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N^1,N^4-Diethynyl-N^1,N^4-diphenylbenzene-1,4-diamine

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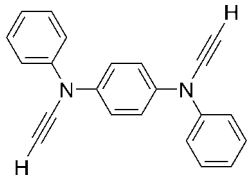
Key indicators: single-crystal X-ray study; T = 93 K; mean σ(C–C) = 0.005 Å; R factor = 0.043; wR factor = 0.093; data-to-parameter ratio = 6.9.

The title compound, $C_{22}H_{16}N_2$, is the first example of an ynamine with H atoms bonded to the terminal C atoms. The environment around each N atom is almost planar. The distances of the N atoms from a least squares plane fitted through each N atom and the surrounding three C atoms, are 0.087 (3) and 0.041 (4) Å. The dihedral angles between these two planes and the central phenylene ring are 23.34 (14) and 34.57 (14)°. The two acetylene groups have an *anti* conformation, keeping a conjugation through the central benzene ring. The freely refined lengths of C_{sp}—H are 1.00 (5) and 0.93 (4) Å, consistent with those of reported acetylenes. The H atoms bound to terminal C atoms have short contacts with the neighboring acetylenic C and N atoms. The closest contacts are an H···N distance of 2.67 (5) Å and an H···C distance of 2.74 (5) Å.

Related literature

For the related structures of ynamine compounds where a diphenylamino group is connected to a diacetylene in the terminal position, see: Galli *et al.* (1988, 1989). For the related structures of a diacetylene compound having 9-carbazolyl groups at both ends, see: Mayerle & Flandera (1978). For the related structures of ynamine compounds incorporating a phenothiazine-10-yl group, see: Okuno *et al.* (2006). For our work on the preparation and the structure of the related ynamine molecule incoporating a part of the title compound, see: Tabata *et al.* (2011).



Experimental

Crystal data

$C_{22}H_{16}N_2$
M_r = 308.38
Monoclinic, $P2_1$
a = 9.228 (3) Å
b = 7.752 (2) Å
c = 11.359 (4) Å
β = 100.880 (4)°
V = 798.0 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 93 K
0.25 × 0.12 × 0.08 mm

Data collection

Rigaku Saturn724 diffractometer
Absorption correction: numerical (*NUMABS*; Rigaku, 1999)
T_{min} = 0.984, T_{max} = 0.994
6457 measured reflections
1942 independent reflections
1627 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.093
S = 1.03
1939 reflections
282 parameters
1 restraint
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
The CH···π interactions of C_{sp}—H with the acetylenic carbon and the nitrogen atoms (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C20—H1···N1^{i}	1.00 (5)	2.67 (5)	3.540 (5)	145 (4)
C22—H2···C20^{ii}	0.93 (4)	2.74 (5)	3.478 (6)	137 (4)

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2117).

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supporting information

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N^1,N^4-Diethynyl-N^1,N^4-diphenylbenzene-1,4-diamine

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S1. Comment

Ynamines, where amino groups are connected to acetylene groups, are known to be unstable because of their high reactivity. Therefore, reports of crystal structures are limited to rather stable ynamines (Galli *et al.*, 1988; Galli *et al.*, 1989; Mayerle & Flandera, 1978; Okuno *et al.*, 2006;) which carry some substituents, except for H atoms, on all C– and N-terminals. When H atoms are connected to C– or N-terminals, the stability of ynamines decreases drastically. In the course of our research in ynamine compounds to develop a conjugated linker, (Tabata *et al.*, 2011) we have succeeded in preparation and characterization of the title compound. It is the first example of ynamines with H atoms in the C-terminals.

In the molecular structure, (Fig. 1) the geometric parameters are consistent with those of other reported ynamines. (Table 1) The bond lengths of C_{sp}—H are 1.00 (5) Å and 0.93 (4) Å, where a marked difference is not recognized compared with those of other acetylenic compounds. The structures around the nitrogen atoms, plane (N1/C1/C7/C19) and plane (N2/C4/C13/C21), are almost planar, where the distances of the nitrogen atoms from the least squares planes are 0.087 (3) Å and 0.041 (4) Å, respectively. The dihedral angles of the plane (N1/C1/C7/C19) with the phenylene (C1/C2/C3/C4/C5/C6) and the phenyl rings (C7/C8/C9/C10/C11/C12) are 23.34 (14)° and 48.74 (15)°, respectively. The dihedral angles of the plane (N2/C4/C13/C21) with the phenylene (C1/C2/C3/C4/C5/C6) and the phenyl rings (C13/C14/C15/C16/C17/C18) are 34.57 (14)° and 29.28 (14)°, respectively. The two acetylene groups have an *anti* conformation, keeping a conjugation through the phenylene ring.

