Crystal structure and fluorescence of 1-[8-phenyl-9-(phenylethynyl)-4H-benzo[def]carbazol-4-yl]-ethan-1-one

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The crystal of the title compound, C_{60}H_{38}N_{2}O_{2}, which crystallizes in the monoclinic space group P2_{1}/n, was obtained by thermal evaporation of a 1:1 dichloromethane and hexanes solution of the pure compound. The crystal structure is stabilized by π–π interactions between benzo[def]carbazole moieties and carbonyl–carbonyl interactions between the two acetyl groups.

1. Chemical context

For recent background literature on the chemistry of related carbazole-derived compounds and their applications, including syntheses of bioactive carbazoles, see: (Chakraborty et al., 1965; Bondock et al., 2019) and references cited therein. The syntheses of related benzo[def]carbazoles are described by Pocock et al. (2021) and Geng et al. (2016). For applications of benzo[def]carbazole derivatives, see: Vespa et al. (2018), Atakan & Gunbas (2016) and Myśliwiec et al. (2015).

The photophysical properties of 4H-benzo[def]carbazole have been studied over the past few decades (Bender et al., 1964; Zander et al., 1966; Favini et al., 1971; Horaguchi et al., 1980). The spectra show that the wavelengths of absorption and emission maxima are in the ranges 230–410 nm and 345–520 nm, respectively, at different temperatures and for different solvents. The effect of the solvent on absorption and fluorescence bands as well as comparisons with theoretical expectations have been used to estimate the dipole moment of the first excited state. Geng et al. (2016) reported the optimized geometry, electron-density distributions, and HOMO and LUMO of carbazole and 4H-benzo[def]carbazole. Changes in the HOMO–LUMO gap (E_g) and the design of molecules for material applications can be realized by comparing frontier molecular orbitals, HOMO and LUMO energy levels, and exploring their electron-density maps.

In order to obtain the benzo[def]carbazole 2 efficiently, we utilized the pathway through the conversion of diphenylphenanthrene 1 to N-acetyl benzo[def]carbazole 2. We
obtained N-acetyl carbazole 2 in quantitative yield utilizing Buchwalds’ method by treatment of diphenylphenanthrene 1 as a substrate in the presence of Pd(OAc)₂ (10 mol %), NaOAc (1.0 equiv.), Cu(OAc)₂ (2.0 equiv.) and powdered molecular sieves in toluene under oxygen at 393 K for 24 h. Single crystals of 2 were grown from a mixture of hexanes and DCM (v/v = 1:1) at room temperature by slow thermal evaporation.

2. Structural commentary

Compound 2 crystallizes in the monoclinic space group P2₁⁄n with two independent molecules in the asymmetric unit. The atomic labelling scheme is shown in Fig. 1. The C—C bond lengths are within the expected values known for aromatic systems (Allen et al., 1987).

In the structure of 2, both independent conformers occupy their own coordinates in the asymmetric unit, but are in the same configuration. On the other hand, owing to the space group of the title compound, P2₁⁄n, which is centrosymmetric, both molecules will produce two identical configurations that are 180° inverted from each other. In the stereo view, we can observe that the phenyl group and the phenyl alkynyl moiety in the two independent conformers have different dihedral angles with respect to the benzo[def]carbazole, which are 22.2 (1), 25.7 (2)⁰ and 50.8 (2), 59.7 (2)⁰, respectively.

3. Supramolecular features

In the crystal, there are no classical hydrogen bonds present and the crystal packing of 2 (Fig. 2) is mainly determined by intermolecular π–π interactions between the benzo[def]carbazole moieties with centroid–centroid distances of 3.795 (2) to 4.553 (1) Å (Fig. 3a, grey dashed line), acetyl–acetyl dipolar interactions of 3.459 (3) to 3.689 (3) Å (Fig. 3a, blue dashed line), C—H···π interactions of 2.935 (2) to 3.314 (3) Å (Fig. 3b, green dashed line), and π–π interactions with centroid–centroid distances of 3.801 (2) to 5.672 (2) Å (Fig. 3b, red dashed lines) between phenyl alkynyl moieties.

Specifically, the crystal is stabilized by the phenyl groups of the alkynyl moiety, which interacts weakly with each other (Fig. 3b, red dashed lines) through π–π stacking. Furthermore, the phenyl group also interacts with another neighboring phenyl moiety and with the phenyl alkynyl moiety through C—H···π interactions (Table 1). In addition, π–π stacking and carbonyl–carbonyl interactions with δC+ and δO− between the two acetyl groups are observed. The molecules are ordered into infinite ribbons extending along the [001] direction through alternating intermolecular C—H···π and π–π stacking interactions.

