

STRUCTURAL
CHEMISTRY

ISSN 2053-2296

Co-operative halogen bonds and nonconventional $sp\text{-C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds in 1:1 cocrystals formed between diethynylpyridines and *N*-halosuccinimides

Eric Bosch^{a*} and Nathan P. Bowling^b

Received 25 May 2022

Accepted 27 June 2022

Edited by A. Lemmerer, University of the Witwatersrand, South Africa

Keywords: halogen bonding; $sp\text{-C}\cdots\text{H}\cdots\text{O}$ hydrogen bonding; crystal structure; nonconventional hydrogen bonding; diethynylpyridine; halosuccinimide; Sonogashira coupling.

CCDC references: 2170323; 2170322; 2170321

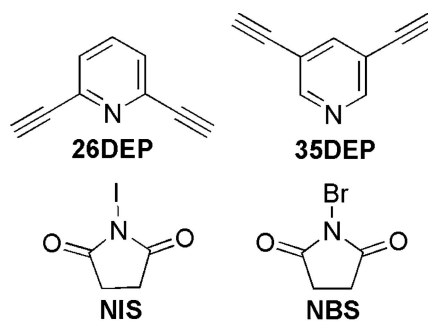
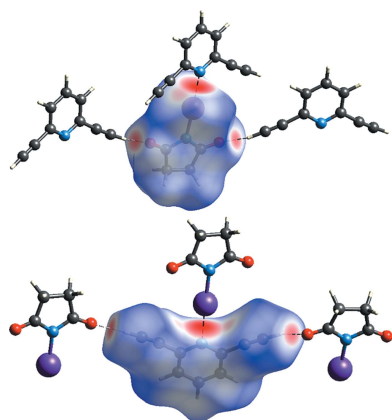
Supporting information: this article has supporting information at journals.iucr.org/c

^aDepartment of Chemistry and Biochemistry, Missouri State University, 901 South National Avenue, Springfield, Missouri 6589, USA, and ^bDepartment of Chemistry, University of Wisconsin–Stevens Point, 2101 Fourth Avenue, Stevens Point, WI 54481, USA. *Correspondence e-mail: ericbosch@missouristate.edu

The rapid evaporation of 1:1 solutions of diethynylpyridines and *N*-halosuccinimides, that react together to form haloalkynes, led to the isolation of unreacted 1:1 cocrystals of the two components. The 1:1 cocrystal formed between 2,6-diethynylpyridine and *N*-iodosuccinimide ($\text{C}_4\text{H}_4\text{INO}_2\cdot\text{C}_9\text{H}_5\text{N}$) contains an *N*-iodosuccinimide–pyridine $\text{I}\cdots\text{N}$ halogen bond and two terminal alkyne–succinimide carbonyl $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. The three-dimensional extended structure features interwoven double-stranded supramolecular polymers that are interconnected through halogen bonds. The cocrystal formed between 3,5-diethynylpyridine and *N*-iodosuccinimide ($\text{C}_4\text{H}_4\text{INO}_2\cdot\text{C}_9\text{H}_5\text{N}$) also features an $\text{I}\cdots\text{N}$ halogen bond and two $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. However, the components form essentially planar double-stranded one-dimensional zigzag supramolecular polymers. The cocrystal formed between 3,5-diethynylpyridine and *N*-bromosuccinimide ($\text{C}_4\text{H}_4\text{BrNO}_2\cdot\text{C}_9\text{H}_5\text{N}$) is isomorphous to the cocrystal formed between 3,5-diethynylpyridine and *N*-iodosuccinimide, with a $\text{Br}\cdots\text{N}$ halogen bond instead of an $\text{I}\cdots\text{N}$ halogen bond.

1. Introduction

Halogen bonding is widely recognized as a functional tool in molecular recognition, supramolecular chemistry, and crystal engineering (Metrangolo & Resnati, 2008; Costa, 2017). Fundamental studies comparing the variation in halogen-bond strength for a variety of halogen-bond donors have established that iodoalkynes are versatile and strong halogen-bond donors (Aakeröy *et al.*, 2015; Perkins *et al.*, 2012; Goroff *et al.*, 2005). Traditional methods for the formation of iodoalkynes involved the reaction of metal acetylides with iodine (Jager & Viehe, 1977), while amine bases, including morpholine and *N,N*-dimethylaminopyridine, have also been used along with iodine



Scheme 1

(Southwick & Kirchner, 1962; Meng *et al.*, 2008). Hypervalent iodine sources have also been used, as have oxidants, as co-

Table 1

Experimental details.

For all structures: monoclinic, $P2_1/n$, $Z = 4$. Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker APEX-I CCD diffractometer. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2014). Refinement was on 171 parameters with 2 restraints. H atoms were treated by a mixture of independent and constrained refinement.

	26DEP·NIS	35DEP·NIS	35DEP·NBS
Crystal data			
Chemical formula	$C_4H_4INO_2 \cdot C_9H_5N$	$C_4H_4INO_2 \cdot C_9H_5N$	$C_4H_4BrNO_2 \cdot C_9H_5N$
M_r	352.12	352.12	305.13
a, b, c (Å)	9.4503 (8), 12.7805 (11), 10.9605 (9)	10.4088 (9), 5.3200 (4), 23.5462 (19)	10.2264 (9), 5.3123 (5), 23.281 (2)
β (°)	100.687 (1)	91.606 (1)	92.048 (1)
V (Å ³)	1300.84 (19)	1303.35 (18)	1264.0 (2)
μ (mm ⁻¹)	2.46	2.45	3.25
Crystal size (mm)	0.22 × 0.21 × 0.13	0.20 × 0.20 × 0.02	0.40 × 0.20 × 0.10
Data collection			
T_{min}, T_{max}	0.685, 0.746	0.572, 0.746	0.597, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15683, 2935, 2659	15299, 2931, 2463	13338, 2869, 2462
R_{int}	0.042	0.044	0.036
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.646	0.647	0.649
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.055, 1.05	0.022, 0.046, 1.02	0.025, 0.064, 1.06
No. of reflections	2935	2931	2869
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.68, -0.39	0.51, -0.56	0.52, -0.48

Computer programs: SMART (Bruker, 2014), SAINT (Bruker, 2014), SHELXT2018 (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b) and X-SEED (Barbour, 2020).

reactants (Liu *et al.* 2017). Amongst the milder methods reported, several have focused on the application of *N*-iodosuccinimide in acetic acid (Yao *et al.*, 2020a), with γ -alumina (Yao *et al.*, 2020b), and in acetone with silver nitrate as catalyst (Hofmeister *et al.*, 1984). Herein we report the unexpected isolation and characterization of the unreacted 1:1 cocrystals formed on rapid evaporation of mixtures of the diethynylpyridines 2,6-diethynylpyridine (**26DEP**) and 3,5-diethynylpyridine (**35DEP**), and the *N*-halosuccinimides *N*-bromosuccinimide (**NBS**) and *N*-iodosuccinimide (**NIS**) in acetone (Scheme 1).

2. Experimental

2.1. Synthesis of diethynylpyridines

The diethynylpyridines were formed by palladium-catalyzed Sonogashira coupling of the corresponding dibromopyridine with trimethylsilylacetylene, followed by base-catalyzed deprotection. The spectral data are consistent with those reported previously for 2,6-diethynylpyridine (Dana *et al.*, 2002) and 3,5-diethynylpyridine (Bosch & Barnes, 2000).

