	0.0661	0.3806	−0.0763	0.0493 (12)*
C25	−0.03656 (17)	0.31923 (12)	0.02107 (8)	0.0337 (3)
C26	−0.02005 (16)	0.28995 (12)	0.10212 (8)	0.0310 (3)
H26A	−0.0974	0.2628	0.1315	0.0493 (12)*
C31	0.22574 (17)	0.35753 (14)	0.41039 (8)	0.0343 (3)
C32	0.34167 (19)	0.30339 (16)	0.46879 (8)	0.0423 (4)
H32A	0.3984	0.2246	0.4717	0.0493 (12)*
C33	0.3750 (2)	0.36363 (19)	0.52283 (9)	0.0508 (5)
C34	0.2907 (2)	0.47823 (19)	0.51759 (9)	0.0543 (5)
H34A	0.3127	0.5197	0.5541	0.0493 (12)*
C35	0.1740 (2)	0.53512 (16)	0.46021 (9)	0.0453 (4)
C36	0.14317 (18)	0.47275 (14)	0.40718 (8)	0.0376 (3)
H36A	0.0640	0.5098	0.3680	0.0493 (12)*
C41	0.50935 (14)	0.55846 (11)	0.22440 (7)	0.0249 (3)
C42	0.51641 (15)	0.67694 (11)	0.20718 (7)	0.0274 (3)
C43	0.65678 (17)	0.70169 (13)	0.21674 (9)	0.0355 (3)
H43A	0.6633	0.7813	0.2040	0.0493 (12)*
C44	0.78655 (17)	0.61237 (14)	0.24442 (10)	0.0405 (4)
H44A	0.8805	0.6308	0.2516	0.0493 (12)*
C45	0.77815 (17)	0.49539 (13)	0.26156 (9)	0.0372 (3)
H45A	0.8671	0.4344	0.2808	0.0493 (12)*
C46	0.64164 (15)	0.46580 (12)	0.25103 (7)	0.0288 (3)
C51	0.37757 (15)	0.77520 (11)	0.17859 (8)	0.0281 (3)
C52	0.38282 (16)	0.86209 (11)	0.11207 (8)	0.0310 (3)
H52A	0.4751	0.8583	0.0860	0.0493 (12)*
C53	0.25486 (18)	0.95470 (12)	0.08299 (9)	0.0356 (3)
C54	0.12087 (18)	0.95858 (12)	0.12200 (10)	0.0401 (4)
H54A	0.0329	1.0203	0.1022	0.0493 (12)*
C55	0.11196 (17)	0.87449 (13)	0.18925 (10)	0.0389 (4)
C56	0.24141 (16)	0.78290 (12)	0.21704 (9)	0.0334 (3)
H56A	0.2369	0.7249	0.2628	0.0493 (12)*
C61	0.64236 (15)	0.33803 (12)	0.26545 (8)	0.0310 (3)
C62	0.60754 (16)	0.28933 (12)	0.20536 (9)	0.0341 (3)
H62A	0.5830	0.3383	0.1545	0.0493 (12)*
C63	0.60795 (18)	0.17052 (13)	0.21815 (11)	0.0431 (4)
C64	0.6460 (2)	0.10049 (14)	0.29319 (12)	0.0530 (5)
H64A	0.6452	0.0197	0.3032	0.0493 (12)*
C65	0.6850 (2)	0.14580 (15)	0.35396 (11)	0.0546 (5)
C66	0.6827 (2)	0.26500 (14)	0.33937 (9)	0.0452 (4)
H66A	0.7090	0.2968	0.3804	0.0493 (12)*
C231	0.3311 (2)	0.41188 (14)	−0.03091 (9)	0.0439 (4)
H23A	0.2859	0.4722	−0.0776	0.124 (2)*
H23B	0.3995	0.3446	−0.0463	0.124 (2)*
H23C	0.3888	0.4451	0.0009	0.124 (2)*