### Table 1

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C12—H12···O2i | 0.95 | 2.48 | 3.417 (3) | 169 |
| C19—H19···O1ii | 0.95 | 2.42 | 3.294 (2) | 153 |
| C19—H19···Cg22ii | 0.95 | 2.94 | 3.652 (2) | 132 |
| C33—H33···Cg6iii | 0.05 | 2.96 | 3.756 (2) | 142 |

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

4. Database survey

A search of the Cambridge Structural Database (WebCSD accessed 21 April 2022; Groom et al., 2016) results in over a thousand carbazole derivatives of which 45 are derivatives of benzo[def]carbazole. Most of the compounds are cyclized with the benzo moiety to the skeleton of benzo[def]carbazole. Of these, 31 molecular structures are derivatives of the main structure of phenanthro[1,10,9,8-cdef][2]carbazole that is commonly used to design functional molecules, such as organic transistors or n-doped thermoelectric devices (KUTZUX (Cann et al., 2020); ZAJMUW (Martell et al., 2021)), white-light emissive material (ILIGIW; Chatsiriuspachai et al., 2021), N-annulated perylene diimide for stable organic materials with unique optical, electronic, magnetic properties (MEHDUB; Wei et al., 2017), organic solar cells.
Other compounds have benzo[def]carbazole derivatives as the skeleton, for instance, 4,5-iminophenanthrene (IMNPHN; Ern et al., 1971), aka 4H-benzo[def]carbazole, capped [3]cyclo(2,6)benzo[def]carbazole dichloromethane solvate (ROZQAA; Myśliwiec et al., 2015), picenoporphyrins [QUQYAC01 (Nath et al., 2003); QUQYAC (Aihara et al., 2001)] and 4H-naphtho[1,2,3,4-def]carbazole (IWOBEE; Pocock et al., 2021). In addition, there is no alkynyl phenyl group on C8 and a phenyl group on C9 of the benzo[def]carbazole as in the title compound in any structure found in the WebCSD search. The title compound is the only one with an N-acetyl group attached to the benzo[def]carbazole unit.

5. Synthesis and crystallization

To a dried reaction tube, phenanthrene 1 (0.1 mmol), Pd(OAc)$_2$ (2.25 mg, 0.01 mmol), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol), NaOAc (16.4 mg, 0.2 mmol) and powdered molecular sieves (40 mg, activated 3 Å) were added under air and covered with a septum. The tube was evacuated and refilled with N$_2$. Under a positive N$_2$ pressure, toluene (2 mL) was added via a syringe followed by degassing under a weak vacuum to this tube, and it was refilled with O$_2$ three times. The reaction mixture was sealed and stirred at 293 K for 24 h under an O$_2$ atmosphere. After completion of the reaction, the solution was cooled to room temperature and diluted with ethyl acetate followed by filtration through a thin pad of Celite. The crude product was purified by flash chromatography (hexanes/EtOAc) on silica gel to afford N-acetyl benzo[def]carbazole 2. Crystals of the title compound were obtained by thermal evaporation of the pure compound from a 1:1 solution of dichloromethane and hexanes.
6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically (C—H = 0.95–0.98 Å) and refined using a riding model, with $U_{	ext{iso}}(H) = 1.2$ or $1.5U_{eq}(C)$.

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Crystal structure and fluorescence of 1-[8-phenyl-9-(phenylethynyl)-4H-benzo[def]carbazol-4-yl]ethan-1-one

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Computing details
Data collection: APEX2 (Bruker, 2013); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT (Bruker, 2013); program(s) used to solve structure: SHELXD (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014/6 (Sheldrick, 2015); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

1-[8-Phenyl-9-(phenylethynyl)-4H-benzo[def]carbazol-4-yl]ethan-1-one

Crystal data
C₆₀H₃₈N₂O₂  
Mr = 818.92
Monoclinic, P2₁/n
a = 15.835 (2) Å  
b = 7.0408 (8) Å  
c = 37.245 (4) Å  
β = 96.464 (4)°  
V = 4126.0 (8) Å³  
Z = 4
F(000) = 1712  
Dₐ = 1.318 Mg m⁻³
Cell parameters from 4269 reflections
θ = 2.6–26.2°  
µ = 0.08 mm⁻¹
T = 100 K
Lamellar, colorless
0.10 × 0.04 × 0.01 mm

Data collection
Bruker APEXII CCD
diffractometer
Detector resolution: 8.3333 pixels mm⁻¹
φ and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2013)
Tmin = 0.663, Tmax = 0.745
24738 measured reflections
8499 independent reflections
5655 reflections with I > 2σ(I)
Rint = 0.050
θmax = 26.5°, θmin = 2.6°
h = −19→19  
k = −7→8  
l = −46→29