2.2. Preparation of cocrystals

Equimolar amounts of the *N*-halosuccinimide and the corresponding diethynylpyridine were weighed out and placed at the center of a watch glass. Acetone was added dropwise and the mixture swirled with a spatula until a clear solution was obtained. The watch glass was covered to block light, as **NIS** and **NBS** are light sensitive, and the solvent allowed to evaporate over the course of several hours, resulting in the formation of small crystals suitable for X-ray analysis of each of **26DEP·NIS**, **35DEP·NIS**, and **35DEP·NBS**. Our efforts to

form the cocrystal **26DEP·NBS** under similar conditions were unsuccessful.

2.3. X-ray structure determination

Aromatic and aliphatic H atoms were located in difference maps, placed in idealized positions, and refined with a riding model. Alkynyl protons located in the difference maps were refined with a distance restraint of 0.95 (2) Å. Crystallographic details are collected in Table 1.

3. Results and discussion

When planning the preparation of bis(iodoalkynyl)pyridines for an as-yet unpublished project, we chose the reaction of terminal alkynes with *N*-iodosuccinimide catalysed by silver(I) nitrate in acetone (Hofmeister *et al.*, 1984). While formulating exact reaction conditions for the reaction of 2,6-diethynylpyridine (**26DEP**) and *N*-iodosuccinimide (**NIS**), we were surprised to observe some colorless crystalline material on evaporation of an incomplete reaction. X-ray analysis revealed this solid to be the 1:1 cocrystal **26DEP·NIS**. This cocrystal was then formed independently by evaporation of the solvent from a 1:1 mixture of the components in acetone on a watch glass in the dark. While the formation of this cocrystal was not expected, the formation of pyridyl cocrystals with *N*-iodosuccinimide has been reported previously (Makhotkina *et al.*, 2015).

The cocrystal **26DEP·NIS** crystallized in the monoclinic space group $P2_1/n$. The asymmetric unit has one molecule of each component, as shown in Fig. 1, with a halogen bond from **NIS** to the pyridine N atom, with an I1...N1 separation of

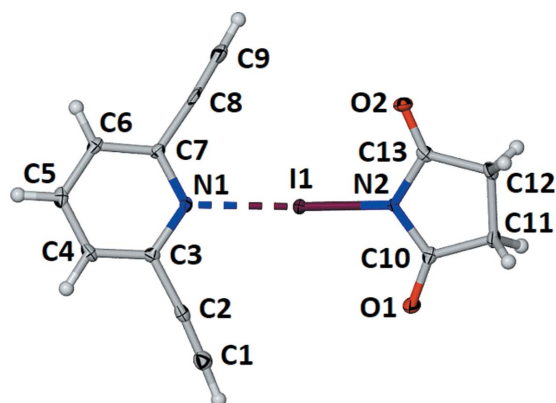


Figure 1

The labeled asymmetric unit of **26DEP·NIS**. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms, while H atoms are shown as spheres of arbitrary size. The halogen bond is shown as a dashed line

2.540 (2) Å and a near linear N2—I1···N1 angle of 177.43 (8)°.

The halogen-bond separation is short at 72% of the sum of the van der Waals radii (Bondi, 1964). It should however be noted that this I···N separation is slightly longer than the 2.43 Å I···N separation in the cocrystal formed between **NIS** and pyridine and the 2.407 Å I···N separation in the cocrystal formed with the strong base 4-(dimethylamino)pyridine (Makhotkina *et al.*, 2015). The three-dimensional structure is complex. First, the pyridine and succinimide rings are twisted along the N1—I1 bond, with an interplanar angle of 21.34 (6)°. The flanking alkynyl H atoms have close contacts to succinimide O atoms of two separate **NIS** molecules. The shorter, more linear, *sp*-C—H hydrogen bond has an H1···O2ⁱ separation of 2.22 (2) Å, 82% of the sum of the van der Waals radii, with a C1—H1···O2ⁱ angle of 171 (2)° [symmetry code: (i) $x + 1, y, z$]. Proton H9 has an H9···O1ⁱⁱ separation of 2.30 (2) Å, 82% of the sum of the van der Waals radii, with a C9—H9···O1ⁱⁱ angle of 150.0 (3)° [symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$]. It is noteworthy that to accommodate these interactions the alkyne groups are bowed and atoms C1 and

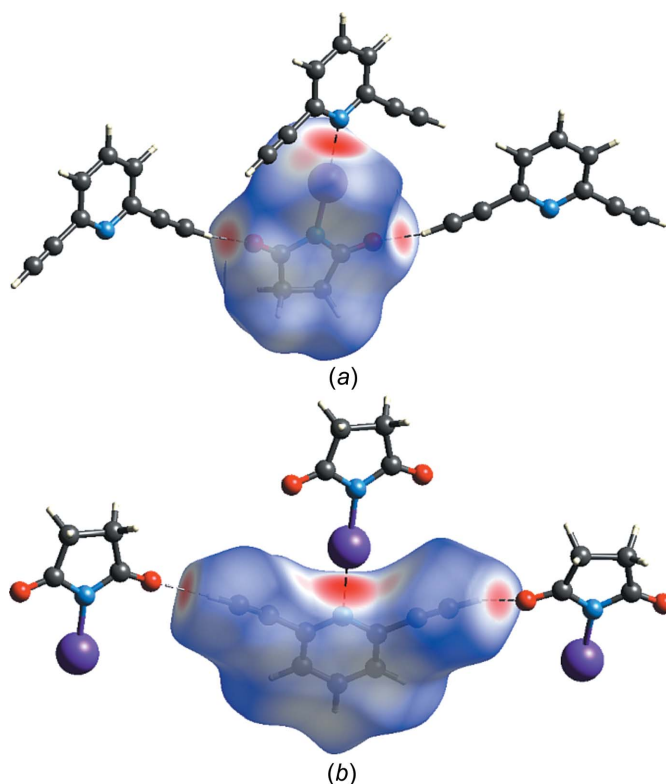


Figure 2

(a) Hirshfeld surface of cocrystal **26DEP·NIS** mapped over d_{norm} for **NIS**, showing the I···N halogen bonds and C—H···O interactions as dashed lines. (b) Complementary Hirshfeld surface of cocrystal **26DEP·NIS** mapped over d_{norm} for **26DEP**.

C9 lie above the plane defined by the pyridyl atoms by 0.274 (6) and 0.171 (6) Å, respectively. These close contacts are well visualized using Hirshfeld surface analysis (Spackman *et al.*, 2021) individually for each of the two components, as shown in Fig. 2, where the red areas denote contacts shorter than the sum of the van der Waals radii.

