Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Crystal structure and Hirshfeld surface analysis of 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazol-3-ium benzoate

Ruby Ahmed,[a] Onur Erman Doğan,[b] Farman Ali,[a] Musheer Ahmad,[a] Adeeba Ahmed,[a] Necmi Dege[c]* and Irina A. Golenia[d]*

[a]Department of Applied Chemistry, ZHCET, Aligarh Muslim University, Aligarh, 202002, UP, India, [b]Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Chemistry, 55139 Samsun, Turkey, [c]Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, 55139 Samsun, Turkey, and [d]Department of Chemistry, Taras Shecchenko National University of Kyiv, 64, Vladimirska Str., Kiev 01601, Ukraine. *Correspondence e-mail: necmid@omu.edu.tr, igolenya@ua.fm

Received 16 March 2020
Accepted 16 April 2020

Edited by J. T. Mague, Tulane University, USA

Keywords: crystal structure; 2-phenyl-1-*H*-phenanthro[9,10-*d*]imidazole; hydrogen bonding; π–π interactions.

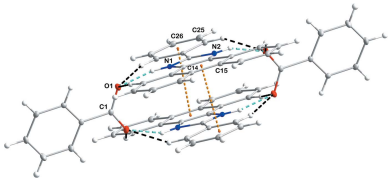
CCDC reference: 1997348

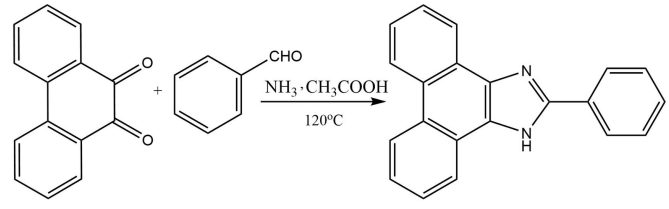
Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, $C_{21}H_{15}N_2^+\cdot C_7H_5O_2^-$, 2-phenyl-1*H*-phenanthro[9,10-*d*]-imidazole and benzoic acid form an ion pair complex. The system is consolidated by hydrogen bonds along with π–π interactions and N—H$\cdots\pi$ interactions between the constituent units. For a better understanding of the crystal structure and intermolecular interactions, a Hirshfeld surface analysis was performed.

1. Chemical context

When phenanthrene is substituted by a heterocyclic moiety, its intermolecular charge-transfer ability is increased (Xu *et al.*, 2017). Such a donor–π–acceptor (D–π–A) arrangement has tunable properties that can be controlled by suitable substituents (Cao *et al.*, 2017). The presence of a heteroatom such as N, O or S may give electron-rich heterocycles (thiophene, pyrrole, or furan) or electron-deficient heterocycles (pyridine, phenanthroline) (Xu *et al.*, 2017). The dipole moment and λ_{max} can be modulated by the selection of D and A. Thus the photophysical properties can be controlled (Wang *et al.*, 2017). The inclusion of heterocycles enhances the polarizability, thermal and chemical stabilities of such adducts. The π-conjugated heterocyclic systems increase delocalization, thus enhancing the stability and photophysical properties (Gu *et al.*, 2017, Zhang *et al.*, 2012). By proper selection of the heterocyclic substituent, good fluorescence with higher sensitivity can be achieved (Li *et al.*, 2016; Huang *et al.*, 2012). The synthesis of selective chromo-fluorogenic sensors for anions, cations and neutral molecules can be achieved (Chou *et al.*, 2012; Zhuang *et al.*, 2012). Herein we report the crystal structure of the title compound, which was synthesized from 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole and benzoic acid.





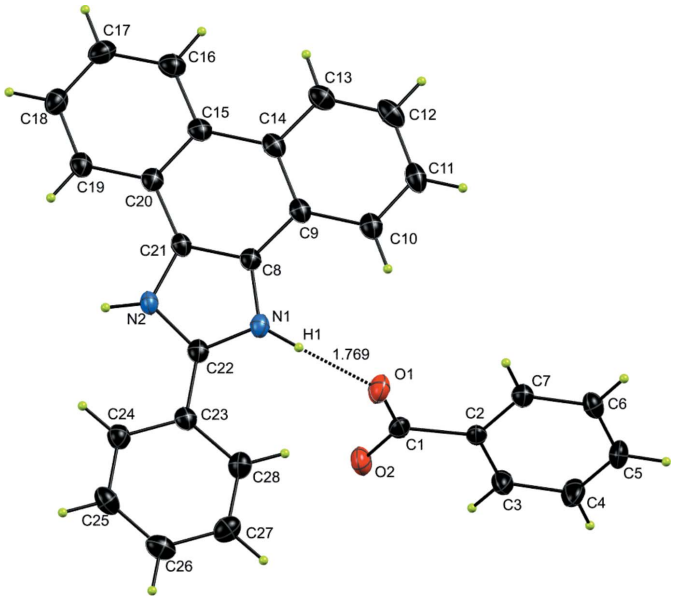


Figure 1
The molecular structure of the title compound with atom labelling. The dashed line indicates the N—H···O hydrogen bond. Displacement ellipsoids are drawn at the 50% probability level.