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.050
wR(F²) = 0.113
S = 1.00
8499 reflections
579 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
w = 1/[σ²(Fo²) + (0.0436P)² + 1.1066P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max = 0.001
Δρmax = 0.21 e Å⁻³
Δρmin = −0.21 e Å⁻³
**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.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|  | x   | y   | z   | Uiso*/Ueq |
|---|-----|-----|-----|-----------|
| O1 | 0.74487 (10) | 0.1747 (2) | 0.68964 (4) | 0.0415 (4) |
| O2 | 0.22802 (9)  | 0.3551 (2)  | 0.34700 (4)  | 0.0362 (4)  |
| N1 | 0.65540 (10) | 0.1891 (2)  | 0.63820 (4)  | 0.0240 (4)  |
| N2 | 0.34803 (10) | 0.2839 (2)  | 0.32282 (4)  | 0.0206 (4)  |
| C1 | 0.80629 (14) | 0.1151 (4)  | 0.63534 (6)  | 0.0419 (6)  |
| H1A | 0.8596 | 0.1073 | 0.6514 | 0.063* |
| H1B | 0.8110 | 0.2147 | 0.6173 | 0.063* |
| H1C | 0.7950 | -0.0070 | 0.6231 | 0.063* |
| C2 | 0.73527 (13) | 0.1615 (3)  | 0.65688 (6)  | 0.0303 (5)  |
| C3 | 0.58209 (13) | 0.2340 (3)  | 0.65598 (5)  | 0.0224 (4)  |
| C4 | 0.51389 (13) | 0.2467 (3)  | 0.62913 (5)  | 0.0201 (4)  |
| C5 | 0.43028 (13) | 0.2837 (3)  | 0.63400 (5)  | 0.0208 (4)  |
| C6 | 0.37150 (12) | 0.2849 (2)  | 0.60078 (5)  | 0.0186 (4)  |
| C7 | 0.28426 (13) | 0.3221 (3)  | 0.60435 (5)  | 0.0211 (4)  |
| C8 | 0.21214 (13) | 0.3538 (3)  | 0.60968 (5)  | 0.0219 (4)  |
| C9 | 0.12705 (12) | 0.4010 (3)  | 0.61566 (5)  | 0.0210 (4)  |
| C10 | 0.05863 (13) | 0.3555 (3)  | 0.59016 (5)  | 0.0249 (5)  |
| H10 | 0.0683 | 0.2903 | 0.5687 | 0.030* |
| C11 | -0.02299 (14) | 0.4048 (3)  | 0.59603 (5)  | 0.0308 (5)  |
| H11 | -0.0692 | 0.3734 | 0.5785 | 0.037* |
| C12 | -0.03801 (14) | 0.4993 (3)  | 0.62720 (6)  | 0.0316 (5)  |
| H12 | -0.0943 | 0.5333 | 0.6311 | 0.038* |
| C13 | 0.62873 (12) | 0.1764 (3)  | 0.59994 (5)  | 0.0208 (4)  |
| C14 | 0.66663 (12) | 0.1343 (3)  | 0.56942 (5)  | 0.0235 (4)  |
| H14 | 0.7255 | 0.1056 | 0.5706 | 0.028* |
| C15 | 0.61385 (12) | 0.1359 (3)  | 0.53622 (5)  | 0.0227 (4)  |
| H15 | 0.6392 | 0.1070 | 0.5149 | 0.027* |
| C16 | 0.52804 (12) | 0.1766 (3)  | 0.53256 (5)  | 0.0196 (4)  |
| H16 | 0.4963 | 0.1764 | 0.5093 | 0.024* |
| C17 | 0.48803 (12) | 0.2183 (2)  | 0.56351 (5)  | 0.0167 (4)  |
| C18 | 0.39959 (12) | 0.2569 (2)  | 0.56697 (5)  | 0.0173 (4)  |
| C19 | 0.11147 (13) | 0.4960 (3)  | 0.64717 (5)  | 0.0253 (5)  |
| H19 | 0.1573 | 0.5273 | 0.6649 | 0.030* |
| C20 | 0.02936 (14) | 0.5442 (3)  | 0.65260 (6)  | 0.0305 (5)  |
| H20 | 0.0191 | 0.6089 | 0.6741 | 0.037* |
| C21 | 0.41488 (14) | 0.3148 (3)  | 0.67003 (5)  | 0.0245 (5)  |
| H21 | 0.3592 | 0.3426 | 0.6758 | 0.029* |
| C22 | 0.48259 (14) | 0.3041 (3)  | 0.69689 (5)  | 0.0299 (5)  |
| H22 | 0.4711 | 0.3260 | 0.7210 | 0.036* |
| Atom | U1   | U2   | U3   | U12  |
