Isomorphous crystal structures of chlorodiacetylene and iododiacetylene derivatives: simultaneous hydrogen and halogen bonds on carbonyl

Pierre Baillargeon,[a]* Tarik Rahem,[a] Édouard Caron-Duval,[a] Jacob Tremblay,[a] Cloé Fortin,[a] Étienne Blais,[a] Victor Fan,[a] Daniel Fortin[b] and Yves L. Dory[c]

[a]Département de Chimie, Cégep de Sherbrooke, 475 rue du Cégep, Sherbrooke, Québec, J1E 4K1, Canada, [b]Laboratoire d'Analyses Structurales par Diffraction des Rayons-X, Département de Chimie, Université de Sherbrooke, 2500, boulevard de l'Université, Sherbrooke, Québec, J1K 2R1, Canada, and [c]Laboratoire de Synthèse Supramoléculaire, Département de Chimie, Institut de Pharmacologie, Université de Sherbrooke, 3001 12e avenue nord, Sherbrooke, QC, J1H 5N4, Canada. *Correspondence e-mail: pierre.baillargeon@usherbrooke.ca

The crystal structures of tert-butyl (5-chloropenta-2,4-diyn-1-yl)carbamate, $C_{10}H_{12}ClNO_2$ **(II)**, and tert-butyl (5-iodopenta-2,4-diyn-1-yl)carbamate, $C_{10}H_{12}INO_2$ **(IV)**, are isomorphous to previously reported structures and accordingly their molecular and supramolecular structures are similar. In the crystals of **(II)** and **(IV)**, molecules are linked into very similar two-dimensional wall organizations with antiparallel carbamate groups involved in a combination of hydrogen and halogen bonds (bifurcated N—H···O=C and C≡C—X···O=C interactions on the same carbonyl group). There is no long-range parallel stacking of diynes, so the topochemical polymerization of diacetylene is prevented. A Cambridge Structural Database search revealed that C≡C—X···O=C contacts shorter than the sum of the van der Waals radii are scarce (only one structure for the C≡C—Cl···O=C interaction and 13 structures for the similar C≡C—I···O=C interaction).

1. Chemical context

Hydrogen bonds (HBs) and halogen bonds (XBs) are considered to be useful noncovalent synthetic tools in crystal engineering (Aakeröy et al., 2015; Grabowski, 2016; Resnati et al., 2015; Cinčić et al., 2008). Indeed, these directional intermolecular interactions facilitate the preparation of the desired solid-state motifs and architectures (Gilday et al., 2015; Cavallo et al., 2016; Priimagi et al., 2013; Mukherjee et al., 2014; Shirman et al., 2015; Mukherjee et al., 2017). For example, using HBs and XBs, the specific organization of terminal diacetylenes (Li et al., 2009; Ouyang et al., 2003), bromodiacetylenes (Jin et al., 2015) and iododiacetylenes (Jin et al., 2013; Sun et al., 2006) has been obtained to achieve the solid-state topochemical polymerization of diacetylenes. On the other hand, to the best of our knowledge, no chlorodiacetylene topochemical polymerizations have been reported. Our results show that chlorodiacetylene **(II)** is isostructural to iododiacetylene **(IV)** and the previously reported bromodiacetylene **(III)** and terminal diacetylene **(I)** (Baillargeon et al., 2016) (see Scheme). Although the arrangement of diynes in the present article stands no chance of undergoing topochemical polymerization, we suggest that in other systems prone to polymerization, replacing Br, I or H atoms by Cl atoms in their diyne groups might result in successful PolyChloroDiAcetylene (PCDA) formation as well. This work also contributes to an emerging research theme, namely the

1175
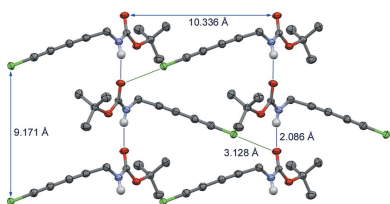
concept of orthogonal molecular interactions such as HBs and XBs (Kratzer *et al.*, 2015; Takemura *et al.*, 2014; Voth *et al.*, 2009), which may find applications in medicinal chemistry and chemical biology (Wilcken *et al.*, 2013).