C251	−0.1741 (2)	0.30356 (16)	−0.01978 (10)	0.0503 (4)
H25A	−0.2480	0.2853	0.0186	0.124 (2)*

H25B	−0.1418	0.2388	−0.0462	0.124 (2)*
H25C	−0.2211	0.3765	−0.0581	0.124 (2)*
C331	0.5011 (3)	0.3029 (2)	0.58593 (11)	0.0757 (7)
H33A	0.5323	0.3624	0.6073	0.124 (2)*
H33B	0.5885	0.2576	0.5636	0.124 (2)*
H33C	0.4636	0.2497	0.6275	0.124 (2)*
C351	0.0832 (2)	0.66077 (18)	0.45559 (12)	0.0598 (5)
H35A	−0.0205	0.6715	0.4349	0.124 (2)*
H35B	0.1320	0.7155	0.4212	0.124 (2)*
H35C	0.0794	0.6766	0.5077	0.124 (2)*
C531	0.2619 (2)	1.04761 (14)	0.01049 (11)	0.0520 (4)
H53A	0.1667	1.0679	−0.0212	0.124 (2)*
H53B	0.3474	1.0170	−0.0195	0.124 (2)*
H53C	0.2760	1.1182	0.0252	0.124 (2)*
C551	−0.0355 (2)	0.88193 (16)	0.23127 (14)	0.0594 (5)
H55A	−0.0749	0.9620	0.2389	0.124 (2)*
H55B	−0.0161	0.8257	0.2820	0.124 (2)*
H55C	−0.1105	0.8630	0.2001	0.124 (2)*
C631	0.5684 (3)	0.11844 (17)	0.15313 (15)	0.0714 (7)
H63A	0.5549	0.1777	0.1038	0.124 (2)*
H63B	0.4738	0.0940	0.1638	0.124 (2)*
H63C	0.6509	0.0499	0.1496	0.124 (2)*
C651	0.7302 (3)	0.0670 (2)	0.43513 (13)	0.0911 (9)
H65A	0.6618	0.0149	0.4483	0.124 (2)*
H65B	0.7226	0.1161	0.4730	0.124 (2)*
H65C	0.8351	0.0194	0.4362	0.124 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0296 (6)	0.0238 (5)	0.0213 (5)	−0.0067 (4)	−0.0063 (4)	−0.0011 (4)
N2	0.0274 (6)	0.0289 (6)	0.0217 (5)	−0.0055 (4)	−0.0020 (4)	−0.0027 (4)
N3	0.0295 (6)	0.0213 (5)	0.0268 (5)	−0.0067 (4)	−0.0022 (4)	−0.0036 (4)
C11	0.0281 (6)	0.0254 (6)	0.0222 (6)	−0.0069 (5)	−0.0020 (5)	−0.0009 (5)
C12	0.0367 (7)	0.0264 (7)	0.0252 (6)	−0.0096 (6)	−0.0017 (5)	−0.0022 (5)
C13	0.0709 (11)	0.0355 (8)	0.0344 (8)	−0.0262 (8)	−0.0034 (7)	−0.0034 (6)
C14	0.0968 (15)	0.0386 (9)	0.0360 (9)	−0.0358 (10)	−0.0007 (9)	0.0063 (7)
C15	0.0710 (12)	0.0440 (9)	0.0230 (7)	−0.0236 (8)	−0.0044 (7)	0.0065 (6)
C16	0.0377 (8)	0.0344 (7)	0.0226 (6)	−0.0094 (6)	−0.0029 (5)	−0.0017 (5)
C21	0.0365 (7)	0.0209 (6)	0.0239 (6)	−0.0053 (5)	−0.0037 (5)	−0.0063 (5)
C22	0.0343 (7)	0.0218 (6)	0.0270 (6)	−0.0049 (5)	−0.0027 (5)	−0.0062 (5)
C23	0.0436 (8)	0.0196 (6)	0.0255 (6)	−0.0023 (5)	0.0005 (6)	−0.0053 (5)
C24	0.0527 (9)	0.0228 (6)	0.0228 (6)	−0.0011 (6)	−0.0095 (6)	−0.0049 (5)