|------|------|------|------|------|
| C23  | 0.56690 (14) | 0.2634 (3) | 0.69129 (5) | 0.0287 (5) |
| H23  | 0.6110 | 0.2564 | 0.7108 | 0.034* |
| C24  | 0.54160 (12) | 0.2140 (3) | 0.59572 (5) | 0.0188 (4) |
| C25  | 0.33834 (11) | 0.2660 (3) | 0.53370 (5) | 0.0177 (4) |
| C26  | 0.34917 (12) | 0.3975 (3) | 0.50668 (5) | 0.0202 (4) |
| H26  | 0.3961 | 0.4823 | 0.5095 | 0.024* |
| C27  | 0.29199 (13) | 0.4057 (3) | 0.47564 (5) | 0.0247 (5) |
| H27  | 0.2998 | 0.4966 | 0.4574 | 0.030* |
| C28  | 0.22389 (12) | 0.2826 (3) | 0.47107 (5) | 0.0253 (5) |
| H28  | 0.1848 | 0.2886 | 0.4498 | 0.030* |
| C29  | 0.21288 (12) | 0.1506 (3) | 0.49758 (5) | 0.0251 (5) |
| H29  | 0.1664 | 0.0647 | 0.4945 | 0.030* |
| C30  | 0.26971 (12) | 0.1436 (3) | 0.52868 (5) | 0.0218 (4) |
| H30  | 0.2614 | 0.0531 | 0.5469 | 0.026* |
| C31  | 0.98472 (13) | 0.2404 (3) | 0.48214 (5) | 0.0291 (5) |
| H31  | 1.0332 | 0.2476 | 0.4996 | 0.035* |
| C32  | 0.90969 (13) | 0.3266 (3) | 0.48863 (5) | 0.0263 (5) |
| H32  | 0.9069 | 0.3943 | 0.5105 | 0.032* |
| C33  | 0.83845 (12) | 0.3151 (3) | 0.46351 (5) | 0.0219 (4) |
| H33  | 0.7868 | 0.3739 | 0.4682 | 0.026* |
| C34  | 0.84273 (12) | 0.2167 (3) | 0.43118 (5) | 0.0185 (4) |
| C35  | 0.76930 (12) | 0.2040 (3) | 0.40509 (5) | 0.0189 (4) |
| C36  | 0.70893 (12) | 0.1952 (3) | 0.38286 (5) | 0.0185 (4) |
| C37  | 0.63290 (12) | 0.1977 (2) | 0.35821 (5) | 0.0175 (4) |
| C38  | 0.55469 (12) | 0.2330 (2) | 0.37392 (5) | 0.0179 (4) |
| C39  | 0.48281 (12) | 0.2459 (2) | 0.34919 (5) | 0.0177 (4) |
| C40  | 0.40077 (12) | 0.2841 (3) | 0.35681 (5) | 0.0196 (4) |
| C41  | 0.26149 (13) | 0.3182 (3) | 0.32008 (5) | 0.0254 (5) |
| C42  | 0.21216 (13) | 0.3046 (3) | 0.28353 (5) | 0.0331 (5) |
| H42A | 0.1520 | 0.3293 | 0.2855 | 0.050* |
| H42B | 0.2186 | 0.1770 | 0.2737 | 0.050* |
| H42C | 0.2336 | 0.3987 | 0.2674 | 0.050* |
| C43  | 0.98923 (13) | 0.1438 (3) | 0.45019 (5) | 0.0283 (5) |
| H43  | 1.0409 | 0.0847 | 0.4457 | 0.034* |
| C44  | 0.91876 (12) | 0.1324 (3) | 0.42466 (5) | 0.0237 (5) |
| H44  | 0.9224 | 0.0667 | 0.4026 | 0.028* |
| C45  | 0.63535 (12) | 0.1767 (2) | 0.32106 (5) | 0.0176 (4) |
| C46  | 0.55753 (12) | 0.1896 (2) | 0.29627 (5) | 0.0175 (4) |
| C47  | 0.54453 (12) | 0.1717 (3) | 0.25823 (5) | 0.0214 (4) |
| H47  | 0.5908 | 0.1441 | 0.2449 | 0.026* |
| C48  | 0.46346 (12) | 0.1948 (3) | 0.24062 (5) | 0.0232 (4) |
| H48  | 0.4565 | 0.1837 | 0.2150 | 0.028* |
| C49  | 0.39071 (12) | 0.2335 (3) | 0.25765 (5) | 0.0224 (4) |
| H49  | 0.3365 | 0.2495 | 0.2442 | 0.027* |
| C50  | 0.40171 (12) | 0.2472 (3) | 0.29484 (5) | 0.0196 (4) |
| C51  | 0.48426 (12) | 0.2248 (2) | 0.31221 (5) | 0.0181 (4) |
| C52  | 0.71793 (12) | 0.1450 (3) | 0.30673 (5) | 0.0184 (4) |
| C53  | 0.74376 (12) | 0.2607 (3) | 0.27948 (5) | 0.0213 (4) |