The C—H···O and I···N interactions lead to a complex three-dimensional structure, shown partially in Fig. 3, that

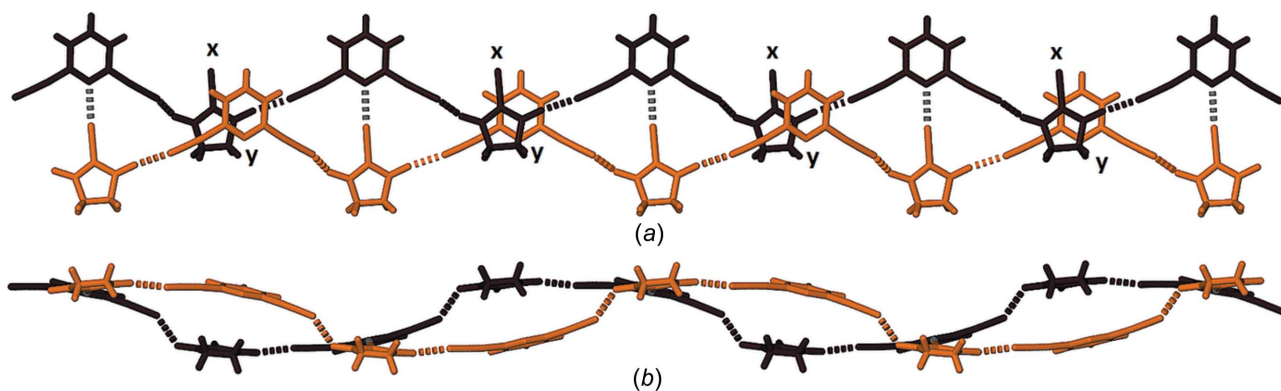


Figure 3

(a) View along the *b* axis of two interwoven strands (shown in different colors) of C—H···O-connected molecules of the cocrystal **26DEP·NIS**. Adjacent molecules in each strand are connected through C—H···O interactions, which are shown as dashed lines. Halogen bonds are shown as grey dashed lines. (b) An orthogonal view of the same interwoven strands.

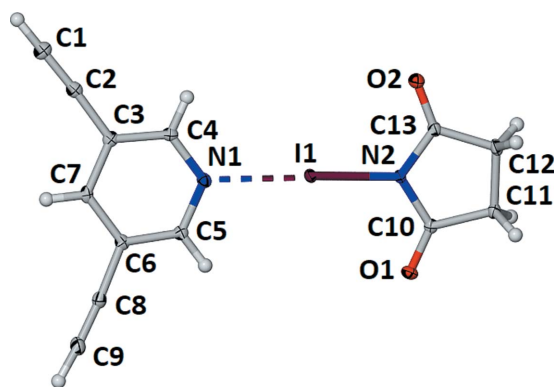


Figure 4

The labeled asymmetric unit of **35DEP·NIS**. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms, while H atoms are shown as spheres of arbitrary size. The halogen bond is shown as a dashed line.

highlights an interwoven double strand of C—H...O-connected molecules that are cross connected through halogen bonds. These interwoven strands are connected to

other interwoven double strands through halogen bonds to outward facing I and pyridine atoms labeled as **x** and **y**, respectively, in Fig. 3. There is a unique close-stacked pair of **NIS** and **26DEP** molecules, with a centroid-to-centroid distance of 3.7513 (16) Å.

Inspired by this serendipitous structure, we attempted to form similar cocrystals between other combinations of diethynylpyridines and *N*-halosuccinimides. Thus, rapid evaporation of acetone from a 1:1 mixture of **NIS** and 3,5-diethynylpyridine in the dark yielded the cocrystal **35DEP·NIS**, that also crystallized in the monoclinic space group $P2_1/n$, with one molecule of each component in the asymmetric unit (Fig. 4).

The halogen bond from **NIS** to the pyridine N atom has an I...N separation of 2.498 (2) Å and an N2—I1...N1 angle of 176.71 (8)°. The halogen-bond distance is slightly shorter than that in cocrystal **26DEP·NIS** at 71% of the sum of the van der Waals radii, and the pyridine and succinimide rings are less twisted along the N—I bond, with an interplanar angle of 11.35 (18)°. The flanking alkynyl H atoms also have close contacts to succinimide O atoms. The proton H1 has an H1...O2ⁱⁱⁱ separation of 2.22 (2) Å, 82% of the sum of the van

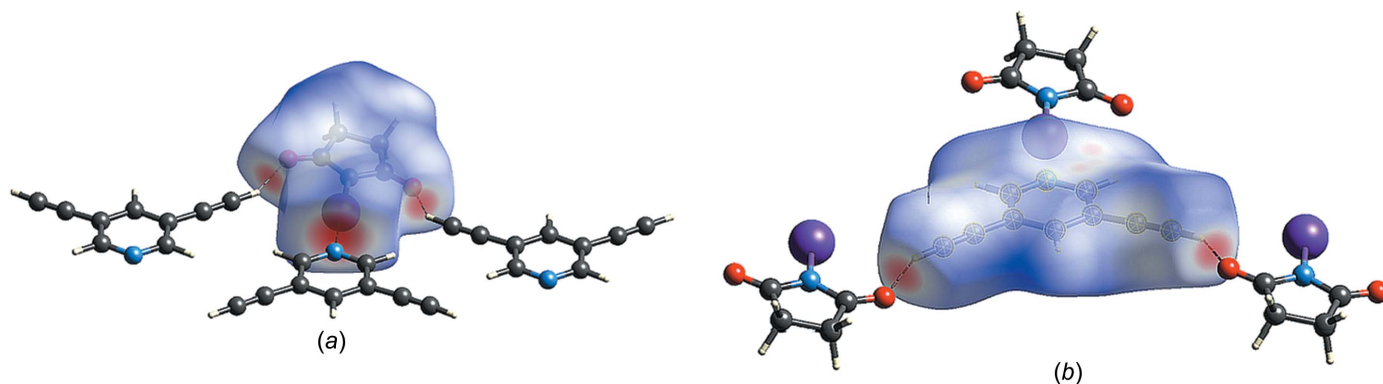


Figure 5

(a) Hirshfeld surface of cocrystal **35DEP·NIS** mapped over d_{norm} on **NIS**, where the I...N halogen bonds and C—H...O interactions are shown as dashed lines. (b) Hirshfeld surface of cocrystal **35DEP·NIS** mapped over d_{norm} on **35DEP**.

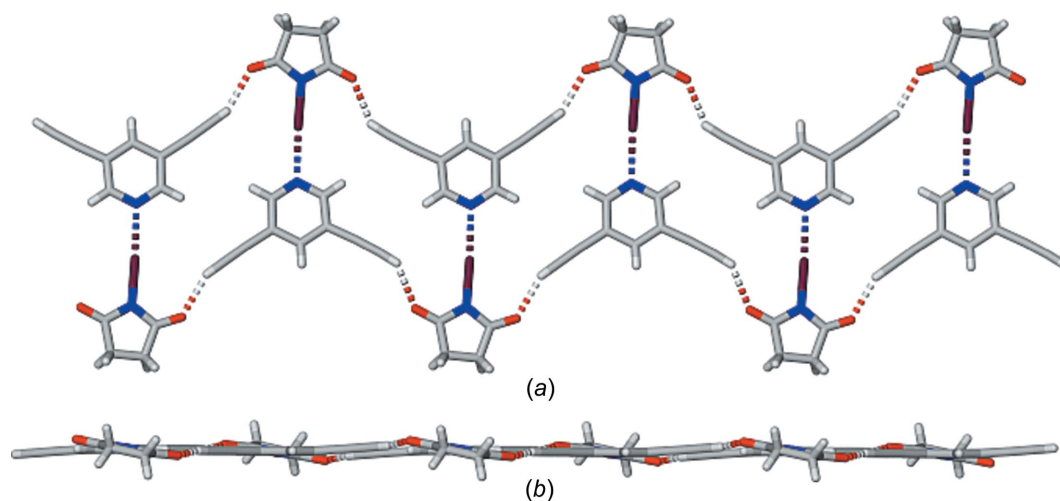


Figure 6

(a) Double-stranded zigzag supramolecular polymer within the structure of **35DEP·NIS**. Halogen bonds and hydrogen bonds are shown as dashed lines. (b) An orthogonal view of the same zigzag polymer.