The H-atoms bound to C-terminals have short contacts with the neighboring acetylenic carbon and nitrogen atoms, giving C_{sp}—H···π interactions. (Fig. 2, Table 2) The C20—H1 bond points to the C2($-x+1, y+1/2, -z$) atom, where the closest contact is C20—H1···N1($-x+1, y+1/2, -z$) of 2.67 (5) Å, indicating the interaction with the lone pair of N1. The H2 atom interacts with *p*-orbitals of an adjacent acetylenic carbon atom. The C22—H2 bond directs to the N1($x, y, z+1$) atom, with close contact C22—H2···C20($x, y, z+1$) of 2.74 (5) Å.

S2. Experimental

N^1,N^4-diethynyl-N^1,N^4-diphenyl-1,4- phenylenediamine

n-BuLi in *n*-hexane (15.5 ml, 24.6 mmol) was added dropwise to a solution of N^1,N^4-bis(trichloroethenyl)-N^1, N^4-diphenyl-1,4-phenylenediamine (2.00 g, 3.85 mmol) in dry THF (100 ml) at -78 °C under an argon atmosphere. After the solution was stirred for 1 h, methanol (1.3 ml) was added to the solution. It was allowed to warm to -10 °C and poured into water (50 ml). The water layer was extracted with ether (100 ml), and the combined organic layer was washed with saturated brine (20 ml), and dried over anhydrous sodium sulfate. After the solvent was evaporated, the residue was purified by GPC to give 0.60 g (yield 50%) of the title compound as a reddish brown powder. The single crystals with sufficient quality were obtained by slow evaporation from a solution of chloroform in a refrigerator.

S3. Refinement

Friedel pairs were merged because the molecule itself was achiral and because there were not any anomalous scattering effects. Four reflections whose 2θ angles were lower than 8° were not used for refinement because of the effect of a beam stop. The C-bound H atoms were obtained from a difference Fourier map and were refined isotropically with the restriction of C_{sp}—H range between 0.95 (4) Å and 1.15 (4) Å.

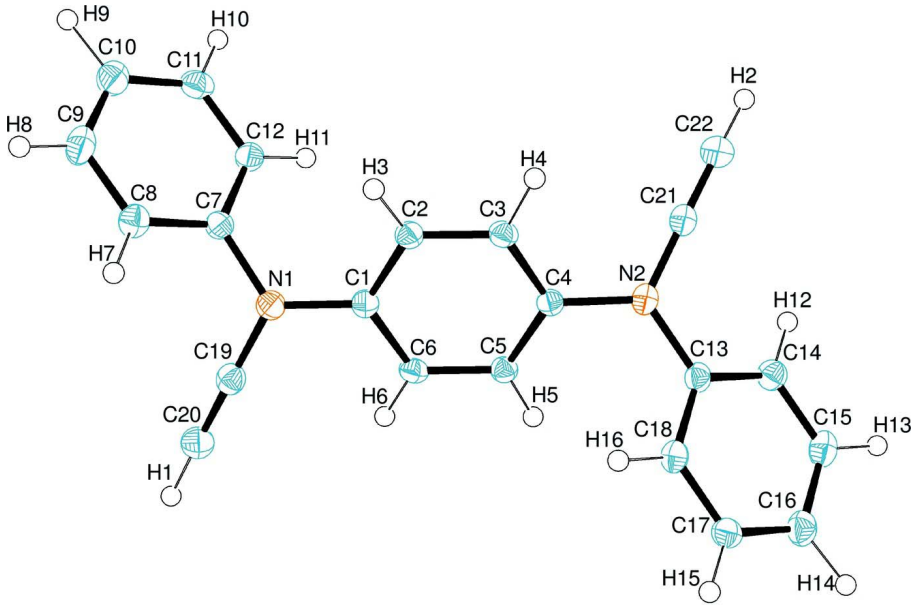

Figure 1

The asymmetric unit of the title compound with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