C25	0.0443 (8)	0.0216 (6)	0.0323 (7)	−0.0017 (6)	−0.0133 (6)	−0.0078 (5)
C26	0.0366 (7)	0.0257 (7)	0.0315 (7)	−0.0090 (6)	−0.0039 (6)	−0.0067 (5)
C31	0.0397 (8)	0.0454 (8)	0.0192 (6)	−0.0158 (7)	0.0008 (5)	−0.0045 (6)
C32	0.0433 (9)	0.0587 (10)	0.0225 (7)	−0.0130 (7)	−0.0020 (6)	−0.0045 (7)
C33	0.0496 (10)	0.0829 (14)	0.0235 (7)	−0.0248 (9)	−0.0032 (7)	−0.0105 (8)

C34	0.0628 (11)	0.0845 (14)	0.0309 (8)	−0.0337 (11)	0.0043 (8)	−0.0275 (9)
C35	0.0516 (10)	0.0586 (10)	0.0354 (8)	−0.0234 (8)	0.0111 (7)	−0.0203 (7)
C36	0.0419 (8)	0.0476 (9)	0.0253 (7)	−0.0152 (7)	0.0013 (6)	−0.0085 (6)
C41	0.0295 (7)	0.0259 (6)	0.0186 (6)	−0.0069 (5)	−0.0032 (5)	−0.0042 (5)
C42	0.0312 (7)	0.0258 (6)	0.0250 (6)	−0.0073 (5)	−0.0022 (5)	−0.0053 (5)
C43	0.0376 (8)	0.0303 (7)	0.0405 (8)	−0.0131 (6)	−0.0047 (6)	−0.0069 (6)
C44	0.0327 (8)	0.0406 (8)	0.0493 (9)	−0.0123 (6)	−0.0091 (7)	−0.0088 (7)
C45	0.0306 (7)	0.0356 (8)	0.0397 (8)	−0.0022 (6)	−0.0094 (6)	−0.0036 (6)
C46	0.0327 (7)	0.0281 (7)	0.0225 (6)	−0.0052 (5)	−0.0037 (5)	−0.0019 (5)
C51	0.0343 (7)	0.0201 (6)	0.0317 (7)	−0.0079 (5)	−0.0052 (5)	−0.0083 (5)
C52	0.0380 (7)	0.0208 (6)	0.0345 (7)	−0.0071 (5)	−0.0020 (6)	−0.0070 (5)
C53	0.0455 (8)	0.0190 (6)	0.0413 (8)	−0.0050 (6)	−0.0092 (6)	−0.0080 (6)
C54	0.0380 (8)	0.0209 (7)	0.0592 (10)	0.0003 (6)	−0.0101 (7)	−0.0134 (6)
C55	0.0356 (8)	0.0264 (7)	0.0582 (10)	−0.0070 (6)	0.0004 (7)	−0.0179 (7)
C56	0.0371 (8)	0.0252 (7)	0.0400 (8)	−0.0096 (6)	0.0004 (6)	−0.0098 (6)
C61	0.0295 (7)	0.0258 (7)	0.0310 (7)	−0.0005 (5)	−0.0023 (5)	−0.0002 (5)
C62	0.0331 (7)	0.0257 (7)	0.0377 (8)	0.0002 (6)	−0.0033 (6)	−0.0039 (6)
C63	0.0377 (8)	0.0269 (7)	0.0608 (10)	0.0009 (6)	−0.0024 (7)	−0.0122 (7)
C64	0.0550 (10)	0.0227 (7)	0.0721 (12)	−0.0025 (7)	0.0082 (9)	−0.0007 (8)
C65	0.0668 (12)	0.0333 (8)	0.0466 (10)	0.0006 (8)	0.0034 (9)	0.0101 (7)
C66	0.0585 (10)	0.0337 (8)	0.0326 (8)	−0.0005 (7)	−0.0054 (7)	0.0022 (6)
C231	0.0565 (10)	0.0408 (9)	0.0334 (8)	−0.0119 (7)	0.0104 (7)	−0.0073 (7)
C251	0.0575 (10)	0.0474 (9)	0.0465 (9)	−0.0106 (8)	−0.0226 (8)	−0.0145 (8)