2. Structural commentary

The structure of the title compound is shown in Fig. 1. The proton from benzoic acid (BA) is completely transferred to the N atom of the imidazole ring of 2-phenyl-1-*H*-phenanthro[9,10-*d*]imidazole (M1), leading to the formation of a $M1^{+}BA^{-}$ co-crystal. The space group is monoclinic, $P2_1/n$ and two asymmetric units, two $M1^{+}$ ions and two benzoate ions, are combined in an inversion dimer of ion pairs (unit *A*, Fig. 2). The benzoate ion and $M1^{+}$ are nearly perpendicular [67.82 (4)°] to one another and the torsional angle C1—O1—N1—C22 is 78.24 **(su?)**°. Unit *A* is stabilized by hydrogen bonds (N1—H1···O1, 1.77 Å, and N2—H2···O2, 1.83 Å; Fig. 2). Beside the hydrogen bonds, there are weak π interactions between the two $M^{+}1$ moieties [intercentroid separations between the C23–C28 and C8/C9/C14/C15/C20/C21 rings = 3.4590 (9) Å].

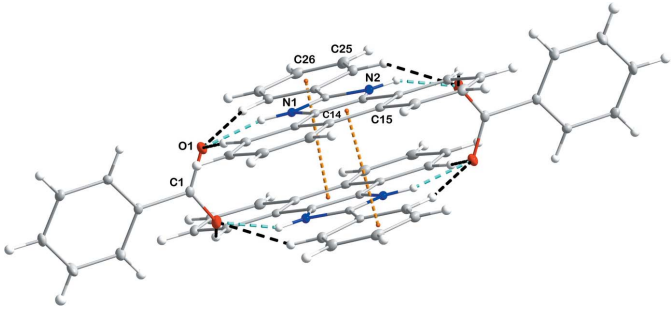


Figure 2
Unit *A* consisting of two entities each of benzoate ions and M1 moieties, linked by hydrogen bonds and π–π interactions.

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

*Cg*4 is the centroid of the C15–C20 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.77	2.6159 (17)	168
N2—H2···O2^{i}	0.86	1.83	2.6523 (16)	158
C7—H7···*Cg*4^{ii}	0.93	2.79	3.585 (2)	145
C10—H10···O1	0.93	2.40	3.265 (2)	155
C19—H19···O2^{i}	0.93	2.54	3.372 (2)	150
C24—H24···O2^{i}	0.93	2.50	3.343 (2)	152
C28—H28···O1	0.93	2.48	3.365 (2)	159

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

3. Supramolecular features

In the crystal, the *A* units are associated through weak, slipped, π-stacking interactions between the C9–C14 benzene rings and N1/C22/N2/C21/C8 imidazole rings across inversion centers [centroid–centroid distance = 3.5675 (9) Å, dihedral angle = 1.57 (8)°, slippage = 1.532 Å). The stepped stacks thus formed extend alternately in the directions of the normals to (111) and (1$\bar{1}$1) and are connected *via* C7—H7···*Cg*4 interactions (Table 1, Fig. 3).

4. Hirshfeld surface analysis

The Hirshfeld surfaces provide an extended qualitative and quantitative analysis of the interactions between the constituents of the co-crystal. The analysis shows the presence of C—H···O and N—H···O hydrogen bonds leading to multi-directional interactions to form the three-dimensional structure. The red spots in the Hirshfeld surface (Fig. 4) are centered on the N1—H1···O1, C10—H10···O1 and C28—H28···O1 interactions of the benzoate ion with the phenanthrene and with the N—H of the imidazole. Their bond lengths are 1.77, 2.40, and 2.48 Å, respectively. The fingerprint plots (Fig. 5) show the percentage contribution of the various interactions. Those of H···H and H···C dominate at 44.8% and 30.6%, respectively. The H···O interactions involve oxygen atoms from the benzoate anion and the N—H group of the imidazole ring of $M1^{+}$.