Previous work	This work
(**I**) $X = H$	(**II**) $X = Cl$
(**III**) $X = Br$	(**IV**) $X = I$
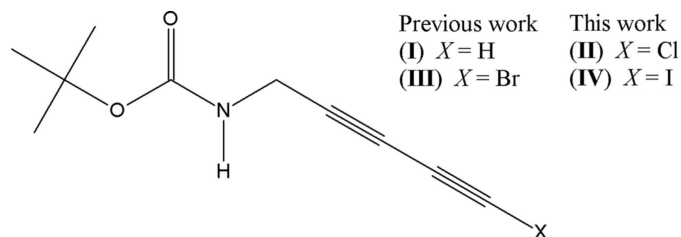
2. Structural commentary

The molecular structures of compounds (**II**) and (**IV**) are shown in Fig. 1. All bond lengths and angles are within normal ranges. For example, the internal diyne C2—C3 bonds lengths [1.376 (3) Å for (**II**) and 1.385 (4) Å for (**IV**)] follow the useful rule of thumb describing a C—C single-bond distance (1.54 Å) decreasing by 0.04 Å each time one of the participating C atoms changes hybridization from sp^3 to sp^2 or from sp^2 to sp (Bent, 1961). Moreover, the observed distances are almost identical to those found recently in the literature for similar halodiynes (Hoheisel *et al.*, 2013; Baillargeon *et al.*, 2016). The relative orientation between the diacetylenic moiety and the carbamate functional group can be established by the absolute value of the torsion angles C4—C5—N1—C6 [111.07 (19)°] for (**II**) and [103.8 (3)°] for (**IV**).

3. Supramolecular features

In the crystals of compounds (**II**) and (**IV**), molecules are linked *via* an N—H···O=C hydrogen bond between their
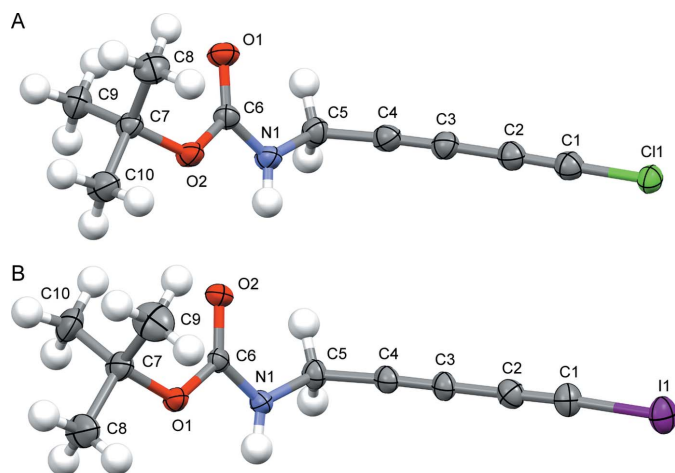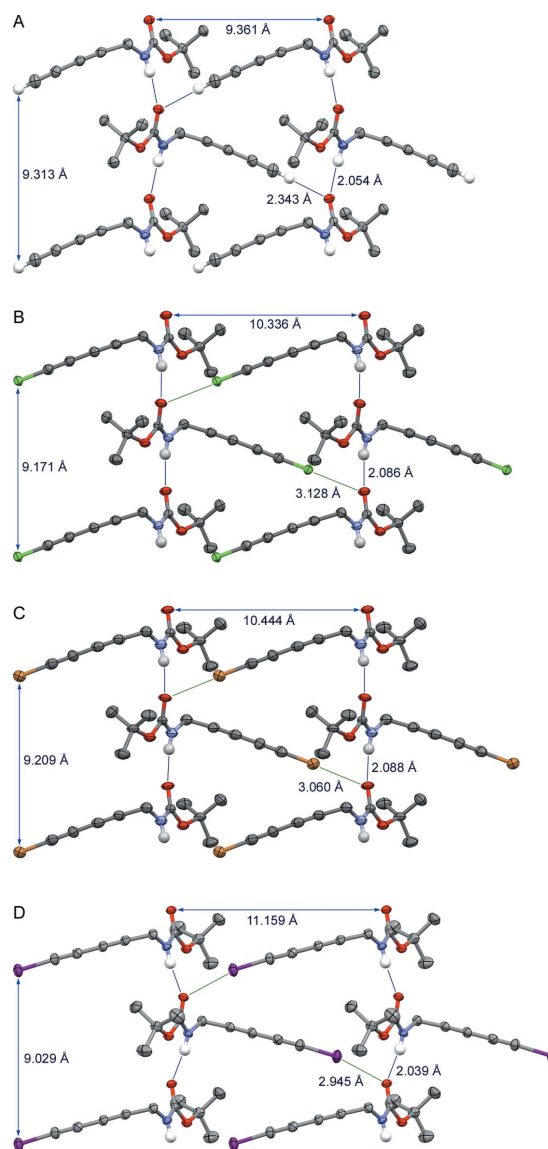

Figure 1
The molecular structure of (A) compound (**II**) and (B) compound (**IV**), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as fixed-size spheres of 0.30 Å.

Table 1
Hydrogen-bond and halogen-bond geometries (Å, °) for (**II**).