C331	0.0702 (14)	0.120 (2)	0.0358 (10)	−0.0263 (14)	−0.0193 (9)	−0.0135 (11)
C351	0.0715 (13)	0.0626 (12)	0.0573 (11)	−0.0235 (10)	0.0172 (10)	−0.0312 (10)
C531	0.0671 (12)	0.0261 (8)	0.0518 (10)	−0.0012 (7)	−0.0065 (9)	0.0021 (7)
C551	0.0394 (9)	0.0400 (9)	0.0971 (16)	−0.0061 (7)	0.0141 (10)	−0.0171 (10)
C631	0.0791 (14)	0.0367 (10)	0.0964 (17)	0.0042 (9)	−0.0255 (12)	−0.0314 (10)
C651	0.132 (2)	0.0508 (12)	0.0584 (13)	0.0010 (13)	0.0017 (14)	0.0264 (11)

Geometric parameters (Å, °)

N1—N2	1.3525 (15)	C46—C61	1.4998 (19)
N2—N3	1.2650 (15)	C51—C52	1.3953 (19)
N1—H1	0.892 (17)	C51—C56	1.400 (2)
N1—C11	1.4213 (16)	C52—C53	1.4001 (19)
N3—C41	1.4317 (16)	C52—H52A	0.9500
C11—C12	1.4088 (19)	C53—C54	1.391 (2)
C11—C16	1.4109 (18)	C53—C531	1.511 (2)
C12—C13	1.397 (2)	C54—C55	1.393 (2)
C12—C21	1.4973 (18)	C54—H54A	0.9500
C13—C14	1.386 (2)	C55—C56	1.398 (2)
C13—H13A	0.9500	C55—C551	1.520 (2)
C14—C15	1.386 (2)	C56—H56A	0.9500
C14—H14A	0.9500	C61—C66	1.3928 (19)
C15—C16	1.395 (2)	C61—C62	1.396 (2)
C15—H15A	0.9500	C62—C63	1.396 (2)
C16—C31	1.499 (2)	C62—H62A	0.9500
C21—C22	1.3983 (19)	C63—C64	1.394 (3)

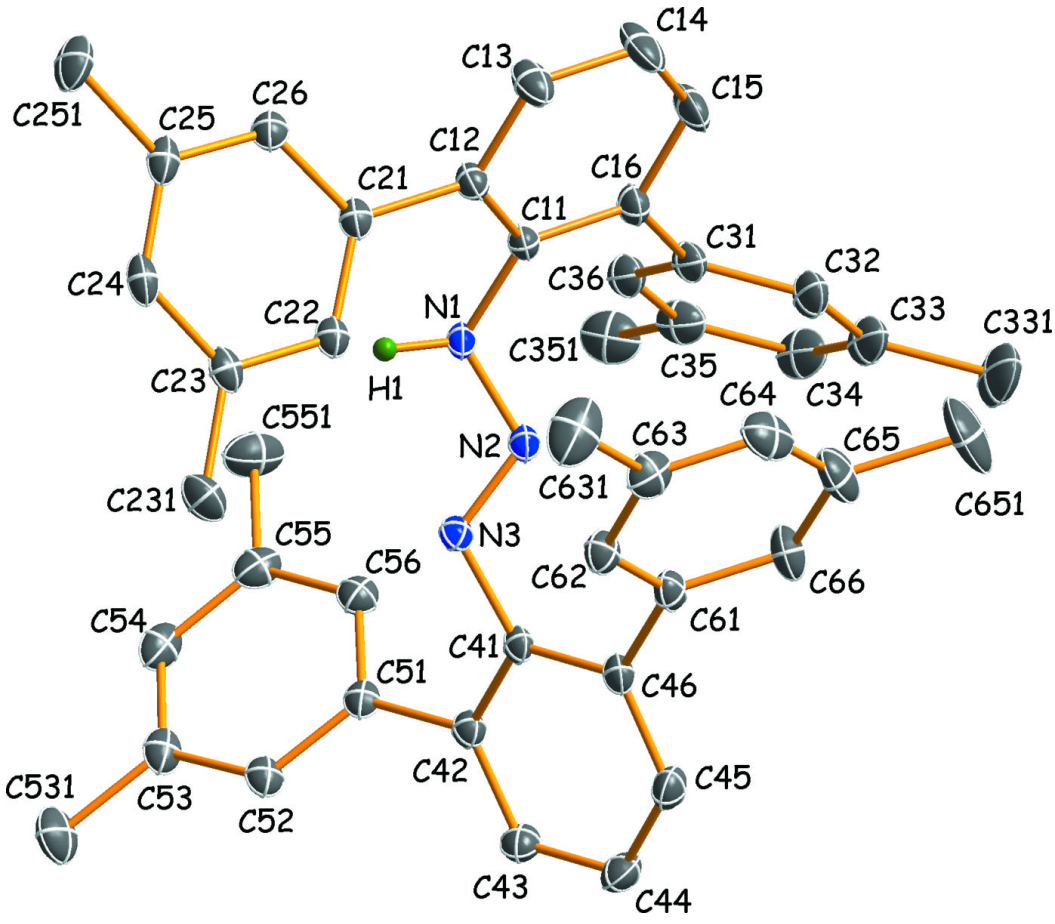
C21—C26	1.4059 (19)	C63—C631	1.512 (3)
C22—C23	1.3990 (18)	C64—C65	1.394 (3)
C22—H22A	0.9500	C64—H64A	0.9500
C23—C24	1.399 (2)	C65—C66	1.395 (2)
C23—C231	1.508 (2)	C65—C651	1.524 (2)
C24—C25	1.391 (2)	C66—H66A	0.9500
C24—H24A	0.9500	C231—H23A	0.9800
C25—C26	1.3949 (19)	C231—H23B	0.9800
C25—C251	1.519 (2)	C231—H23C	0.9800
C26—H26A	0.9500	C251—H25A	0.9800
C31—C36	1.391 (2)	C251—H25B	0.9800
C31—C32	1.402 (2)	C251—H25C	0.9800
C32—C33	1.398 (2)	C331—H33A	0.9800
C32—H32A	0.9500	C331—H33B	0.9800
C33—C34	1.384 (3)	C331—H33C	0.9800
C33—C331	1.523 (3)	C351—H35A	0.9800
C34—C35	1.400 (3)	C351—H35B	0.9800
C34—H34A	0.9500	C351—H35C	0.9800
C35—C36	1.395 (2)	C531—H53A	0.9800
C35—C351	1.516 (3)	C531—H53B	0.9800
C36—H36A	0.9500	C531—H53C	0.9800
C41—C42	1.4075 (18)	C551—H55A	0.9800
C41—C46	1.4181 (18)	C551—H55B	0.9800
C42—C43	1.3997 (19)	C551—H55C	0.9800
C42—C51	1.4962 (19)	C631—H63A	0.9800
C43—C44	1.386 (2)	C631—H63B	0.9800
C43—H43A	0.9500	C631—H63C	0.9800