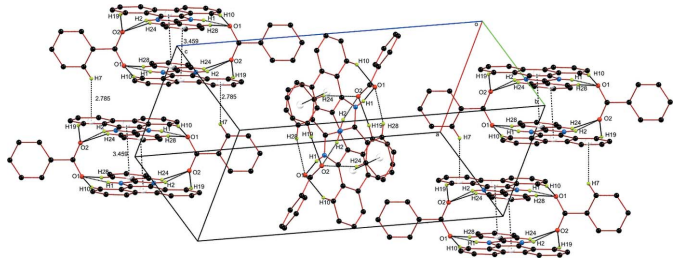


Figure 3
Supramolecular structure showing *A* units stacked over adjacent rows of *A* units running perpendicular to each other.

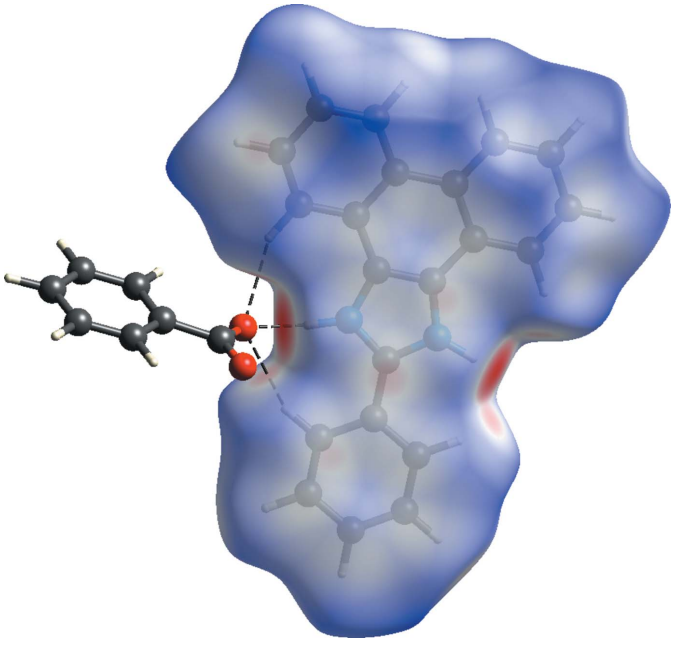


Figure 4
View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm}.

5. Database survey

A search of the Cambridge Structural database (CSD, version 5.41, update November 2019; Groom *et al.*, 2016) for the 2,3-dihydro-1*H*-phenanthro[9,10-*d*]imidazole moiety revealed 45 hits of which the most similar to the title compound are imidazole derivatives (CEZWEL: Mormul *et al.*, 2013; ODEDAD: Li *et al.*, 2016; QORJUD: Tapu *et al.*, 2009; REKXOX: Akula *et al.*, 2017; YUMTEG: Ullah *et al.*, 2009; ZACSAA: Therrien *et al.*, 2014). The N—C bond lengths of the imidazole ring in these structures vary from 1.312 (2) to 1.365 (2) Å. The molecular conformations of these structures are also planar.

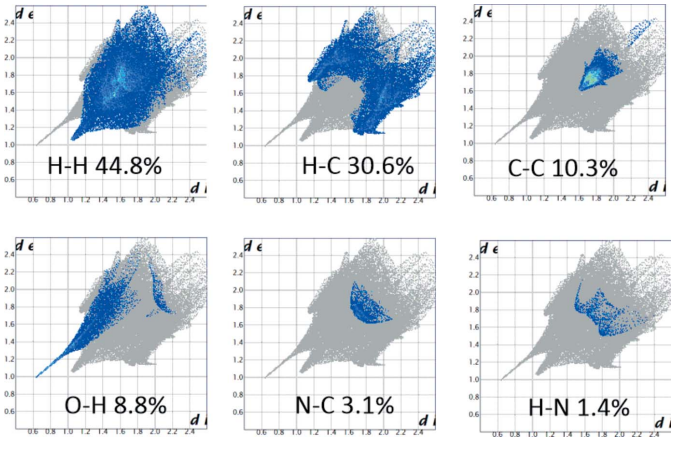


Figure 5
Two-dimensional fingerprint plots of the crystal with the relative contributions of the atom pairs to the Hirshfeld surface.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{15}N_2^+ \cdot C_7H_5O_2^-$
M_r	416.46
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.4693 (4), 8.7384 (3), 24.5049 (9)
β (°)	91.792 (1)
V (Å^3)	2026.70 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.39 × 0.28 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.708, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25446, 3979, 3269
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.104, 1.10
No. of reflections	3979
No. of parameters	289
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.33

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2018/3* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2020).