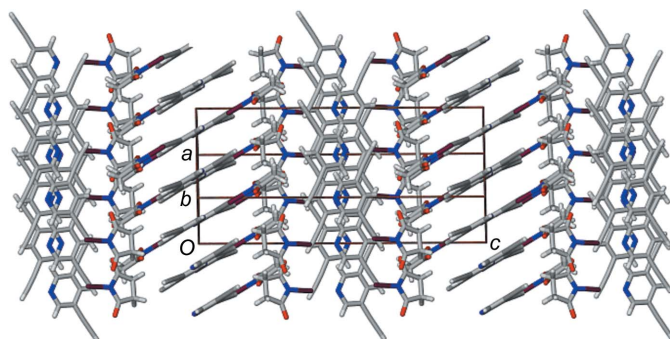


Figure 7
The three-dimensional packing within the structure of **35DEP·NIS**.

der Waals radii, with a $C1-H1\cdots O2^{iii}$ angle of $156(2)^\circ$ [symmetry code: (iii) $-x+1, -y, -z+1$]. Similarly, proton H9 has an $H9\cdots O1^{iv}$ separation of $2.27(2)$ Å, 82% of the sum of the van der Waals radii, with a $C9-H9\cdots O1^{ii}$ angle of $145(2)^\circ$ [symmetry code: (iv) $-x+2, -y+2, -z+1$]. While the location of the alkynes on pyridine **35DEP** is different to pyridine **26DEP**, the close contacts on the Hirshfeld surface of each component of cocrystal **35DEP·NIS** are also dominated by the $I\cdots N$ interaction and the $C-H\cdots O$ interactions, as shown in Fig. 5.

The orientation of the dialkynyl moieties in **35DEP** facilitates the formation of discrete infinite planar double-stranded zigzag supramolecular polymers, shown in Fig. 6, in contrast to the interwoven strands in the structure of **26DEP·NIS**. Within the three-dimensional crystal, these double strands are offset slip stacked, while adjacent double strands have a herringbone type of arrangement, as shown in Fig. 7.

Similar rapid evaporation of acetone from a 1:1 mixture of **NBS** and 3,5-diethynylpyridine provided the cocrystal **35DEP·NBS**. The two cocrystals with **35DEP** are isomorphous and cocrystal **35DEP·NBS** also has one molecule of each component in the asymmetric unit, as shown in Fig. 8.

The halogen bond to the pyridine N atom has a $Br\cdots N$ separation of $2.4704(17)$ Å, 71% of the sum of the van der

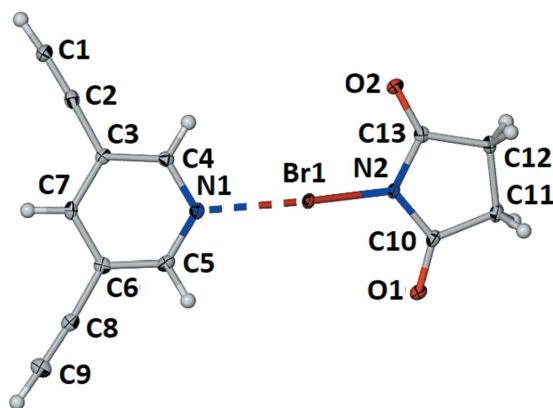


Figure 8
The labeled asymmetric unit of **35DEP·NBS**. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms, while H atoms are shown as spheres of arbitrary size. The halogen bond is shown as a dashed line.

Waals radii, and an $N2-Br1\cdots N1$ angle of $176.35(7)^\circ$. The pyridine and succinimide rings have a similar slight twist, with an interplanar angle of $11.43(14)^\circ$. The alkynyl H atoms have close contacts to succinimide O atoms. Proton H1 has an $H\cdots O$ separation of $2.25(2)$ Å, with a $C-H\cdots O$ angle of $155.1(18)^\circ$, while proton H9 has an $H\cdots O$ separation of $2.30(2)$ Å, with a $C-H\cdots O$ angle of $142(2)^\circ$. The halogen bond coupled with the two $sp-C-H\cdots O$ interactions leads to the formation of a similar double-stranded linear supramolecular polymer.

4. Conclusion

We have described here the isolation and characterization of 1:1 cocrystals formed between two components that undergo reaction in the same solvent. While this was unintentional, the cocrystals provide an example of the combination of a halogen-bond donor with two hydrogen-bond acceptor sites, and a halogen-bond acceptor with two hydrogen-bond donor sites. Indeed, the observed halogen bonds between the two components are complemented by two $sp-C-H\cdots O$ hydrogen bonds in all three structures. These unexpected cocrystals complement our earlier isolation of cocrystals formed between the product iodoalkyne 1,2-bis(iodoethynyl)benzene and the base *N,N*-dimethylaminopyridine, used in the preparation of the iodoalkyne (Bosch, 2014). The results highlight the potential for the deliberate design of supramolecular systems with co-operative nonconventional hydrogen bonding and halogen bonding.

Funding information

Funding for this research was provided by: National Science Foundation, Directorate for Mathematical and Physical Sciences (grant No. CHE-1903593).

References

- Aakeröy, C. B., Wijethunga, T. K., Desper, J. & Đaković, M. (2015). *Cryst. Growth Des.* **15**, 3853–3861.
- Barbour, L. J. (2020). *J. Appl. Cryst.* **53**, 1141–1146.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bosch, E. (2014). *Cryst. Growth Des.* **14**, 126–130.
- Bosch, E. & Barnes, C. L. (2000). *Organometallics*, **19**, 5522–5524.
- Bruker (2014). *SMART, SAINT, and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Costa, P. J. (2017). *Phys. Sci. Rev.* **2**, 2010136.
- Dana, B. H., Robinson, B. H. & Simpson, J. (2002). *J. Organomet. Chem.* **648**, 251–269.
- Goroff, N. S., Curtis, S. M., Webb, J. A., Fowler, F. W. & Lauher, J. W. (2005). *Org. Lett.* **7**, 1891–1893.
- Hofmeister, H., Annen, K., Laurent, H. & Wiechert, R. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 727–729.
- Jager, V. & Viehe, H. G. (1977). *Houben-Weyl Methoden der Organische Chemie*, Vol. 2, p. 601. Stuttgart: George Thieme Verlag.
- Liu, Y., Huang, D., Huang, J. & Maruoka, K. (2017). *J. Org. Chem.* **82**, 11865–11871.
- Makhotkina, O., Lieffrig, J., Jeannin, O., Fourmigué, M., Aubert, E. & Espinosa, E. (2015). *Cryst. Growth Des.* **15**, 3464–3473.
- Meng, L. G., Cai, P. J., Guo, Q. X. & Xue, S. (2008). *Synth. Commun.* **38**, 1257.

- Metrangolo, P. & Resnati, G. (2008). In *Halogen Bonding: Fundamentals and Applications*. Berlin, Heidelberg: Springer.
- Perkins, C., Libri, S., Adams, H. & Brammer, L. (2012). *CrystEngComm*, **14**, 3033–3038.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Southwick, P. L. & Kirchner, J. R. (1962). *J. Org. Chem.* **27**, 3305–3308.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Yao, M., Zhang, J., Yang, S., Liu, E. & Xiong, H. (2020a). *Synlett*, **31**, 1102–1106.
- Yao, M., Zhang, J., Yang, S., Xiong, H., Li, L., Liu, E. & Shi, H. (2020b). *RSC Adv.* **10**, 3946–3950.

supporting information

Acta Cryst. (2022). C78, 424–429 [https://doi.org/10.1107/S2053229622006635]

Co-operative halogen bonds and nonconventional *sp*-C—H $\cdots$ O hydrogen bonds in 1:1 cocrystals formed between diethynylpyridines and *N*-halosuccinimides

Eric Bosch and Nathan P. Bowling

Computing details

For all structures, data collection: *SMART* (Bruker, 2014); cell refinement: *SMART* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXT2018* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *X-SEED* (Barbour, 2020); software used to prepare material for publication: *X-SEED* (Barbour, 2020).