|   | X       | Y       | Z       | U11   | U22   | U33   | U12   | U13   | U23   |
|---|---------|---------|---------|-------|-------|-------|-------|-------|-------|-------|
| O1| 0.0442 (10) | 0.0477 (10) | 0.0288 (9) | -0.0090 (8) | -0.0134 (7) | 0.0041 (7) |
| O2| 0.0260 (8)  | 0.0502 (10) | 0.0333 (9) | 0.0050 (7)  | 0.0069 (7)  | 0.0010 (7) |
| N1| 0.0293 (10) | 0.0201 (9)  | 0.0207 (8) | -0.0037 (7) | -0.0054 (7) | 0.0012 (7) |
| N2| 0.0204 (9)  | 0.0200 (9)  | 0.0208 (8) | -0.0013 (7) | 0.0002 (7)  | 0.0002 (7) |
| C1| 0.0284 (13) | 0.0526 (16) | 0.0417 (14) | -0.0024 (11) | -0.0091 (11) | 0.0081 (11) |
| C2| 0.0311 (12) | 0.0246 (12) | 0.0319 (12) | -0.0068 (9) | -0.0109 (10) | 0.0046 (9) |
| C3| 0.0301 (11) | 0.0140 (10) | 0.0224 (10) | -0.0064 (9) | -0.0003 (9) | 0.0014 (8) |
| C4| 0.0327 (12) | 0.0111 (10) | 0.0162 (9)  | -0.0051 (8) | 0.0011 (8)  | 0.0002 (7) |
| C5| 0.0335 (12) | 0.0105 (9)  | 0.0190 (10) | -0.0055 (8) | 0.0051 (8)  | 0.0006 (7) |
| C6| 0.0263 (11) | 0.0092 (9)  | 0.0209 (10) | -0.0028 (8) | 0.0047 (8)  | 0.0008 (7) |
| C7| 0.0324 (12) | 0.0138 (10) | 0.0176 (10) | -0.0010 (9) | 0.0053 (9)  | 0.0016 (7) |
| C8| 0.0335 (12) | 0.0127 (10) | 0.0201 (10) | -0.0024 (9) | 0.0062 (9)  | 0.0029 (8) |
| C9| 0.0286 (11) | 0.0148 (10) | 0.0209 (10) | -0.0008 (8) | 0.0086 (9)  | 0.0038 (8) |
| C10| 0.0349 (12) | 0.0189 (11) | 0.0215 (10) | -0.0031 (9) | 0.0059 (9)  | -0.0026 (8) |
| C11| 0.0307 (12) | 0.0308 (12) | 0.0305 (12) | -0.0039 (10) | 0.0018 (10) | 0.0014 (9) |
| C12| 0.0257 (12) | 0.0291 (13) | 0.0418 (13) | -0.0011 (10) | 0.0116 (10) | -0.0002 (10) |
| C13| 0.0281 (11) | 0.0119 (10) | 0.0210 (10) | -0.0047 (8) | -0.0026 (8) | 0.0006 (8) |
| C14| 0.0208 (11) | 0.0201 (11) | 0.0292 (11) | -0.0014 (8) | 0.0014 (9)  | 0.0006 (8) |
| C15| 0.0278 (11) | 0.0198 (11) | 0.0214 (10) | -0.0014 (9) | 0.0059 (9)  | -0.0010 (8) |
| C16| 0.0249 (11) | 0.0160 (10) | 0.0174 (9)  | -0.0035 (8) | 0.0003 (8)  | 0.0010 (7) |
| C17| 0.0245 (10) | 0.0093 (9)  | 0.0161 (9)  | -0.0025 (8) | 0.0022 (8)  | 0.0003 (7) |
| C18| 0.0237 (10) | 0.0093 (9)  | 0.0190 (9)  | -0.0025 (8) | 0.0025 (8)  | 0.0015 (7) |
| C19| 0.0319 (12) | 0.0237 (11) | 0.0212 (10) | -0.0050 (9) | 0.0072 (9)  | -0.0024 (8) |
| C20| 0.0368 (13) | 0.0281 (12) | 0.0294 (11) | -0.0044 (10) | 0.0155 (10) | -0.0078 (9) |
| C21| 0.0398 (13) | 0.0161 (11) | 0.0189 (10) | -0.0057 (9) | 0.0087 (9)  | -0.0009 (8) |
| C22| 0.0514 (15) | 0.0230 (12) | 0.0161 (10) | -0.0101 (10) | 0.0066 (10) | -0.0016 (8) |
| C23| 0.0476 (14) | 0.0197 (11) | 0.0170 (10) | -0.0106 (10) | -0.0045 (9) | 0.0002 (8) |
| C24| 0.0256 (11) | 0.0116 (9)  | 0.0191 (9)  | -0.0039 (8) | 0.0021 (8)  | -0.0007 (7) |
| C25| 0.0200 (10) | 0.0163 (10) | 0.0173 (9)  | 0.0027 (8)  | 0.0048 (8)  | -0.0004 (7) |
### Geometric parameters (Å, °)