6. Synthesis and crystallization

A condensation reaction was performed between equimolar quantities of phenanthrene-9,10-dione and benzaldehyde. 1 mmol of phenanthrene-9,10-dione, 1 mmol of benzaldehyde, 5 mmol of ammonium acetate and 30 mL of glacial acetic acid were added to single-neck 100 mL round-bottom flask. The mixture was refluxed for 12 h under nitrogen. After completion of the reaction, the reaction mixture was cooled to room temperature and then 50 mL of deionized cold water were added. The product precipitated out as pale-brown solid. The solid product was filtered, washed with deionized water and dried in a vacuum oven to give 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (M1) as the final product. Crystals were prepared using 20 mg of M1 and 20 mg of benzoic acid dissolved in 5mL of ethanol. The clear solution was left undisturbed for crystallization. Fine crystals were obtained after 15 days.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH hydrogen atoms were located in difference-Fourier maps and, together with the carbon-bound hydrogen atoms, were included as riding contributions in calculated positions [N—H = 0.86, C—H = 0.93 Å; U_{iso}(H) = 1.2U_{eq}(C,N)].

Acknowledgements

The authors are grateful to the Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India, for providing laboratory facilities.

Funding information

Dr Farman Ali acknowledges the DST for INSPIRE Faculty Funding.

References

Akula, S. B., Chen, H.-S., Su, C., Chen, B.-R., Chiou, J.-J., Shieh, C.-H., Lin, Y.-F. & Li, W.-R. (2017). *Inorg. Chem.* **56**, 12987–12995.
Bruker (2016). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cao, L., Zhang, D., Xu, L., Fang, Z., Jiang, X.-F. & Lu, F. (2017). *Eur. J. Org. Chem.* **2017**, 2495–2500.
Chou, H. H., Chen, Y. H., Hsu, H. P., Chang, W. H., Chen, Y. H. & Cheng, C. H. (2012). *Adv. Mater.* **24**, 5867–5871.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Gu, P.-Y., Wang, Z., Liu, G., Yao, H., Wang, Z., Li, Y., Zhu, J., Li, S. & Zhang, Q. (2017). *Chem. Mater.* **29**, 4172–4175.
Huang, H., Wang, Y., Zhuang, S., Yang, X., Wang, L. & Yang, C. (2012). *J. Phys. Chem. C*, **116**, 19458–19466.
Li, J., Chen, S., Wang, Z. & Zhang, Q. (2016). *Chem. Rec.* **16**, 1518–1530.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Mormul, J., Steimann, M., Maichle–Mössmer, C. & Nagel, U. (2013). *Eur. J. Inorg. Chem.* pp. 3421–3428.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Tapu, D., Owens, C., VanDerveer, D. & Gwaltney, K. (2009). *Organometallics*, **28**, 270–276.
Therrien, J. A., Wolf, M. O. & Patrick, B. O. (2014). *Inorg. Chem.* **53**, 12962–12972.
Ullah, F., Kindermann, M. K., Jones, P. G. & Heinicke, J. (2009). *Organometallics*, **28**, 2441–2449.
Wang, Z., Gu, P., Liu, G., Yao, H., Wu, Y., Li, Y., Rakesh, G., Zhu, J., Fu, H. & Zhang, Q. (2017). *Chem. Commun.* **53**, 7772–7775.
Xu, L., Zhang, D., Zhou, Y., Zheng, Y., Cao, L., Jiang, X.-F. & Lu, F. (2017). *Opt. Mater.* **70**, 131–137.
Zhang, Y., Lai, S.-L., Tong, Q.-X., Lo, M.-F., Ng, T.-W., Chan, M.-Y., Wen, Z.-C., He, J., Jeff, K.-S., Tang, X.-L., Liu, W., Ko, C., Wang, P. & Lee, C. (2012). *Chem. Mater.* **24**, 61–70.
Zhuang, S., Shangguan, R., Jin, J., Tu, G., Wang, L., Chen, J., Ma, D. & Zhu, X. (2012). *Org. Electron.* **13**, 3050–3059.

supporting information

Acta Cryst. (2020). E**76**, 724-727 [https://doi.org/10.1107/S2056989020005344]

Crystal structure and Hirshfeld surface analysis of 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazol-3-ium benzoate

Ruby Ahmed, Onur Erman Doğan, Farman Ali, Musheer Ahmad, Adeeba Ahmed, Necmi Dege and Irina A. Golenia

Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT2018/3* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2020).