C44—C45	1.394 (2)	C651—H65A	0.9800
C44—H44A	0.9500	C651—H65B	0.9800
C45—C46	1.398 (2)	C651—H65C	0.9800
C45—H45A	0.9500		
N3—N2—N1	111.74 (10)	C51—C52—H52A	119.3
N2—N1—H1	115.6 (11)	C53—C52—H52A	119.3
C11—N1—H1	116.7 (11)	C54—C53—C52	118.44 (14)
N2—N1—C11	116.07 (10)	C54—C53—C531	120.81 (14)
N2—N3—C41	114.02 (10)	C52—C53—C531	120.75 (15)
C12—C11—C16	121.24 (12)	C53—C54—C55	121.85 (14)
C12—C11—N1	118.55 (11)	C53—C54—H54A	119.1
C16—C11—N1	120.19 (12)	C55—C54—H54A	119.1
C13—C12—C11	118.53 (12)	C54—C55—C56	118.54 (14)
C13—C12—C21	118.68 (13)	C54—C55—C551	120.68 (15)
C11—C12—C21	122.79 (11)	C56—C55—C551	120.79 (15)
C14—C13—C12	120.87 (15)	C55—C56—C51	121.16 (14)
C14—C13—H13A	119.6	C55—C56—H56A	119.4
C12—C13—H13A	119.6	C51—C56—H56A	119.4
C13—C14—C15	119.84 (14)	C66—C61—C62	118.86 (14)
C13—C14—H14A	120.1	C66—C61—C46	119.92 (13)
C15—C14—H14A	120.1	C62—C61—C46	121.19 (12)
C14—C15—C16	121.68 (13)	C63—C62—C61	121.65 (14)

C14—C15—H15A	119.2	C63—C62—H62A	119.2
C16—C15—H15A	119.2	C61—C62—H62A	119.2
C15—C16—C11	117.80 (13)	C64—C63—C62	117.95 (16)
C15—C16—C31	118.69 (12)	C64—C63—C631	120.56 (16)
C11—C16—C31	123.49 (12)	C62—C63—C631	121.50 (16)
C22—C21—C26	118.50 (12)	C65—C64—C63	121.76 (15)
C22—C21—C12	121.95 (12)	C65—C64—H64A	119.1
C26—C21—C12	119.46 (12)	C63—C64—H64A	119.1
C21—C22—C23	121.38 (13)	C64—C65—C66	118.88 (15)
C21—C22—H22A	119.3	C64—C65—C651	120.96 (18)
C23—C22—H22A	119.3	C66—C65—C651	120.2 (2)
C24—C23—C22	118.34 (13)	C61—C66—C65	120.86 (16)
C24—C23—C231	121.23 (13)	C61—C66—H66A	119.6
C22—C23—C231	120.39 (13)	C65—C66—H66A	119.6
C25—C24—C23	121.87 (12)	C23—C231—H23A	109.5
C25—C24—H24A	119.1	C23—C231—H23B	109.5
C23—C24—H24A	119.1	H23A—C231—H23B	109.5
C24—C25—C26	118.61 (13)	C23—C231—H23C	109.5
C24—C25—C251	121.12 (13)	H23A—C231—H23C	109.5
C26—C25—C251	120.25 (14)	H23B—C231—H23C	109.5
C25—C26—C21	121.29 (13)	C25—C251—H25A	109.5
C25—C26—H26A	119.4	C25—C251—H25B	109.5
C21—C26—H26A	119.4	H25A—C251—H25B	109.5
C36—C31—C32	118.79 (14)	C25—C251—H25C	109.5
C36—C31—C16	121.76 (13)	H25A—C251—H25C	109.5
C32—C31—C16	119.28 (14)	H25B—C251—H25C	109.5
C33—C32—C31	121.01 (17)	C33—C331—H33A	109.5