| Bond/Distance | Value (Å) | Bond/Distance | Value (Å) |
|---------------|-----------|---------------|-----------|
| O1—C2         | 1.216     | C28—H28       | 0.9500    |
| O2—C41        | 1.214     | C29—C30       | 1.386 (3) |
| N1—C2         | 1.387     | C29—H29       | 0.9500    |
| N1—C3         | 1.435     | C30—H30       | 0.9500    |
| N1—C13        | 1.443     | C31—C32       | 1.379 (3) |
| N2—C41        | 1.384     | C31—C43       | 1.380 (3) |
| N2—C40        | 1.436     | C31—H31       | 0.9500    |
| N2—C50        | 1.440     | C32—C33       | 1.385 (3) |
| C1—C2         | 1.489     | C32—H32       | 0.9500    |
| C1—H1A        | 0.9800    | C33—C34       | 1.397 (2) |

**Notes:**
- Geometric parameters include bond lengths, bond angles, and other structural parameters.
- Values are given with standard deviations in parentheses.
- The structure is from Acta Cryst. (2022), E78, 590-593.
C1—H1B 0.9800
C1—H1C 0.9800
C3—C23 1.379 (3)
C3—C4 1.390 (3)
C4—C5 1.381 (3)
C4—C24 1.385 (3)
C5—C21 1.408 (2)
C5—C6 1.462 (3)
C6—C18 1.396 (2)
C6—C7 1.427 (3)
C7—C8 1.202 (3)
C8—C9 1.429 (3)
C9—C10 1.395 (3)
C9—C19 1.396 (3)
C10—C11 1.379 (3)
C10—H10 0.9500
C11—C12 1.382 (3)
C11—H11 0.9500
C12—C20 1.380 (3)
C12—H12 0.9500
C13—C14 1.376 (3)
C13—C24 1.396 (3)
C14—C15 1.412 (3)
C14—H14 0.9500
C15—C16 1.380 (3)
C15—H15 0.9500
C16—C17 1.380 (2)
C16—H16 0.9500
C17—C24 1.390 (2)
C17—C18 1.447 (3)
C18—C25 1.487 (2)
C19—C20 1.380 (3)
C19—H19 0.9500
C20—H20 0.9500
C21—C22 1.384 (3)
C21—H21 0.9500
C22—C23 1.404 (3)
C22—H22 0.9500
C23—C24 1.396 (3)
C23—C22 0.9500
C24—C25 1.383 (3)
C25—C26 1.392 (2)
C26—C27 1.387 (2)
C26—H26 0.9500
C27—C28 1.379 (3)
C27—H27 0.9500
C28—C29 1.382 (3)
C2—N1—C3 122.60 (16)
C33—H33 0.9500
C34—C44 1.388 (3)
C34—C35 1.432 (3)
C35—C36 1.194 (2)
C36—C37 1.430 (3)
C37—C38 1.396 (2)
C38—C39 1.384 (2)
C38—C58 1.406 (2)
C39—C40 1.387 (3)
C39—C51 1.388 (2)
C40—C60 1.380 (3)
C41—C42 1.494 (3)
C42—H42A 0.9800
C42—H42B 0.9800
C42—H42C 0.9800
C43—C44 1.384 (3)
C43—H43 0.9500
C44—H44 0.9500
C45—C46 1.457 (2)
C45—C52 1.484 (3)
C46—C47 1.414 (2)
C46—C51 1.384 (3)
C47—C48 1.384 (3)
C47—H47 0.9500
C48—C49 1.403 (3)
C48—H48 0.9500
C49—C50 1.380 (2)
C49—H49 0.9500
C50—C51 1.401 (3)
C52—C53 1.398 (3)
C52—C57 1.392 (2)
C53—C54 1.382 (3)
C53—C54 1.382 (3)
C54—C55 1.383 (3)
C54—H54 0.9500
C55—H55 0.9500
C55—C56 1.383 (3)
C56—C57 1.383 (3)
C56—H56 0.9500
C57—H57 0.9500
C58—C59 1.384 (3)
C58—H58 0.9500
C59—C60 1.409 (3)
C59—H59 0.9500
C60—H60 0.9500
C25—C30—C29 121.13 (18)
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| C2—N1—C13           | 129.48 (17)  | C25—C30—H30         | 119.4        |
| C3—N1—C13           | 107.90 (15)  | C29—C30—H30         | 119.4        |
| C41—N2—C40          | 122.53 (16)  | C32—C31—C43         | 119.82 (18)  |
| C41—N2—C50          | 129.64 (15)  | C32—C31—H31         | 120.1        |
| C40—N2—C50          | 107.81 (14)  | C43—C31—H31         | 120.1        |
| C2—C1—H1A           | 109.5        | C31—C32—C33         | 120.55 (18)  |
| C2—C1—H1B           | 109.5        | C31—C32—H32         | 119.7        |
| H1A—C1—H1B          | 109.5        | C33—C32—H32         | 119.7        |
| C2—C1—H1C           | 109.5        | C32—C33—C34         | 119.76 (19)  |
| H1A—C1—H1C          | 109.5        | C32—C33—H33         | 120.1        |
| H1B—C1—H1C          | 109.5        | C34—C33—H33         | 120.1        |
| O1—C2—N1            | 119.8 (2)    | C44—C34—C33         | 119.34 (17)  |
| O1—C2—C1            | 122.72 (19)  | C44—C34—C35         | 120.57 (17)  |