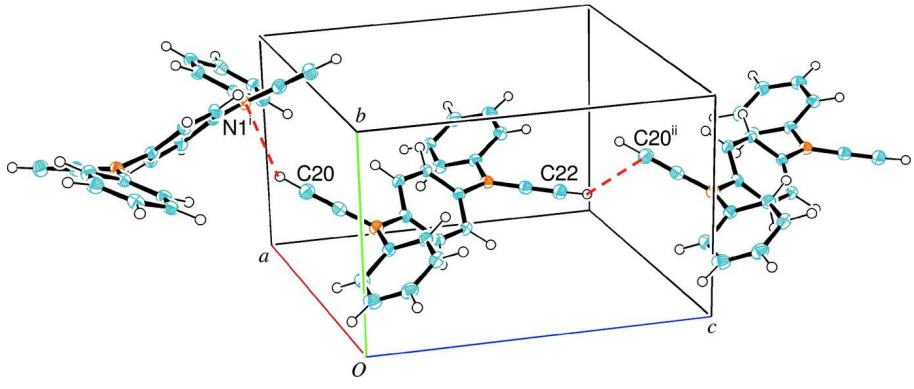

Figure 2

C–H···π interactions between H-atoms of the C-terminals and the acetylenic carbon and the nitrogen atoms. [Symmetry codes: (i) -x + 1, y + 1/2, -z; (ii) x, y, z + 1]

N^1,N^4-Diethynyl-N^1,N^4-diphenylbenzene- 1,4-diamine

Crystal data

$C_{22}H_{16}N_2$
M_r = 308.38

Monoclinic, $P2_1$
Hall symbol: P 2yb

a = 9.228 (3) Å
b = 7.752 (2) Å
c = 11.359 (4) Å
β = 100.880 (4)°
V = 798.0 (5) Å^3
Z = 2
F(000) = 324.00
D_x = 1.283 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 2741 reflections
θ = 3.2–27.5°
μ = 0.08 mm^{-1}
T = 93 K
Prism, colourless
0.25 × 0.12 × 0.08 mm

Data collection

Rigaku Saturn724 diffractometer
Detector resolution: 28.445 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Rigaku, 1999)
T_{min} = 0.984, T_{max} = 0.994
6457 measured reflections

1942 independent reflections
1627 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.040
θ_{max} = 27.5°
h = −11→11
k = −10→10
l = −14→10

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.093
S = 1.03
1939 reflections
282 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.116 (10)

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

	x	y	z	U_{iso}*/U_{eq}
N1	0.3719 (3)	0.3729 (3)	0.1482 (2)	0.0205 (6)
N2	0.7581 (3)	0.3249 (4)	0.5970 (2)	0.0199 (6)
C1	0.4697 (3)	0.3595 (4)	0.2614 (3)	0.0179 (7)
C2	0.4381 (3)	0.2478 (4)	0.3489 (3)	0.0185 (7)
C3	0.5345 (3)	0.2341 (4)	0.4589 (3)	0.0189 (7)
C4	0.6630 (3)	0.3317 (4)	0.4816 (3)	0.0169 (7)
C5	0.6951 (3)	0.4417 (4)	0.3933 (3)	0.0178 (7)
C6	0.5999 (3)	0.4552 (4)	0.2837 (3)	0.0190 (7)
C7	0.2146 (3)	0.3531 (4)	0.1369 (3)	0.0193 (7)
C8	0.1366 (4)	0.2700 (4)	0.0355 (3)	0.0240 (8)
C9	−0.0163 (4)	0.2602 (5)	0.0191 (3)	0.0291 (9)
C10	−0.0907 (4)	0.3317 (5)	0.1017 (3)	0.0286 (9)
C11	−0.0121 (4)	0.4117 (4)	0.2036 (3)	0.0249 (8)
C12	0.1407 (3)	0.4234 (4)	0.2211 (3)	0.0208 (7)
C13	0.9137 (3)	0.3538 (4)	0.6126 (3)	0.0194 (7)
C14	0.9879 (3)	0.4337 (4)	0.7169 (3)	0.0226 (8)
C15	1.1393 (4)	0.4586 (4)	0.7329 (3)	0.0263 (8)
C16	1.2172 (4)	0.4105 (4)	0.6452 (3)	0.0262 (8)