2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazol-3-ium benzoate

Crystal data

$C_{21}H_{15}N_2^+ \cdot C_7H_5O_2^-$
M_r = 416.46
Monoclinic, $P2_1/n$
a = 9.4693 (4) Å
b = 8.7384 (3) Å
c = 24.5049 (9) Å
β = 91.792 (1)°
V = 2026.70 (13) Å^3
Z = 4
$F(000)$ = 872
D_x = 1.365 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9121 reflections
θ = 3.2–28.1°
μ = 0.09 mm^{-1}
T = 100 K
Block, pink
0.39 × 0.28 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.708, T_{max} = 0.746
25446 measured reflections
3979 independent reflections
3269 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 26.0°, θ_{min} = 2.3°
h = −11→11
k = −10→10
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.10
3979 reflections
289 parameters
0 restraints
Primary atom site location: iterative
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 1.042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 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*	U_{iso}*/U_{eq}
O1	0.23573 (12)	0.35667 (14)	0.39271 (5)	0.0272 (3)
O2	0.43116 (12)	0.21182 (14)	0.39047 (5)	0.0277 (3)
N1	0.27589 (13)	0.51384 (15)	0.48272 (5)	0.0174 (3)
H1	0.259534	0.474240	0.451017	0.021*
N2	0.36868 (13)	0.65362 (15)	0.54849 (5)	0.0177 (3)
H2	0.421794	0.718335	0.565817	0.021*
C1	0.30537 (16)	0.24344 (19)	0.37667 (6)	0.0190 (3)
C2	0.23159 (16)	0.13699 (18)	0.33666 (6)	0.0174 (3)
C3	0.30647 (17)	0.0201 (2)	0.31269 (7)	0.0260 (4)
H3	0.400888	0.004987	0.322848	0.031*
C4	0.24293 (19)	−0.0746 (2)	0.27379 (7)	0.0327 (4)
H4	0.294737	−0.151762	0.257587	0.039*
C5	0.10194 (18)	−0.0537 (2)	0.25920 (7)	0.0261 (4)
H5	0.059013	−0.115598	0.232633	0.031*
C6	0.02506 (17)	0.05930 (19)	0.28422 (7)	0.0225 (4)
H6	−0.070461	0.071109	0.275216	0.027*
C7	0.08921 (16)	0.15524 (18)	0.32262 (6)	0.0194 (3)
H7	0.037017	0.231785	0.338992	0.023*
C8	0.20749 (15)	0.47649 (18)	0.52979 (6)	0.0172 (3)
C9	0.09665 (15)	0.36873 (18)	0.53830 (6)	0.0185 (3)
C10	0.03891 (16)	0.27684 (18)	0.49600 (7)	0.0214 (4)
H10	0.070829	0.286745	0.460668	0.026*
C11	−0.06499 (16)	0.17229 (19)	0.50718 (7)	0.0241 (4)
H11	−0.102982	0.111124	0.479346	0.029*
C12	−0.11351 (17)	0.1577 (2)	0.56009 (7)	0.0267 (4)
H12	−0.183127	0.086184	0.567421	0.032*
C13	−0.05897 (17)	0.2486 (2)	0.60154 (7)	0.0243 (4)
H13	−0.093418	0.238283	0.636479	0.029*
C14	0.04783 (15)	0.35686 (18)	0.59221 (7)	0.0201 (3)
C15	0.10846 (15)	0.45281 (18)	0.63613 (6)	0.0197 (3)
C16	0.06231 (17)	0.4443 (2)	0.69008 (7)	0.0244 (4)
H16	−0.010480	0.377451	0.698225	0.029*
C17	0.12253 (17)	0.5328 (2)	0.73112 (7)	0.0263 (4)
H17	0.090928	0.523517	0.766521	0.032*
C18	0.23025 (17)	0.6361 (2)	0.72023 (7)	0.0243 (4)
H18	0.269913	0.695635	0.748191	0.029*
C19	0.27759 (16)	0.64963 (19)	0.66800 (6)	0.0213 (4)
H19	0.348675	0.719290	0.660521	0.026*
C20	0.21874 (15)	0.55833 (18)	0.62580 (6)	0.0187 (3)