| N1—C2—C1            | 117.51 (18)  | C33—C34—C35         | 120.09 (17)  |
| C23—C3—C4           | 118.14 (19)  | C36—C35—C34         | 178.7 (2)    |
| C23—C3—N1           | 135.25 (18)  | C35—C36—C37         | 174.6 (2)    |
| C4—C3—N1            | 106.60 (16)  | C45—C37—C36         | 121.32 (17)  |
| C5—C4—C24           | 123.70 (17)  | C45—C37—C38         | 122.58 (16)  |
| C5—C4—C3            | 126.63 (17)  | C36—C37—C38         | 116.03 (15)  |
| C24—C4—C3           | 109.67 (18)  | C39—C38—C37         | 114.75 (16)  |
| C4—C5—C21           | 115.21 (17)  | C39—C38—C37         | 114.75 (16)  |
| C4—C5—C6            | 114.73 (16)  | C58—C38—C37         | 130.20 (16)  |
| C21—C5—C6           | 130.06 (19)  | C38—C39—C40         | 126.57 (17)  |
| C18—C6—C7           | 121.34 (16)  | C38—C39—C51         | 123.29 (18)  |
| C18—C6—C5           | 121.69 (17)  | C40—C39—C51         | 110.13 (16)  |
| C7—C6—C5            | 116.94 (16)  | C40—C39—C51         | 118.30 (17)  |
| C8—C7—C6            | 175.84 (19)  | C60—C40—N2          | 135.14 (18)  |
| C7—C8—C9            | 177.2 (2)    | C39—C40—N2          | 106.55 (15)  |
| C10—C9—C19          | 119.00 (18)  | O2—C41—N2           | 119.81 (18)  |
| C10—C9—C8           | 120.92 (17)  | O2—C41—C42          | 122.28 (18)  |
| C19—C9—C8           | 120.07 (18)  | N2—C41—C42          | 117.89 (18)  |
| C11—C10—C9          | 120.27 (18)  | C41—C42—H42A        | 109.5        |
| C11—C10—H10         | 119.9        | C41—C42—H42B        | 109.5        |
| C9—C10—H10          | 119.9        | H42A—C42—H42B       | 109.5        |
| C10—C11—C12         | 120.49 (19)  | C41—C42—H42C        | 109.5        |
| C10—C11—H11         | 119.8        | H42A—C42—H42C       | 109.5        |
| C12—C11—H11         | 119.8        | H42B—C42—H42C       | 109.5        |
| C20—C12—C11         | 119.5 (2)    | C31—C43—C44         | 120.33 (19)  |
| C20—C12—H12         | 120.2        | C31—C43—H43         | 119.8        |
| C11—C12—H12         | 120.2        | C44—C43—H43         | 119.8        |
| C14—C13—C24         | 117.72 (17)  | C43—C44—C34         | 120.20 (18)  |
| C14—C13—N1          | 136.29 (18)  | C43—C44—H44         | 119.9        |
| C24—C13—N1          | 105.97 (16)  | C34—C44—H44         | 119.9        |
| C13—C14—C15         | 116.82 (18)  | C37—C45—C46         | 120.36 (17)  |
| C13—C14—H14         | 121.6        | C37—C45—C52         | 119.74 (16)  |
| C15—C14—H14         | 121.6        | C46—C45—C52         | 119.89 (15)  |
| C16—C15—C14         | 124.55 (18)  | C51—C46—C47         | 114.29 (16)  |
| C16—C15—H15         | 117.7        | C51—C46—C45         | 115.42 (15)  |
C14—C15—H15 117.7 C47—C46—C45 130.29 (17)
C15—C16—C17 119.42 (17) C48—C47—C46 119.14 (18)
C15—C16—H16 120.3 C48—C47—H47 120.4
C17—C16—H16 120.3 C46—C47—H47 120.4
C24—C17—C16 114.54 (17) C47—C48—C49 125.01 (17)
C24—C17—C18 115.48 (16) C47—C48—H48 117.5
C16—C17—C18 129.93 (16) C49—C48—H48 117.5
C6—C18—C17 121.13 (16) C50—C49—C48 116.75 (17)
C6—C18—C25 120.12 (17) C50—C49—H49 121.6
C17—C18—C25 118.75 (15) C48—C49—H49 121.6
C20—C19—C9 119.95 (19) C49—C50—C48 117.50 (17)
C20—C19—H19 120.0 C49—C50—N2 136.11 (17)
C9—C19—H19 120.0 C51—C50—N2 106.38 (15)
C19—C20—C12 120.75 (19) C46—C51—C39 123.59 (16)
C19—C20—H20 119.6 C46—C51—C50 127.29 (16)
C12—C20—H20 119.6 C39—C51—C48 109.12 (17)
C22—C21—C5 118.5 (2) C57—C52—C53 125.01 (17)
C22—C21—H21 120.7 C57—C52—C45 120.77 (16)
C5—C21—H21 120.7 C53—C52—C45 121.00 (16)
C21—C22—C23 125.18 (18) C54—C53—C52 120.64 (17)
C21—C22—H22 117.4 C54—C53—H53 119.7
C23—C22—H22 117.4 C52—C53—H53 119.7