$D—X···A$	$D—X$	$X···A$	$D···A$	$D—X···A$
N1—H1···O1[i]	0.88	2.09	2.934 (2)	162
C1—Cl1···O1[ii]	1.665 (2)	3.127 (2)	4.792 (3)	179.01 (7)

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

respective carbamate functionalities [N1—H1···O1[i] (Table 1) and N1—H1···O2[i] (Table 2)], generating an antiparallel stacking pattern which orients the diacetylene skeleton on each side of the one-dimensional carbamate tape (parts B and D in Fig. 2). For both crystals, the simultaneous presence of halogen and hydrogen bonds with the carbamate O atom have been found. Indeed, additional halogen-bond interactions

Figure 2
Halogen (green lines) and/or hydrogen bonds (blue lines) inside the supramolecular walls of (A) diyne (**I**), (B) chlorodiyne (**II**), (C) bromodiyne (**III**) and (D) iododiyne (**IV**). The nonpolar H atoms have been omitted for clarity.

Table 2
Hydrogen-bond and halogen-bond geometries (Å, °) for (IV).

$D-X\cdots A$	$D-X$	$X\cdots A$	$D\cdots A$	$D-X\cdots A$
N1—H1···O2^i	0.88	2.04	2.881 (2)	160
C1—I1···O2^{ii}	1.999 (2)	2.945 (2)	4.919 (3)	168.31 (8)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{3}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{3}{2}, -z + \frac{3}{2}$.

occur with the carbamate O atom [Cl1···O1^{ii} for (II) and I1···O2^{ii} for (IV)], resulting in an infinite two-dimensional network that can be considered as polar supramolecular walls. This arrangement is similar to our previous work (Baillargeon *et al.*, 2016) on the terminal diacetylene (I) (part A in Fig. 2) and the bromodiacetylene (III) (part C in Fig. 2). In fact, diynes (I)–(IV) (Fig. 2) constitute a complete set of truly isomorphous crystals that can be carefully examined to evaluate the differences and similarities that exist between halogen and hydrogen bonds. Thus, the $X\cdots O\cdots H$ angle increases as the size of the halogen atom becomes larger. This angle, which is pretty open in the chlorine crystal (II) (Cl1···O1···H1; part B in Fig. 2; 69°) adopts a near orthogonal geometry with the iodine (I1···O2···H1; part D in Fig. 2; 83°). It is not a surprise that the bromine crystal (III) represents an intermediate case (part C in Fig. 2; 72°). The value for the terminal diacetylene (I) X = H (part A in Fig. 2; 76°) is closely related to the bromodiacetylene (Baillargeon *et al.*, 2016).

4. Database survey

A survey of the Cambridge Structural Database (*Conquest* Version 1.19; CSD, Version 5.38, November 2016 plus 3 updates; Groom *et al.*, 2016) furnished 404 hits of terminal alkynes CC—H having close contacts with carbonyl O=C (shorter than the sum of their van der Waals radii). On the other hand, similar contacts from halogenoalkyne analogs are scarce (1 hit for the chloroalkyne, 4 hits for the bromoalkyne

and 13 hits for the iodoalkyne; Table 3). For the iodoalkyne, results are limited to monovalent iodine and for a structure in which the carbonyl group is not involved in an organometallic complex.

5. Synthesis and crystallization

5.1. Compound (II)

Tetra-*n*-butylammonium fluoride (TBAF, 0.437 ml, 1 *M* in THF, 0.437 mmol), AgNO$_3$ (39 mg, 0.23 mmol) and NCS (190 mg, 1.42 mmol) were added to a solution of BocNHCH$_2$—C≡C—C≡C—TMS (183 mg, 0.728 mmol) in acetonitrile (3 ml) at room temperature. The resulting mixture was stirred for 2.5 h under N$_2$ in the absence of light. Purification of the crude product by flash chromatography on silica gel, eluting with mixtures of Hex/DCM/Et$_2$O (gradient from 9:1:1 to 1:1:1), provided compound (II) as a beige solid (yield 72 mg, 46%). Single crystals suitable for X-ray diffraction were prepared by diffusion of pentane into a chloroform solution of (II) at 263 K. R_F = 0.43 (2:1:1 Hex/DCM/Et$_2$O); IR (UATR, ν, cm^{-1}): 3326, 2977, 2920, 2255, 2168, 1673, 1531, 1421, 1368, 1278, 1248, 1222, 1158, 1143, 1042, 1028, 933, 849, 761, 718, 655; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.72 (*br*, 1H), 3.99 (*d*, 2H), 1.45 (*s*, 9H); HRMS (*m/z*): calculated for C$_{10}$H$_{12}$ClNNaO$_2$ [MNa$^+$]: 236.0449, found: 236.0448.