C17	1.1418 (3)	0.3325 (4)	0.5412 (3)	0.0229 (8)
C18	0.9911 (3)	0.3013 (4)	0.5250 (3)	0.0212 (7)
C19	0.4187 (3)	0.4520 (4)	0.0562 (3)	0.0223 (7)
C20	0.4608 (4)	0.5242 (4)	−0.0232 (3)	0.0266 (9)
C21	0.6955 (3)	0.3114 (4)	0.6945 (3)	0.0208 (7)
C22	0.6419 (4)	0.3023 (4)	0.7811 (3)	0.0258 (8)
H1	0.498 (5)	0.586 (6)	−0.089 (4)	0.056 (13)*
H2	0.601 (4)	0.299 (6)	0.850 (3)	0.039 (10)*
H3	0.352 (4)	0.178 (5)	0.330 (3)	0.017 (8)*
H4	0.502 (4)	0.162 (5)	0.523 (3)	0.024 (9)*
H5	0.785 (4)	0.509 (5)	0.404 (3)	0.021 (8)*
H6	0.624 (4)	0.529 (5)	0.223 (3)	0.033 (10)*
H7	0.194 (3)	0.217 (4)	−0.021 (3)	0.014 (7)*
H8	−0.064 (4)	0.207 (5)	−0.054 (3)	0.025 (9)*
H9	−0.218 (4)	0.329 (6)	0.084 (3)	0.038 (10)*
H10	−0.065 (4)	0.464 (5)	0.262 (3)	0.028 (9)*
H11	0.191 (4)	0.486 (5)	0.294 (3)	0.033 (10)*
H12	0.934 (4)	0.468 (5)	0.779 (3)	0.028 (9)*
H13	1.195 (4)	0.509 (5)	0.811 (3)	0.033 (10)*
H14	1.336 (4)	0.424 (6)	0.662 (3)	0.038 (10)*
H15	1.196 (4)	0.298 (5)	0.478 (3)	0.025 (8)*
H16	0.939 (4)	0.242 (5)	0.449 (3)	0.028 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0205 (12)	0.0205 (12)	0.0205 (12)	−0.0003 (10)	0.0036 (10)	0.0013 (10)
N2	0.0194 (11)	0.0194 (12)	0.0194 (12)	0.0000 (10)	0.0000 (9)	0.0000 (10)
C1	0.0179 (13)	0.0179 (14)	0.0179 (13)	0.0027 (11)	0.0034 (11)	−0.0016 (11)
C2	0.0186 (14)	0.0186 (14)	0.0186 (14)	−0.0024 (11)	0.0039 (11)	−0.0004 (11)
C3	0.0192 (14)	0.0192 (13)	0.0192 (14)	0.0003 (11)	0.0056 (11)	0.0029 (11)
C4	0.0170 (13)	0.0170 (13)	0.0170 (13)	0.0017 (11)	0.0040 (10)	−0.0007 (12)
C5	0.0179 (14)	0.0179 (13)	0.0179 (13)	−0.0012 (12)	0.0039 (11)	−0.0003 (11)
C6	0.0194 (14)	0.0194 (14)	0.0194 (13)	−0.0005 (12)	0.0070 (11)	0.0025 (12)
C7	0.0192 (14)	0.0192 (14)	0.0192 (14)	−0.0002 (12)	0.0031 (11)	0.0032 (11)
C8	0.0238 (15)	0.0238 (15)	0.0238 (15)	0.0005 (12)	0.0027 (13)	−0.0014 (12)
C9	0.0278 (16)	0.0278 (17)	0.0278 (17)	−0.0046 (13)	−0.0046 (14)	0.0009 (13)
C10	0.0280 (17)	0.0280 (16)	0.0280 (17)	−0.0030 (14)	0.0005 (13)	0.0080 (15)
C11	0.0254 (16)	0.0254 (15)	0.0254 (15)	0.0012 (13)	0.0088 (13)	0.0054 (13)
C12	0.0207 (14)	0.0207 (14)	0.0207 (14)	−0.0018 (12)	0.0030 (12)	0.0017 (12)
C13	0.0190 (14)	0.0190 (14)	0.0190 (14)	−0.0004 (12)	0.0009 (11)	0.0029 (11)
C14	0.0225 (15)	0.0225 (14)	0.0225 (15)	−0.0008 (13)	0.0034 (12)	−0.0011 (13)
C15	0.0253 (16)	0.0253 (16)	0.0253 (16)	−0.0015 (13)	−0.0031 (13)	0.0007 (13)
C16	0.0256 (16)	0.0256 (16)	0.0256 (16)	0.0004 (13)	0.0000 (13)	0.0055 (13)
C17	0.0232 (15)	0.0232 (15)	0.0232 (14)	0.0068 (13)	0.0068 (12)	0.0067 (13)
C18	0.0208 (14)	0.0208 (14)	0.0208 (14)	0.0021 (12)	0.0005 (12)	0.0015 (12)
C19	0.0221 (14)	0.0221 (14)	0.0221 (14)	−0.0003 (12)	0.0028 (11)	−0.0043 (12)
C20	0.0267 (17)	0.0267 (16)	0.0267 (16)	−0.0017 (13)	0.0057 (13)	0.0010 (13)