C21	0.26552 (15)	0.56429 (18)	0.57097 (6)	0.0173 (3)
C22	0.37202 (15)	0.62210 (18)	0.49467 (6)	0.0174 (3)
C23	0.46252 (15)	0.69837 (18)	0.45586 (6)	0.0180 (3)
C24	0.55209 (16)	0.81660 (19)	0.47343 (7)	0.0224 (4)
H24	0.554159	0.846890	0.509828	0.027*
C25	0.63769 (17)	0.8886 (2)	0.43664 (7)	0.0264 (4)
H25	0.697088	0.967356	0.448523	0.032*
C26	0.63607 (17)	0.8448 (2)	0.38243 (7)	0.0264 (4)
H26	0.695022	0.892778	0.358048	0.032*
C27	0.54566 (18)	0.7287 (2)	0.36468 (7)	0.0260 (4)
H27	0.543584	0.699591	0.328159	0.031*
C28	0.45880 (17)	0.65616 (19)	0.40079 (7)	0.0224 (4)
H28	0.397852	0.579232	0.388489	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0306 (6)	0.0247 (6)	0.0259 (6)	−0.0004 (5)	−0.0033 (5)	−0.0090 (5)
O2	0.0214 (6)	0.0332 (7)	0.0279 (6)	−0.0035 (5)	−0.0069 (5)	−0.0051 (5)
N1	0.0161 (6)	0.0172 (7)	0.0185 (7)	0.0026 (5)	−0.0037 (5)	−0.0023 (5)
N2	0.0151 (6)	0.0177 (7)	0.0200 (7)	−0.0006 (5)	−0.0035 (5)	−0.0032 (5)
C1	0.0211 (8)	0.0216 (8)	0.0144 (7)	−0.0032 (7)	0.0002 (6)	0.0011 (6)
C2	0.0184 (7)	0.0192 (8)	0.0146 (7)	−0.0039 (6)	0.0010 (6)	0.0011 (6)
C3	0.0166 (7)	0.0336 (10)	0.0277 (9)	0.0000 (7)	−0.0019 (7)	−0.0089 (8)
C4	0.0264 (9)	0.0371 (11)	0.0343 (10)	0.0034 (8)	−0.0006 (8)	−0.0185 (9)
C5	0.0269 (9)	0.0285 (9)	0.0226 (8)	−0.0054 (7)	−0.0046 (7)	−0.0076 (7)
C6	0.0180 (7)	0.0245 (9)	0.0245 (8)	−0.0022 (7)	−0.0051 (7)	0.0006 (7)
C7	0.0192 (8)	0.0187 (8)	0.0203 (8)	0.0010 (6)	−0.0007 (6)	−0.0003 (6)
C8	0.0145 (7)	0.0173 (8)	0.0197 (8)	0.0042 (6)	−0.0019 (6)	−0.0001 (6)
C9	0.0143 (7)	0.0156 (8)	0.0254 (8)	0.0045 (6)	−0.0036 (6)	0.0004 (6)
C10	0.0177 (8)	0.0183 (8)	0.0281 (9)	0.0042 (6)	−0.0035 (7)	−0.0017 (7)
C11	0.0182 (8)	0.0171 (8)	0.0364 (10)	0.0028 (7)	−0.0075 (7)	−0.0035 (7)
C12	0.0178 (8)	0.0200 (9)	0.0420 (11)	0.0001 (7)	−0.0019 (7)	0.0058 (8)
C13	0.0185 (8)	0.0255 (9)	0.0288 (9)	0.0015 (7)	−0.0009 (7)	0.0054 (7)
C14	0.0141 (7)	0.0181 (8)	0.0278 (9)	0.0046 (6)	−0.0025 (6)	0.0019 (7)
C15	0.0147 (7)	0.0207 (8)	0.0234 (8)	0.0060 (6)	−0.0007 (6)	0.0013 (7)
C16	0.0192 (8)	0.0275 (9)	0.0264 (9)	0.0037 (7)	0.0013 (7)	0.0027 (7)
C17	0.0241 (8)	0.0347 (10)	0.0201 (8)	0.0076 (8)	0.0022 (7)	0.0002 (7)
C18	0.0217 (8)	0.0299 (9)	0.0212 (8)	0.0068 (7)	−0.0044 (7)	−0.0032 (7)
C19	0.0162 (7)	0.0227 (9)	0.0247 (9)	0.0040 (6)	−0.0035 (6)	−0.0023 (7)
C20	0.0152 (7)	0.0190 (8)	0.0217 (8)	0.0064 (6)	−0.0033 (6)	−0.0002 (6)
C21	0.0137 (7)	0.0166 (8)	0.0214 (8)	0.0026 (6)	−0.0032 (6)	0.0000 (6)
C22	0.0150 (7)	0.0157 (8)	0.0214 (8)	0.0051 (6)	−0.0032 (6)	−0.0016 (6)
C23	0.0144 (7)	0.0171 (8)	0.0224 (8)	0.0051 (6)	−0.0021 (6)	0.0009 (6)
C24	0.0190 (8)	0.0243 (9)	0.0236 (8)	0.0014 (7)	−0.0024 (7)	−0.0011 (7)
C25	0.0194 (8)	0.0265 (9)	0.0330 (10)	−0.0021 (7)	−0.0045 (7)	0.0038 (8)
C26	0.0203 (8)	0.0286 (10)	0.0304 (9)	0.0034 (7)	0.0014 (7)	0.0097 (8)
C27	0.0301 (9)	0.0264 (9)	0.0215 (8)	0.0057 (7)	0.0000 (7)	0.0018 (7)

C28	0.0234 (8)	0.0191 (8)	0.0243 (8)	0.0021 (7)	−0.0029 (7)	−0.0011 (7)

Geometric parameters (Å, º)