2,6-Diethynylpyridine–*N*-iodosuccinimide (1/1) (26DEP_u008226NIS)

Crystal data

C₄H₄INO₂·C₉H₅N
 $M_r = 352.12$
 Monoclinic, $P2_1/n$
 $a = 9.4503$ (8) Å
 $b = 12.7805$ (11) Å
 $c = 10.9605$ (9) Å
 $\beta = 100.687$ (1)°
 $V = 1300.84$ (19) Å³
 $Z = 4$

$F(000) = 680$
 $D_x = 1.798$ Mg m^{−3}
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4626 reflections
 $\theta = 2.6$ – 27.0 °
 $\mu = 2.46$ mm^{−1}
 $T = 100$ K
 Cut from cube, colourless
 $0.22 \times 0.21 \times 0.13$ mm

Data collection

Bruker APEX-I CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 8.3660 pixels mm^{−1}
 ϕ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2014)
 $T_{\min} = 0.685$, $T_{\max} = 0.746$

15683 measured reflections
 2935 independent reflections
 2659 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 27.3$ °, $\theta_{\min} = 2.5$ °
 $h = -12 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.055$
 $S = 1.05$
 2935 reflections
 171 parameters
 2 restraints
 Primary atom site location: dual

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 1.2626P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.68$ e Å^{−3}
 $\Delta\rho_{\min} = -0.39$ e Å^{−3}

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. For each complex, a single-crystal was mounted on a Kryoloop using viscous hydrocarbon oil. Data were collected using a Bruker *APEXI* CCD diffractometer equipped with Mo *K* α radiation with $\kappa = 0.71073$ Å. Data collection at 100 K was facilitated by use of a Kryoflex system with an accuracy of ± 1 K. Initial data processing was carried out using the *APEX2* software suite (Bruker, 2016). The structures were solved by dual methods using SHELXT (Sheldrick, 2015a) and refined against F^2 using SHELXL (Sheldrick, 2015b) using the program *X-SEED* as a graphical interface (Barbour, 2020) and for the generation of graphics.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
II	0.47984 (2)	0.62904 (2)	0.27102 (2)	0.01364 (6)
O1	0.5343 (2)	0.62403 (17)	−0.01867 (19)	0.0230 (5)
N1	0.6258 (3)	0.64370 (18)	0.4895 (2)	0.0150 (5)
C1	0.9150 (4)	0.6114 (2)	0.3373 (3)	0.0240 (7)
O2	0.1318 (2)	0.59239 (16)	0.15173 (19)	0.0202 (4)
N2	0.3523 (2)	0.61269 (18)	0.0932 (2)	0.0140 (5)
C2	0.8452 (3)	0.6124 (2)	0.4132 (3)	0.0195 (6)
C3	0.7681 (3)	0.6209 (2)	0.5157 (3)	0.0153 (6)
C4	0.8422 (3)	0.6107 (2)	0.6373 (3)	0.0189 (6)
H4	0.941671	0.593203	0.653462	0.023*
C5	0.7698 (3)	0.6261 (2)	0.7341 (3)	0.0191 (6)
H5	0.818836	0.619484	0.817639	0.023*
C6	0.6261 (3)	0.6512 (2)	0.7085 (3)	0.0172 (6)
H6	0.574839	0.663213	0.774008	0.021*
C7	0.5566 (3)	0.6588 (2)	0.5850 (3)	0.0154 (6)
C8	0.4052 (4)	0.6891 (3)	0.5569 (3)	0.0245 (7)
C9	0.2912 (4)	0.7176 (3)	0.5427 (3)	0.0348 (9)
C10	0.4077 (3)	0.6126 (2)	−0.0148 (3)	0.0160 (6)
C11	0.2866 (3)	0.5959 (2)	−0.1242 (3)	0.0203 (6)
H11A	0.302627	0.531575	−0.170131	0.024*
H11B	0.278095	0.656173	−0.181828	0.024*
C12	0.1517 (3)	0.5855 (2)	−0.0665 (3)	0.0187 (6)
H12A	0.081287	0.641080	−0.097690	0.022*
H12B	0.105560	0.516507	−0.086346	0.022*
C13	0.2045 (3)	0.5967 (2)	0.0719 (3)	0.0157 (6)
H1	0.972 (3)	0.610 (3)	0.276 (2)	0.031 (10)*
H9	0.199 (2)	0.743 (3)	0.532 (3)	0.040 (11)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
II	0.01337 (10)	0.01590 (10)	0.01125 (10)	0.00052 (7)	0.00128 (7)	−0.00083 (7)
O1	0.0172 (11)	0.0352 (13)	0.0175 (11)	−0.0061 (9)	0.0059 (9)	−0.0001 (9)
N1	0.0168 (12)	0.0175 (12)	0.0103 (11)	0.0024 (9)	0.0011 (9)	−0.0009 (9)

C1	0.0223 (16)	0.0255 (16)	0.0234 (17)	0.0002 (13)	0.0017 (13)	−0.0049 (13)
O2	0.0169 (11)	0.0254 (11)	0.0200 (11)	−0.0008 (9)	0.0080 (9)	−0.0024 (9)
N2	0.0108 (11)	0.0203 (12)	0.0105 (11)	−0.0009 (9)	0.0009 (9)	−0.0030 (9)
C2	0.0156 (14)	0.0182 (14)	0.0221 (15)	0.0009 (11)	−0.0029 (12)	−0.0006 (12)
C3	0.0148 (14)	0.0134 (13)	0.0178 (14)	0.0005 (11)	0.0036 (11)	−0.0027 (11)
C4	0.0142 (14)	0.0190 (15)	0.0215 (15)	0.0015 (11)	−0.0022 (12)	−0.0008 (12)
C5	0.0227 (15)	0.0182 (15)	0.0147 (14)	−0.0021 (12)	−0.0010 (12)	0.0028 (11)
C6	0.0209 (15)	0.0182 (14)	0.0133 (14)	−0.0020 (11)	0.0056 (12)	0.0008 (11)
C7	0.0173 (14)	0.0174 (14)	0.0125 (13)	0.0016 (11)	0.0051 (11)	−0.0004 (11)
C8	0.0327 (19)	0.0355 (18)	0.0067 (14)	0.0018 (15)	0.0071 (13)	−0.0009 (12)
C9	0.036 (2)	0.055 (2)	0.0145 (16)	0.0164 (18)	0.0077 (15)	0.0075 (15)
C10	0.0180 (15)	0.0169 (14)	0.0126 (13)	−0.0014 (11)	0.0017 (11)	0.0014 (11)
C11	0.0187 (15)	0.0292 (16)	0.0117 (14)	−0.0037 (12)	−0.0004 (12)	−0.0012 (12)
C12	0.0139 (14)	0.0217 (15)	0.0184 (15)	−0.0012 (11)	−0.0025 (12)	−0.0019 (12)
C13	0.0160 (14)	0.0120 (13)	0.0191 (14)	0.0007 (11)	0.0031 (12)	−0.0022 (11)

Geometric parameters (Å, °)