C33—C32—H32A	119.5	C33—C331—H33B	109.5
C31—C32—H32A	119.5	H33A—C331—H33B	109.5
C34—C33—C32	118.49 (16)	C33—C331—H33C	109.5
C34—C33—C331	121.42 (18)	H33A—C331—H33C	109.5
C32—C33—C331	120.1 (2)	H33B—C331—H33C	109.5
C33—C34—C35	122.14 (16)	C35—C351—H35A	109.5
C33—C34—H34A	118.9	C35—C351—H35B	109.5
C35—C34—H34A	118.9	H35A—C351—H35B	109.5
C36—C35—C34	118.07 (17)	C35—C351—H35C	109.5
C36—C35—C351	120.73 (16)	H35A—C351—H35C	109.5
C34—C35—C351	121.20 (16)	H35B—C351—H35C	109.5
C31—C36—C35	121.49 (15)	C53—C531—H53A	109.5
C31—C36—H36A	119.3	C53—C531—H53B	109.5
C35—C36—H36A	119.3	H53A—C531—H53B	109.5
C42—C41—C46	120.77 (12)	C53—C531—H53C	109.5
C42—C41—N3	116.55 (11)	H53A—C531—H53C	109.5
C46—C41—N3	122.50 (11)	H53B—C531—H53C	109.5
C43—C42—C41	118.70 (12)	C55—C551—H55A	109.5
C43—C42—C51	120.18 (12)	C55—C551—H55B	109.5
C41—C42—C51	121.11 (12)	H55A—C551—H55B	109.5
C44—C43—C42	121.29 (13)	C55—C551—H55C	109.5
C44—C43—H43A	119.4	H55A—C551—H55C	109.5

C42—C43—H43A	119.4	H55B—C551—H55C	109.5
C43—C44—C45	119.51 (13)	C63—C631—H63A	109.5
C43—C44—H44A	120.2	C63—C631—H63B	109.5
C45—C44—H44A	120.2	H63A—C631—H63B	109.5
C44—C45—C46	121.43 (13)	C63—C631—H63C	109.5
C44—C45—H45A	119.3	H63A—C631—H63C	109.5
C46—C45—H45A	119.3	H63B—C631—H63C	109.5
C45—C46—C41	118.26 (12)	C65—C651—H65A	109.5
C45—C46—C61	118.82 (12)	C65—C651—H65B	109.5
C41—C46—C61	122.88 (12)	H65A—C651—H65B	109.5
C52—C51—C56	118.66 (13)	C65—C651—H65C	109.5
C52—C51—C42	119.63 (12)	H65A—C651—H65C	109.5
C56—C51—C42	121.72 (12)	H65B—C651—H65C	109.5
C51—C52—C53	121.34 (14)		
C11—N1—N2—N3	159.72 (11)	C32—C31—C36—C35	0.4 (2)
C41—N3—N2—N1	−179.29 (10)	C16—C31—C36—C35	175.83 (13)
N2—N1—C11—C16	53.75 (16)	C34—C35—C36—C31	−0.3 (2)
N2—N3—C41—C46	43.51 (16)	C351—C35—C36—C31	179.77 (15)
C11—C12—C21—C22	48.47 (19)	N2—N3—C41—C42	−141.40 (12)
C11—C16—C31—C36	53.1 (2)	C46—C41—C42—C43	0.08 (19)
C41—C42—C51—C56	50.48 (18)	N3—C41—C42—C43	−175.11 (12)
C41—C46—C61—C62	61.70 (19)	C46—C41—C42—C51	179.61 (12)
N2—N1—C11—C12	−127.86 (13)	N3—C41—C42—C51	4.43 (18)
C16—C11—C12—C13	−0.3 (2)	C41—C42—C43—C44	−1.6 (2)
N1—C11—C12—C13	−178.65 (13)	C51—C42—C43—C44	178.88 (14)