O1—C1	1.2588 (19)	C12—C13	1.377 (2)
O2—C1	1.2587 (19)	C12—H12	0.9300
N1—C22	1.339 (2)	C13—C14	1.409 (2)
N1—C8	1.380 (2)	C13—H13	0.9300
N1—H1	0.8600	C14—C15	1.467 (2)
N2—C22	1.349 (2)	C15—C16	1.407 (2)
N2—C21	1.379 (2)	C15—C20	1.422 (2)
N2—H2	0.8600	C16—C17	1.378 (2)
C1—C2	1.507 (2)	C16—H16	0.9300
C2—C3	1.384 (2)	C17—C18	1.394 (2)
C2—C7	1.390 (2)	C17—H17	0.9300
C3—C4	1.386 (2)	C18—C19	1.374 (2)
C3—H3	0.9300	C18—H18	0.9300
C4—C5	1.383 (2)	C19—C20	1.407 (2)
C4—H4	0.9300	C19—H19	0.9300
C5—C6	1.382 (2)	C20—C21	1.429 (2)
C5—H5	0.9300	C22—C23	1.461 (2)
C6—C7	1.386 (2)	C23—C24	1.396 (2)
C6—H6	0.9300	C23—C28	1.398 (2)
C7—H7	0.9300	C24—C25	1.382 (2)
C8—C21	1.369 (2)	C24—H24	0.9300
C8—C9	1.430 (2)	C25—C26	1.382 (2)
C9—C10	1.408 (2)	C25—H25	0.9300
C9—C14	1.417 (2)	C26—C27	1.389 (2)
C10—C11	1.376 (2)	C26—H26	0.9300
C10—H10	0.9300	C27—C28	1.381 (2)
C11—C12	1.395 (2)	C27—H27	0.9300
C11—H11	0.9300	C28—H28	0.9300
C22—N1—C8	108.53 (13)	C13—C14—C9	117.21 (15)
C22—N1—H1	125.7	C13—C14—C15	122.08 (15)
C8—N1—H1	125.7	C9—C14—C15	120.70 (14)
C22—N2—C21	108.28 (13)	C16—C15—C20	116.92 (15)
C22—N2—H2	125.9	C16—C15—C14	122.22 (15)
C21—N2—H2	125.9	C20—C15—C14	120.86 (14)
O2—C1—O1	126.11 (15)	C17—C16—C15	121.50 (16)
O2—C1—C2	117.05 (14)	C17—C16—H16	119.3
O1—C1—C2	116.84 (14)	C15—C16—H16	119.3
C3—C2—C7	119.04 (14)	C16—C17—C18	120.82 (16)
C3—C2—C1	119.87 (14)	C16—C17—H17	119.6
C7—C2—C1	121.09 (14)	C18—C17—H17	119.6
C2—C3—C4	121.02 (15)	C19—C18—C17	119.72 (16)
C2—C3—H3	119.5	C19—C18—H18	120.1
C4—C3—H3	119.5	C17—C18—H18	120.1

C5—C4—C3	119.58 (16)	C18—C19—C20	120.15 (16)
C5—C4—H4	120.2	C18—C19—H19	119.9
C3—C4—H4	120.2	C20—C19—H19	119.9
C6—C5—C4	119.83 (15)	C19—C20—C15	120.88 (15)
C6—C5—H5	120.1	C19—C20—C21	122.89 (15)
C4—C5—H5	120.1	C15—C20—C21	116.23 (14)
C5—C6—C7	120.51 (15)	C8—C21—N2	107.21 (14)
C5—C6—H6	119.7	C8—C21—C20	122.93 (14)
C7—C6—H6	119.7	N2—C21—C20	129.85 (14)
C6—C7—C2	119.97 (15)	N1—C22—N2	108.77 (14)
C6—C7—H7	120.0	N1—C22—C23	126.05 (14)
C2—C7—H7	120.0	N2—C22—C23	125.15 (14)
C21—C8—N1	107.20 (13)	C24—C23—C28	119.31 (15)
C21—C8—C9	122.75 (15)	C24—C23—C22	119.99 (14)
N1—C8—C9	130.06 (14)	C28—C23—C22	120.69 (14)
C10—C9—C14	120.94 (15)	C25—C24—C23	119.90 (16)
C10—C9—C8	122.55 (15)	C25—C24—H24	120.0
C14—C9—C8	116.51 (14)	C23—C24—H24	120.0
C11—C10—C9	119.71 (16)	C26—C25—C24	120.80 (16)
C11—C10—H10	120.1	C26—C25—H25	119.6
C9—C10—H10	120.1	C24—C25—H25	119.6
C10—C11—C12	120.25 (16)	C25—C26—C27	119.43 (16)
C10—C11—H11	119.9	C25—C26—H26	120.3
C12—C11—H11	119.9	C27—C26—H26	120.3
C13—C12—C11	120.41 (16)	C28—C27—C26	120.56 (16)
C13—C12—H12	119.8	C28—C27—H27	119.7
C11—C12—H12	119.8	C26—C27—H27	119.7
C12—C13—C14	121.48 (16)	C27—C28—C23	119.98 (16)
C12—C13—H13	119.3	C27—C28—H28	120.0
C14—C13—H13	119.3	C23—C28—H28	120.0