I1—N2	2.103 (2)	C5—H5	0.9500
O1—C10	1.213 (3)	C6—C7	1.394 (4)
N1—C7	1.347 (3)	C6—H6	0.9500
N1—C3	1.354 (4)	C7—C8	1.459 (4)
C1—C2	1.154 (4)	C8—C9	1.121 (5)
C1—H1	0.936 (18)	C9—H9	0.919 (18)
O2—C13	1.210 (3)	C10—C11	1.512 (4)
N2—C10	1.381 (3)	C11—C12	1.530 (4)
N2—C13	1.387 (3)	C11—H11A	0.9900
C2—C3	1.452 (4)	C11—H11B	0.9900
C3—C4	1.392 (4)	C12—C13	1.514 (4)
C4—C5	1.380 (4)	C12—H12A	0.9900
C4—H4	0.9500	C12—H12B	0.9900
C5—C6	1.372 (4)		
C7—N1—C3	118.2 (2)	C9—C8—C7	174.7 (4)
C2—C1—H1	179 (2)	C8—C9—H9	178 (2)
C10—N2—C13	112.7 (2)	O1—C10—N2	124.3 (3)
C10—N2—I1	123.44 (18)	O1—C10—C11	126.6 (3)
C13—N2—I1	123.83 (18)	N2—C10—C11	109.2 (2)
C1—C2—C3	174.2 (3)	C10—C11—C12	104.5 (2)
N1—C3—C4	121.8 (3)	C10—C11—H11A	110.8
N1—C3—C2	118.3 (2)	C12—C11—H11A	110.8
C4—C3—C2	119.9 (3)	C10—C11—H11B	110.8
C5—C4—C3	119.3 (3)	C12—C11—H11B	110.8
C5—C4—H4	120.3	H11A—C11—H11B	108.9
C3—C4—H4	120.3	C13—C12—C11	105.1 (2)
C6—C5—C4	119.3 (3)	C13—C12—H12A	110.7
C6—C5—H5	120.3	C11—C12—H12A	110.7
C4—C5—H5	120.3	C13—C12—H12B	110.7

C5—C6—C7	119.0 (3)	C11—C12—H12B	110.7
C5—C6—H6	120.5	H12A—C12—H12B	108.8
C7—C6—H6	120.5	O2—C13—N2	125.0 (3)
N1—C7—C6	122.3 (3)	O2—C13—C12	126.5 (3)
N1—C7—C8	118.2 (2)	N2—C13—C12	108.5 (2)
C6—C7—C8	119.4 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C6—H6 $\cdots$ O1 ⁱ	0.95	2.43	3.283 (3)	150
C11—H11A $\cdots$ I1 ⁱⁱ	0.99	3.24	4.128 (3)	150
C12—H12B $\cdots$ O2 ⁱⁱⁱ	0.99	2.62	3.506 (3)	148

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) $-x+1$, $-y+1$, $-z$; (iii) $-x$, $-y+1$, $-z$.**3,5-Diethynylpyridine-*N*-iodosuccinimide (1/1) (35DEP_u008226NIS)***Crystal data*C₄H₄INO₂·C₉H₅N*M_r* = 352.12Monoclinic, *P*2₁/*n**a* = 10.4088 (9) Å*b* = 5.3200 (4) Å*c* = 23.5462 (19) Å β = 91.606 (1)°*V* = 1303.35 (18) Å³*Z* = 4*F*(000) = 680*D_x* = 1.794 Mg m⁻³Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 4210 reflections

 θ = 3.2–27.2° μ = 2.45 mm⁻¹*T* = 100 K

Cut block, colourless

0.20 × 0.20 × 0.02 mm

Data collection

Bruker APEX-I CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3660 pixels mm⁻¹ ϕ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

T_{min} = 0.572, *T_{max}* = 0.746

15299 measured reflections

2931 independent reflections

2463 reflections with *I* > 2σ(*I*)*R_{int}* = 0.044 $\theta_{\max}$ = 27.4°, $\theta_{\min}$ = 1.7°*h* = −13→13*k* = −6→6*l* = −30→30*Refinement*Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.022*wR*(*F*²) = 0.046*S* = 1.02

2931 reflections

171 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0155*P*)² + 1.0427*P*]where *P* = (*F_o*² + 2*F_c*²)/3(Δ/σ)_{max} = 0.001Δρ_{max} = 0.51 e Å⁻³Δρ_{min} = −0.56 e Å⁻³

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. For each complex, a single-crystal was mounted on a Kryoloop using viscous hydrocarbon oil. Data were collected using a Bruker *APEXI* CCD diffractometer equipped with Mo *K* α radiation with $\kappa = 0.71073$ Å. Data collection at 100 K was facilitated by use of a Kryoflex system with an accuracy of ± 1 K. Initial data processing was carried out using the *APEX2* software suite (Bruker, 2016). The structures were solved by dual methods using SHELXT (Sheldrick, 2015a) and refined against F^2 using SHELXL (Sheldrick, 2015b) using the program *X-SEED* as a graphical interface (Barbour, 2020) and for the generation of graphics.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.64053 (2)	0.66847 (3)	0.38633 (2)	0.01271 (6)
O1	0.74212 (18)	1.0953 (3)	0.29605 (8)	0.0186 (4)
O2	0.38818 (18)	0.5912 (4)	0.29871 (8)	0.0216 (4)
N2	0.57353 (19)	0.8234 (4)	0.30937 (8)	0.0130 (4)
N1	0.7240 (2)	0.5084 (4)	0.48004 (8)	0.0144 (5)
C2	0.6748 (2)	0.0158 (5)	0.58877 (11)	0.0161 (6)
C10	0.6389 (2)	1.0113 (5)	0.28076 (10)	0.0131 (5)
C4	0.6758 (2)	0.3118 (5)	0.50765 (11)	0.0148 (5)
H4	0.603413	0.226817	0.491411	0.018*
C11	0.5590 (3)	1.0849 (5)	0.22881 (11)	0.0162 (6)
H11A	0.605320	1.046894	0.193663	0.019*
H11B	0.538554	1.266611	0.229472	0.019*
C6	0.8830 (2)	0.5613 (5)	0.55450 (11)	0.0138 (5)
C5	0.8254 (2)	0.6301 (5)	0.50297 (11)	0.0141 (5)
H5	0.859321	0.769463	0.483115	0.017*
C7	0.8337 (2)	0.3556 (5)	0.58288 (10)	0.0140 (5)
H7	0.871685	0.302664	0.618033	0.017*
C3	0.7278 (3)	0.2267 (5)	0.55945 (11)	0.0144 (5)
C1	0.6360 (3)	−0.1574 (6)	0.61448 (12)	0.0194 (6)
C12	0.4365 (3)	0.9272 (5)	0.23197 (11)	0.0188 (6)
H12A	0.360566	1.036019	0.237203	0.023*
H12B	0.422869	0.826974	0.196884	0.023*
C8	0.9874 (3)	0.7069 (5)	0.57894 (11)	0.0160 (6)
C13	0.4584 (3)	0.7580 (5)	0.28265 (11)	0.0151 (6)
C9	1.0722 (3)	0.8197 (6)	0.60178 (11)	0.0202 (6)
H9	1.139 (2)	0.900 (5)	0.6217 (11)	0.027 (9)*
H1	0.605 (3)	−0.294 (4)	0.6351 (12)	0.028 (9)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01124 (9)	0.01543 (9)	0.01138 (8)	−0.00057 (7)	−0.00118 (6)	0.00115 (7)
O1	0.0176 (10)	0.0197 (10)	0.0181 (10)	−0.0060 (8)	−0.0029 (8)	−0.0008 (8)
O2	0.0192 (10)	0.0248 (11)	0.0205 (10)	−0.0072 (8)	−0.0034 (8)	0.0054 (8)