C3—C23—C22 116.31 (18) C55—C54—C53 120.53 (17)
C3—C23—H23 121.8 C55—C54—H54 119.7
C22—C23—C22 121.8 C53—C54—H54 119.7
C4—C24—C17 119.85 (16) C32—C33—C34—C44 −0.3 (3)
C4—C24—C13 109.85 (16) C32—C33—C34—C35 179.92 (17)
C17—C24—C13 126.92 (17) C57—C56—C55 120.80 (17)
C30—C25—C26 118.41 (16) C56—C57—C55 120.37 (18)
C30—C25—C18 120.97 (16) C57—C56—H56 119.8
C26—C25—C18 120.62 (16) C56—C57—H56 119.8
C27—C26—C25 120.55 (18) C56—C57—H57 119.6
C27—C26—H26 119.7 C56—C57—H57 119.6
C25—C26—H26 119.7 C52—C57—C55 120.3
C28—C27—C26 120.31 (18) C59—C58—C38 119.11 (17)
C28—C27—H27 119.8 C59—C58—H58 120.4
C26—C27—H27 119.8 C38—C58—H58 120.4
C27—C28—C29 119.63 (18) C58—C59—C60 124.57 (17)
C27—C28—H28 120.2 C58—C59—H59 117.7
C29—C28—H28 120.2 C60—C59—H59 117.7
C28—C29—C30 119.96 (19) C40—C60—C59 116.42 (18)
C28—C29—H29 120.0 C40—C60—H60 121.8
C30—C29—H29 120.0 C59—C60—H60 121.8
C3—N1—C2—O1 0.2 (3) C43—C31—C32—C33 0.7 (3)
C13—N1—C2—O1 −178.38 (18) C31—C32—C33—C34 −0.5 (3)
C3—N1—C2—C1 179.85 (18) C32—C33—C34—C44 −0.3 (3)
C13—N1—C2—C1 1.3 (3) C32—C33—C34—C35 179.92 (17)
C2—N1—C3—C23 1.0 (3) C45—C37—C38—C39 −0.5 (3)
C13—N1—C3—C23 179.8 (2) C36—C37—C38—C39 176.31 (16)
C2—N1—C3—C4 −178.59 (17) C45—C37—C38—C58 −178.77 (18)
C13—N1—C3—C4 0.2 (2) C36—C37—C38—C58 1.9 (3)
C23—C3—C4—C24 1.1 (3) C58—C38—C39—C40 0.5 (3)
N1—C3—C4—C24 0.6 (2) C37—C38—C39—C40 −178.01 (17)
C2—N1—C3—C4 −178.59 (17) C45—C37—C38—C58 −178.77 (18)
C13—N1—C3—C4 0.2 (2) C36—C37—C38—C58 1.9 (3)
C23—C3—C4—C24 1.1 (3) C58—C38—C39—C40 0.5 (3)
N1—C3—C4—C24 0.6 (2) C37—C38—C39—C40 −178.01 (17)
C2—N1—C3—C4 −178.59 (17) C45—C37—C38—C58 −178.77 (18)
C13—N1—C3—C4 0.2 (2) C36—C37—C38—C58 1.9 (3)
C23—C3—C4—C24 1.1 (3) C58—C38—C39—C40 0.5 (3)
N1—C3—C4—C24 0.6 (2) C37—C38—C39—C40 −178.01 (17)
C2—N1—C3—C4 −178.59 (17) C45—C37—C38—C58 −178.77 (18)
C13—N1—C3—C4 0.2 (2) C36—C37—C38—C58 1.9 (3)
C5—C4—C24—C17 1.2 (3) C38—C39—C51—C50 −179.60 (17)
C3—C4—C24—C17 −179.56 (17) C40—C39—C51—C50 −0.7 (2)
C5—C4—C24—C13 −178.49 (17) C49—C50—C51—C46 −0.1 (3)
C3—C4—C24—C13 0.8 (2) N2—C50—C51—C39 −179.15 (17)
C16—C17—C24—C4 −178.47 (17) C49—C50—C51—C39 0.1 (2)
C18—C17—C24—C4 −1.0 (3) N2—C50—C51—C39 0.1 (2)
C16—C17—C24—C13 1.2 (3) C37—C45—C52—C57 50.8 (2)
C18—C17—C24—C13 178.67 (17) C46—C45—C52—C57 −130.45 (17)
C14—C13—C24—C4 177.94 (17) C37—C45—C52—C53 −126.75 (19)
N1—C13—C24—C4 −0.6 (2) C46—C45—C52—C53 52.0 (2)
C14—C13—C24—C17 −1.7 (3) C57—C52—C53—C54 −1.3 (3)
N1—C13—C24—C17 179.75 (17) C45—C52—C53—C54 176.27 (16)
C6—C18—C25—C30 −59.7 (2) C52—C53—C54—C55 −0.1 (3)
C17—C18—C25—C30 120.12 (19) C53—C54—C55—C56 1.2 (3)
C6—C18—C25—C26 120.7 (2) C54—C55—C56—C57 −0.9 (3)
C17—C18—C25—C26 −59.4 (2) C55—C56—C57—C52 −0.6 (3)
C30—C25—C26—C27 0.4 (3) C53—C52—C57—C56 1.7 (3)
C18—C25—C26—C27 179.97 (17) C45—C52—C57—C56 −175.93 (17)
C25—C26—C27—C28 −0.4 (3) C39—C38—C58—C59 0.1 (2)
C26—C27—C28—C29 −0.1 (3) C37—C38—C58—C59 178.33 (18)
C27—C28—C29—C30 0.6 (3) C38—C58—C59—C60 −0.3 (3)
C26—C25—C30—C29 0.1 (3) C39—C40—C60—C59 0.6 (3)
C18—C25—C30—C29 −179.48 (17) N2—C40—C60—C59 179.69 (19)
C28—C29—C30—C25 −0.6 (3) C58—C59—C60—C40 −0.1 (3)

**Hydrogen-bond geometry (Å, °)**

Cg6 and Cg22 are the centroids of the C25–C30 and C52–C57 rings, respectively.

| D—H···A     | D—H | H···A | D···A  | D—H···A |
|------------|-----|------|-------|---------|
| C12—H12···O2i | 0.95 | 2.48 | 3.417 (3) | 169     |
| C49—H49···O1ii | 0.95 | 2.42 | 3.294 (2) | 153     |
| C19—H19···Cg22iii | 0.95 | 2.94 | 3.652 (2) | 132     |
| C33—H33···Cg6iii | 0.05 | 2.96 | 3.756 (2) | 142     |

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