O2—C1—C2—C3	−6.4 (2)	C15—C16—C17—C18	1.1 (2)
O1—C1—C2—C3	172.81 (15)	C16—C17—C18—C19	−0.3 (2)
O2—C1—C2—C7	174.49 (15)	C17—C18—C19—C20	−0.7 (2)
O1—C1—C2—C7	−6.2 (2)	C18—C19—C20—C15	1.0 (2)
C7—C2—C3—C4	2.3 (3)	C18—C19—C20—C21	−178.48 (15)
C1—C2—C3—C4	−176.81 (16)	C16—C15—C20—C19	−0.2 (2)
C2—C3—C4—C5	−1.0 (3)	C14—C15—C20—C19	−179.56 (14)
C3—C4—C5—C6	−1.2 (3)	C16—C15—C20—C21	179.29 (13)
C4—C5—C6—C7	2.0 (3)	C14—C15—C20—C21	−0.1 (2)
C5—C6—C7—C2	−0.7 (2)	N1—C8—C21—N2	−0.15 (16)
C3—C2—C7—C6	−1.4 (2)	C9—C8—C21—N2	179.75 (13)
C1—C2—C7—C6	177.64 (14)	N1—C8—C21—C20	178.83 (13)
C22—N1—C8—C21	−0.49 (16)	C9—C8—C21—C20	−1.3 (2)
C22—N1—C8—C9	179.62 (15)	C22—N2—C21—C8	0.74 (16)
C21—C8—C9—C10	−178.91 (14)	C22—N2—C21—C20	−178.15 (15)
N1—C8—C9—C10	1.0 (2)	C19—C20—C21—C8	−179.40 (15)
C21—C8—C9—C14	0.3 (2)	C15—C20—C21—C8	1.1 (2)

N1—C8—C9—C14	−179.82 (14)	C19—C20—C21—N2	−0.7 (2)
C14—C9—C10—C11	−1.0 (2)	C15—C20—C21—N2	179.84 (14)
C8—C9—C10—C11	178.22 (14)	C8—N1—C22—N2	0.96 (16)
C9—C10—C11—C12	0.3 (2)	C8—N1—C22—C23	−176.97 (14)
C10—C11—C12—C13	0.6 (2)	C21—N2—C22—N1	−1.05 (16)
C11—C12—C13—C14	−0.8 (2)	C21—N2—C22—C23	176.90 (14)
C12—C13—C14—C9	0.2 (2)	N1—C22—C23—C24	175.89 (14)
C12—C13—C14—C15	−179.05 (15)	N2—C22—C23—C24	−1.7 (2)
C10—C9—C14—C13	0.7 (2)	N1—C22—C23—C28	−3.0 (2)
C8—C9—C14—C13	−178.51 (13)	N2—C22—C23—C28	179.44 (14)
C10—C9—C14—C15	179.95 (14)	C28—C23—C24—C25	−1.2 (2)
C8—C9—C14—C15	0.7 (2)	C22—C23—C24—C25	179.97 (14)
C13—C14—C15—C16	−1.0 (2)	C23—C24—C25—C26	−0.1 (2)
C9—C14—C15—C16	179.84 (14)	C24—C25—C26—C27	1.0 (2)
C13—C14—C15—C20	178.35 (14)	C25—C26—C27—C28	−0.6 (2)
C9—C14—C15—C20	−0.8 (2)	C26—C27—C28—C23	−0.7 (2)
C20—C15—C16—C17	−0.8 (2)	C24—C23—C28—C27	1.5 (2)
C14—C15—C16—C17	178.53 (15)	C22—C23—C28—C27	−179.60 (14)

Hydrogen-bond geometry (Å, º)

Cg4 is the centroid of the C15–C20 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.77	2.6159 (17)	168
N2—H2···O2^{i}	0.86	1.83	2.6523 (16)	158
C7—H7···*Cg*4^{ii}	0.93	2.79	3.585 (2)	145
C10—H10···O1	0.93	2.40	3.265 (2)	155
C19—H19···O2^{i}	0.93	2.54	3.372 (2)	150
C24—H24···O2^{i}	0.93	2.50	3.343 (2)	152
C28—H28···O1	0.93	2.48	3.365 (2)	159

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