N2	0.0117 (11)	0.0158 (11)	0.0113 (10)	−0.0017 (9)	−0.0016 (8)	0.0020 (9)
N1	0.0112 (11)	0.0183 (12)	0.0137 (11)	0.0002 (10)	0.0006 (8)	−0.0002 (9)
C2	0.0152 (13)	0.0156 (14)	0.0176 (13)	0.0032 (11)	0.0010 (11)	−0.0034 (11)
C10	0.0153 (13)	0.0121 (13)	0.0119 (12)	0.0019 (11)	0.0008 (10)	−0.0013 (10)
C4	0.0134 (13)	0.0146 (14)	0.0166 (13)	−0.0016 (11)	0.0013 (10)	−0.0012 (11)
C11	0.0192 (14)	0.0148 (13)	0.0144 (13)	−0.0002 (11)	−0.0019 (11)	0.0028 (10)
C6	0.0121 (13)	0.0136 (13)	0.0157 (13)	0.0042 (10)	0.0005 (10)	−0.0017 (10)
C5	0.0127 (13)	0.0149 (14)	0.0148 (13)	0.0005 (11)	0.0023 (10)	−0.0003 (10)
C7	0.0147 (13)	0.0146 (13)	0.0125 (12)	0.0060 (11)	−0.0003 (10)	−0.0010 (10)
C3	0.0155 (14)	0.0127 (13)	0.0151 (13)	0.0032 (10)	0.0035 (10)	−0.0016 (10)
C1	0.0197 (15)	0.0174 (14)	0.0213 (14)	0.0020 (13)	0.0045 (11)	0.0004 (13)
C12	0.0140 (14)	0.0261 (15)	0.0159 (14)	−0.0018 (12)	−0.0036 (11)	0.0057 (11)
C8	0.0178 (14)	0.0155 (15)	0.0148 (13)	0.0026 (11)	0.0002 (11)	0.0005 (10)
C13	0.0141 (13)	0.0182 (13)	0.0129 (13)	0.0000 (11)	−0.0009 (10)	0.0005 (10)
C9	0.0212 (15)	0.0228 (15)	0.0166 (14)	0.0006 (13)	−0.0027 (11)	0.0011 (12)

Geometric parameters (Å, °)

I1—N2	2.092 (2)	C11—H11B	0.9900
O1—C10	1.209 (3)	C6—C5	1.387 (3)
O2—C13	1.217 (3)	C6—C7	1.388 (4)
N2—C13	1.382 (3)	C6—C8	1.441 (4)
N2—C10	1.393 (3)	C5—H5	0.9500
N1—C4	1.337 (3)	C7—C3	1.398 (4)
N1—C5	1.339 (3)	C7—H7	0.9500
C2—C1	1.180 (4)	C1—H1	0.936 (17)
C2—C3	1.436 (4)	C12—C13	1.507 (4)
C10—C11	1.511 (3)	C12—H12A	0.9900
C4—C3	1.396 (3)	C12—H12B	0.9900
C4—H4	0.9500	C8—C9	1.184 (4)
C11—C12	1.531 (4)	C9—H9	0.932 (17)
C11—H11A	0.9900		
C13—N2—C10	112.9 (2)	N1—C5—H5	118.6
C13—N2—I1	123.98 (17)	C6—C5—H5	118.6
C10—N2—I1	123.08 (16)	C6—C7—C3	119.6 (2)
C4—N1—C5	119.0 (2)	C6—C7—H7	120.2
C1—C2—C3	177.1 (3)	C3—C7—H7	120.2
O1—C10—N2	124.3 (2)	C4—C3—C7	117.9 (2)
O1—C10—C11	127.5 (2)	C4—C3—C2	121.9 (2)
N2—C10—C11	108.2 (2)	C7—C3—C2	120.2 (2)
N1—C4—C3	122.5 (2)	C2—C1—H1	179 (2)
N1—C4—H4	118.8	C13—C12—C11	105.0 (2)
C3—C4—H4	118.8	C13—C12—H12A	110.8
C10—C11—C12	105.0 (2)	C11—C12—H12A	110.8
C10—C11—H11A	110.8	C13—C12—H12B	110.8
C12—C11—H11A	110.8	C11—C12—H12B	110.8
C10—C11—H11B	110.8	H12A—C12—H12B	108.8

C12—C11—H11B	110.8	C9—C8—C6	176.3 (3)
H11A—C11—H11B	108.8	O2—C13—N2	124.2 (2)
C5—C6—C7	118.2 (2)	O2—C13—C12	127.1 (2)
C5—C6—C8	120.7 (2)	N2—C13—C12	108.7 (2)
C7—C6—C8	121.1 (2)	C8—C9—H9	176.1 (19)
N1—C5—C6	122.8 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C11—H11A $\cdots$ I1 ⁱ	0.99	3.35	4.219 (3)	147
C11—H11A $\cdots$ O1 ⁱⁱ	0.99	2.89	3.388 (3)	112
C11—H11B $\cdots$ O1 ⁱ	0.99	2.95	3.474 (3)	114
C11—H11B $\cdots$ O2 ⁱⁱⁱ	0.99	2.87	3.646 (3)	136
C12—H12A $\cdots$ O2 ^{iv}	0.99	2.72	3.545 (3)	141

Symmetry codes: (i) $-x+3/2, y+1/2, -z+1/2$; (ii) $-x+3/2, y-1/2, -z+1/2$; (iii) $x, y+1, z$; (iv) $-x+1/2, y+1/2, -z+1/2$.

3,5-Diethynylpyridine-*N*-bromosuccinimide (1/1) (35DEP_u008226NBS)*Crystal data*

C₄H₄BrNO₂·C₉H₅N

M_r = 305.13

Monoclinic, *P*2₁/*n*

a = 10.2264 (9) Å

b = 5.3123 (5) Å

c = 23.281 (2) Å

β = 92.048 (1)°

V = 1264.0 (2) Å³

Z = 4

F(000) = 608

D_x = 1.603 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 4462 reflections

θ = 2.2–27.5°

μ = 3.25 mm⁻¹

T = 100 K

Cut irregular block, colourless

0.40 × 0.20 × 0.10 mm

Data collection

Bruker APEX-I CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3660 pixels mm⁻¹

ϕ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

*T*_{min} = 0.597, *T*_{max} = 0.746

13338 measured reflections

2869 independent reflections

2462 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.036

$\theta_{\max}$ = 27.5°, $\theta_{\min}$ = 2.2°

h = −13→13

k = −6→6

l = −29→29

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.025

wR (*F*²) = 0.064

S = 1.06

2869 reflections

171 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

w = 1/[σ²(*F*_o²) + (0.0348*P*)² + 0.3269*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.52 e Å⁻³