C21	0.0203 (14)	0.0203 (14)	0.0203 (14)	0.0000 (12)	0.0000 (11)	0.0000 (12)
C22	0.0260 (15)	0.0260 (16)	0.0260 (15)	−0.0004 (13)	0.0067 (13)	0.0003 (13)

Geometric parameters (Å, º)

N1—C1	1.428 (4)	C15—C16	1.385 (6)
N1—C7	1.441 (4)	C16—C17	1.391 (5)
N1—C19	1.351 (5)	C17—C18	1.389 (4)
N2—C4	1.434 (4)	C19—C20	1.187 (5)
N2—C13	1.431 (4)	C21—C22	1.184 (6)
N2—C21	1.346 (5)	C2—H3	0.95 (4)
C1—C2	1.390 (5)	C3—H4	1.01 (4)
C1—C6	1.394 (4)	C5—H5	0.97 (4)
C2—C3	1.394 (5)	C6—H6	0.95 (4)
C3—C4	1.389 (4)	C8—H7	0.99 (4)
C4—C5	1.390 (5)	C9—H8	0.96 (4)
C5—C6	1.386 (5)	C10—H9	1.15 (4)
C7—C8	1.395 (5)	C11—H10	0.98 (4)
C7—C12	1.387 (5)	C12—H11	1.00 (4)
C8—C9	1.390 (6)	C14—H12	0.97 (4)
C9—C10	1.379 (6)	C15—H13	1.02 (4)
C10—C11	1.391 (5)	C16—H14	1.08 (4)
C11—C12	1.389 (5)	C17—H15	0.99 (4)
C13—C14	1.396 (5)	C18—H16	1.02 (4)
C13—C18	1.391 (5)	C20—H1	1.00 (5)
C14—C15	1.388 (5)	C22—H2	0.93 (4)
C1—N1—C7	121.8 (3)	N1—C19—C20	178.7 (4)
C1—N1—C19	119.3 (3)	N2—C21—C22	178.7 (4)
C7—N1—C19	116.3 (3)	C1—C2—H3	118 (2)
C4—N2—C13	122.3 (3)	C3—C2—H3	122 (2)
C4—N2—C21	118.1 (3)	C2—C3—H4	117.6 (19)
C13—N2—C21	119.1 (3)	C4—C3—H4	121.9 (19)
N1—C1—C2	120.4 (3)	C4—C5—H5	122 (2)
N1—C1—C6	120.1 (3)	C6—C5—H5	117 (2)
C2—C1—C6	119.4 (3)	C1—C6—H6	120 (2)
C1—C2—C3	120.2 (3)	C5—C6—H6	120 (2)
C2—C3—C4	120.2 (3)	C7—C8—H7	118.0 (16)
N2—C4—C3	120.2 (3)	C9—C8—H7	122.8 (16)
N2—C4—C5	120.3 (3)	C8—C9—H8	115 (3)
C3—C4—C5	119.4 (3)	C10—C9—H8	124 (3)
C4—C5—C6	120.6 (3)	C9—C10—H9	119.7 (19)
C1—C6—C5	120.1 (3)	C11—C10—H9	120 (2)
N1—C7—C8	118.5 (3)	C10—C11—H10	120 (2)
N1—C7—C12	121.0 (3)	C12—C11—H10	120 (2)
C8—C7—C12	120.4 (3)	C7—C12—H11	124 (3)
C7—C8—C9	119.2 (4)	C11—C12—H11	117 (3)
C8—C9—C10	120.7 (3)	C13—C14—H12	120 (2)

C9—C10—C11	119.8 (4)	C15—C14—H12	120 (2)
C10—C11—C12	120.3 (4)	C14—C15—H13	120 (3)
C7—C12—C11	119.6 (3)	C16—C15—H13	119 (3)
N2—C13—C14	119.6 (3)	C15—C16—H14	120 (2)
N2—C13—C18	120.3 (3)	C17—C16—H14	121 (2)
C14—C13—C18	120.1 (3)	C16—C17—H15	120 (2)
C13—C14—C15	119.5 (3)	C18—C17—H15	119 (2)
C14—C15—C16	121.0 (3)	C13—C18—H16	121 (3)
C15—C16—C17	118.9 (4)	C17—C18—H16	120 (3)
C16—C17—C18	121.1 (4)	C19—C20—H1	179 (3)
C13—C18—C17	119.4 (3)	C21—C22—H2	178 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H1···N1^{i}	1.00 (5)	2.67 (5)	3.540 (5)	145 (4)
C22—H2···C20^{ii}	0.93 (4)	2.74 (5)	3.478 (6)	137 (4)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*; (ii) *x*, *y*, *z*+1.