C16—C11—C12—C21	179.98 (13)	C42—C43—C44—C45	1.4 (2)
N1—C11—C12—C21	1.6 (2)	C43—C44—C45—C46	0.4 (2)
C11—C12—C13—C14	−1.5 (3)	C44—C45—C46—C41	−1.8 (2)
C21—C12—C13—C14	178.27 (17)	C44—C45—C46—C61	175.94 (14)
C12—C13—C14—C15	1.7 (3)	C42—C41—C46—C45	1.59 (19)
C13—C14—C15—C16	−0.1 (3)	N3—C41—C46—C45	176.48 (12)
C14—C15—C16—C11	−1.6 (3)	C42—C41—C46—C61	−176.10 (12)
C14—C15—C16—C31	176.93 (17)	N3—C41—C46—C61	−1.20 (19)
C12—C11—C16—C15	1.8 (2)	C43—C42—C51—C52	49.81 (18)
N1—C11—C16—C15	−179.86 (14)	C41—C42—C51—C52	−129.72 (13)
C12—C11—C16—C31	−176.69 (13)	C43—C42—C51—C56	−129.99 (15)
N1—C11—C16—C31	1.7 (2)	C56—C51—C52—C53	−0.9 (2)
C13—C12—C21—C22	−131.26 (15)	C42—C51—C52—C53	179.28 (12)
C13—C12—C21—C26	45.34 (19)	C51—C52—C53—C54	0.0 (2)
C11—C12—C21—C26	−134.93 (14)	C51—C52—C53—C531	−179.48 (14)
C26—C21—C22—C23	−0.15 (19)	C52—C53—C54—C55	1.1 (2)
C12—C21—C22—C23	176.48 (12)	C531—C53—C54—C55	−179.49 (14)
C21—C22—C23—C24	−0.06 (19)	C53—C54—C55—C56	−1.1 (2)
C21—C22—C23—C231	−178.14 (12)	C53—C54—C55—C551	179.17 (15)
C22—C23—C24—C25	−0.1 (2)	C54—C55—C56—C51	0.1 (2)
C231—C23—C24—C25	177.98 (13)	C551—C55—C56—C51	179.83 (14)
C23—C24—C25—C26	0.4 (2)	C52—C51—C56—C55	0.9 (2)
C23—C24—C25—C251	−177.96 (13)	C42—C51—C56—C55	−179.31 (13)
C24—C25—C26—C21	−0.7 (2)	C45—C46—C61—C66	62.08 (19)

C251—C25—C26—C21	177.76 (13)	C41—C46—C61—C66	−120.24 (16)
C22—C21—C26—C25	0.5 (2)	C45—C46—C61—C62	−115.98 (16)
C12—C21—C26—C25	−176.20 (12)	C66—C61—C62—C63	1.9 (2)
C15—C16—C31—C36	−125.37 (16)	C46—C61—C62—C63	179.97 (13)
C15—C16—C31—C32	50.0 (2)	C61—C62—C63—C64	−0.6 (2)
C11—C16—C31—C32	−131.51 (15)	C61—C62—C63—C631	179.27 (16)
C36—C31—C32—C33	−0.3 (2)	C62—C63—C64—C65	−1.0 (3)
C16—C31—C32—C33	−175.84 (13)	C631—C63—C64—C65	179.08 (18)
C31—C32—C33—C34	0.1 (2)	C63—C64—C65—C66	1.4 (3)
C31—C32—C33—C331	179.80 (16)	C63—C64—C65—C651	−178.4 (2)
C32—C33—C34—C35	0.0 (3)	C62—C61—C66—C65	−1.5 (2)
C331—C33—C34—C35	−179.70 (18)	C46—C61—C66—C65	−179.63 (16)
C33—C34—C35—C36	0.1 (3)	C64—C65—C66—C61	−0.1 (3)
C33—C34—C35—C351	−179.98 (16)	C651—C65—C66—C61	179.70 (19)

Fig. 1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