Δρ_{min} = −0.47 e Å⁻³

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. For each complex, a single-crystal was mounted on a Kryoloop using viscous hydrocarbon oil. Data were collected using a Bruker *APEXI* CCD diffractometer equipped with Mo $K\alpha$ radiation with $\kappa = 0.71073$ Å. Data collection at 100 K was facilitated by use of a Kryoflex system with an accuracy of ± 1 K. Initial data processing was carried out using the *APEX2* software suite (Bruker, 2016). The structures were solved by dual methods using SHELXT (Sheldrick, 2015a) and refined against F^2 using SHELXL (Sheldrick, 2015b) using the program *X-SEED* as a graphical interface (Barbour, 2020) and for the generation of graphics.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.63779 (2)	0.67284 (4)	0.37882 (2)	0.01355 (8)
O1	0.74663 (14)	1.0895 (3)	0.29616 (6)	0.0196 (3)
N1	0.71588 (16)	0.5141 (3)	0.47372 (7)	0.0161 (4)
C1	0.6216 (2)	−0.1493 (4)	0.61004 (10)	0.0206 (5)
O2	0.38906 (14)	0.5748 (3)	0.29840 (6)	0.0226 (3)
N2	0.57628 (16)	0.8139 (3)	0.30863 (7)	0.0138 (4)
C2	0.66177 (19)	0.0240 (4)	0.58408 (9)	0.0169 (4)
C3	0.7177 (2)	0.2357 (4)	0.55483 (9)	0.0148 (4)
C4	0.82446 (19)	0.3649 (4)	0.57930 (9)	0.0150 (4)
H4	0.862136	0.313067	0.615272	0.018*
C5	0.87540 (19)	0.5707 (4)	0.55051 (9)	0.0139 (4)
C6	0.8179 (2)	0.6370 (4)	0.49762 (9)	0.0147 (4)
H6	0.852812	0.775993	0.477586	0.018*
C7	0.6661 (2)	0.3190 (4)	0.50171 (9)	0.0173 (4)
H7	0.592777	0.233238	0.484874	0.021*
C8	0.9816 (2)	0.7151 (4)	0.57585 (9)	0.0163 (4)
C9	1.0686 (2)	0.8306 (4)	0.59860 (10)	0.0207 (5)
C10	0.64207 (19)	1.0029 (4)	0.28019 (8)	0.0139 (4)
C11	0.5594 (2)	1.0729 (4)	0.22734 (9)	0.0161 (4)
H11A	0.606463	1.035557	0.191913	0.019*
H11B	0.536973	1.254153	0.227751	0.019*
C12	0.4359 (2)	0.9113 (5)	0.23041 (9)	0.0201 (5)
H12A	0.357762	1.018460	0.235124	0.024*
H12B	0.422955	0.809537	0.195041	0.024*
C13	0.4586 (2)	0.7437 (4)	0.28209 (9)	0.0157 (4)
H9	1.136 (2)	0.910 (5)	0.6179 (11)	0.034 (7)*
H1	0.596 (2)	−0.289 (4)	0.6303 (10)	0.024 (7)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01186 (11)	0.01761 (12)	0.01104 (11)	−0.00031 (8)	−0.00154 (7)	0.00112 (8)
O1	0.0187 (8)	0.0223 (8)	0.0175 (8)	−0.0070 (7)	−0.0036 (6)	0.0002 (6)
N1	0.0145 (8)	0.0193 (9)	0.0144 (8)	0.0006 (7)	−0.0009 (7)	0.0006 (7)

C1	0.0203 (11)	0.0177 (12)	0.0242 (12)	0.0023 (9)	0.0058 (9)	0.0007 (10)
O2	0.0180 (8)	0.0282 (9)	0.0213 (8)	−0.0087 (7)	−0.0045 (6)	0.0048 (7)
N2	0.0119 (8)	0.0181 (9)	0.0112 (8)	−0.0004 (7)	−0.0018 (6)	0.0014 (7)
C2	0.0150 (10)	0.0170 (11)	0.0188 (10)	0.0027 (9)	0.0005 (8)	−0.0039 (9)
C3	0.0138 (10)	0.0136 (10)	0.0173 (10)	0.0025 (8)	0.0033 (8)	−0.0014 (8)
C4	0.0158 (10)	0.0164 (11)	0.0126 (10)	0.0043 (8)	−0.0013 (8)	0.0001 (8)
C5	0.0123 (10)	0.0147 (10)	0.0149 (10)	0.0026 (8)	0.0002 (8)	−0.0025 (8)
C6	0.0148 (10)	0.0156 (11)	0.0139 (10)	−0.0003 (8)	0.0023 (8)	−0.0002 (8)
C7	0.0152 (10)	0.0176 (11)	0.0189 (11)	−0.0021 (8)	−0.0013 (8)	−0.0035 (9)
C8	0.0175 (10)	0.0185 (11)	0.0130 (10)	0.0028 (9)	0.0020 (8)	0.0008 (8)
C9	0.0198 (11)	0.0243 (12)	0.0176 (11)	−0.0039 (10)	−0.0028 (9)	0.0013 (9)
C10	0.0158 (10)	0.0139 (10)	0.0121 (9)	0.0016 (8)	0.0019 (8)	−0.0029 (8)
C11	0.0193 (11)	0.0161 (11)	0.0128 (10)	0.0021 (9)	−0.0015 (8)	0.0017 (8)
C12	0.0159 (10)	0.0296 (13)	0.0146 (11)	−0.0004 (9)	−0.0033 (8)	0.0040 (9)
C13	0.0120 (10)	0.0214 (11)	0.0136 (10)	0.0004 (9)	−0.0017 (8)	−0.0008 (9)

Geometric parameters (Å, °)

Br1—N2	1.8853 (17)	C3—C4	1.394 (3)
O1—C10	1.210 (2)	C3—C7	1.399 (3)
N1—C7	1.335 (3)	C4—C5	1.393 (3)
N1—C6	1.335 (3)	C5—C6	1.391 (3)
C1—C2	1.183 (3)	C5—C8	1.439 (3)
O2—C13	1.214 (3)	C8—C9	1.189 (3)
N2—C13	1.384 (3)	C10—C11	1.514 (3)
N2—C10	1.390 (3)	C11—C12	1.531 (3)
C2—C3	1.443 (3)	C12—C13	1.508 (3)
C7—N1—C6	118.81 (18)	N1—C6—C5	123.01 (19)
C13—N2—C10	114.21 (17)	N1—C7—C3	122.62 (19)
C13—N2—Br1	122.51 (14)	C9—C8—C5	177.7 (2)
C10—N2—Br1	123.24 (13)	O1—C10—N2	124.44 (19)
C1—C2—C3	176.5 (2)	O1—C10—C11	128.19 (19)
C4—C3—C7	118.06 (19)	N2—C10—C11	107.37 (17)
C4—C3—C2	120.56 (19)	C10—C11—C12	105.21 (17)
C7—C3—C2	121.37 (19)	C13—C12—C11	105.32 (17)
C5—C4—C3	119.39 (19)	O2—C13—N2	124.71 (19)
C6—C5—C4	118.10 (19)	O2—C13—C12	127.60 (19)
C6—C5—C8	121.15 (19)	N2—C13—C12	107.69 (18)
C4—C5—C8	120.72 (19)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C12—H12 <i>A</i> $\cdots$ O2 ⁱ	0.99	2.63	3.477 (3)	143
C11—H11 <i>A</i> $\cdots$ Br1 ⁱⁱ	0.99	3.22	4.066 (2)	144
C11—H11 <i>A</i> $\cdots$ O1 ⁱⁱⁱ	0.99	2.81	3.303 (3)	111

C11—H11B $\cdots$ O1 ⁱⁱ	0.99	2.91	3.442 (3)	115
C11—H11B $\cdots$ O2 ^{iv}	0.99	2.84	3.617 (3)	136

Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $-x+3/2, y+1/2, -z+1/2$; (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $x, y+1, z$.