5.2. Compound (IV)

TBAF (0.437 ml, 1 *M* in THF, 0.437 mmol), AgNO$_3$ (39 mg, 0.23 mmol) and NIS (328 mg, 1.46 mmol) were added to a solution of BocNHCH$_2$—C≡C—C≡C—TMS (183 mg, 0.728 mmol) in acetonitrile (3 ml) at room temperature. The resulting mixture was stirred for 2.5 h under N$_2$ in the absence of light. Purification of the crude product by flash chromatography on silica gel, eluting with mixtures of Hex/DCM/Et$_2$O (gradient from 9:1:1 to 1:1:1) provided compound (IV) as a beige solid (yield 95 mg, 43%). Single crystals suitable for

Table 3
CSD data (Groom *et al.*, 2016) retrieved for the C≡C—X···O=C contacts shorter than the sum of their van der Waals radii.

C≡C—X···O=C contacts	CSD refcode	Space group	X···O distance (Å)	C—X···O angle (°)	Reference
C≡C—Cl···O=C	NIDWAA	$P\bar{1}$	3.111; 3.241	152.59; 158.76	Kawai *et al.* (2013)
C≡C—Br···O=C	HEVWAI	$C2$	2.959	158.12	Hoheisel *et al.* (2013)
C≡C—Br···O=C	HEVWAI01	$P2_12_12_1$	2.966	166.70	Hoheisel *et al.* (2013)
C≡C—Br···O=C	NIDWII	$P2_1/n$	2.867	171.11	Kawai *et al.* (2013)
C≡C—Br···O=C	KAMXII	$P2_1/c$	3.060	178.26	Baillargeon *et al.* (2016)
C≡C—I···O=C	COHYUU	$P\bar{1}$	3.096	164.55	Luo *et al.* (2008)
C≡C—I···O=C	IYAYUC	$Pca2_1$	2.861	170.36	Hou *et al.* (2004)
C≡C—I···O=C	MASVUZ	$P2_1/n$	2.834; 2.887	170.72; 172.97	Perkins *et al.* (2012)
C≡C—I···O=C	TOYPUS	$P2_1/c$	2.933	175.36	Avtomonov *et al.* (1997)
C≡C—I···O=C	HOWXIC	$P2_1/c$	2.887	169.51	Dumele *et al.* (2014)
C≡C—I···O=C	LUNKOW	$P2/c$	2.791	174.12	Kratzer *et al.* (2015)
C≡C—I···O=C	LUNKUC	$P2_1/c$	2.754	172.63	Kratzer *et al.* (2015)
C≡C—I···O=C	LUNLAJ	$P2_1/c$	2.773	173.70	Kratzer *et al.* (2015)
C≡C—I···O=C	LUNLIR	$Pca2_1$	2.858	170.94	Kratzer *et al.* (2015)
C≡C—I···O=C	LUNLOX	$C2/c$	2.763	175.58	Kratzer *et al.* (2015)
C≡C—I···O=C	IBUYAI	$P2_1/m$	2.856	177.96	Dumele *et al.* (2017)
C≡C—I···O=C	IBUYOW	$P2_1/c$	2.830	176.52	Dumele *et al.* (2017)
C≡C—I···O=C	IBUYUC	$P\bar{1}$	2.878	177.89	Dumele *et al.* (2017)

Table 4
Experimental details.

	(II)	(IV)
Crystal data		
Chemical formula	$C_{10}H_{12}ClNO_2$	$C_{10}H_{12}INO_2$
M_r	213.66	305.11
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	173	173
a, b, c (Å)	10.336 (3), 9.171 (3), 11.870 (3)	11.1587 (16), 9.0288 (13), 12.9899 (18)
β (°)	100.656 (5)	108.731 (2)
V (Å^3)	1105.8 (5)	1239.4 (3)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.32	2.56
Crystal size (mm)	$0.34 \times 0.22 \times 0.02$	$0.36 \times 0.3 \times 0.28$
Data collection		
Diffractometer	Bruker APEXII	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.66, 0.745	0.675, 0.745
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	16132, 2249, 1755	17970, 2532, 2342
R_{int}	0.045	0.02
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625	0.626
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.089, 1.06	0.022, 0.054, 1.08
No. of reflections	2249	2532
No. of parameters	130	130
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.22, −0.21	1.32, −0.69

Computer programs: *APEX2* (Bruker, 2008), *SAINT* (Bruker, 2008), *SORTAV* (Blessing, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

X-ray diffraction were prepared by slow evaporation from a chloroform solution of (IV) at room temperature. $R_F = 0.48$ (2:1:1 Hex/DCM/Et$_2$O); IR (UATR, ν, cm^{-1}): 3328, 2980, 2933, 2230, 2159, 1661, 1532, 1451, 1420, 1367, 1284, 1250, 1154, 1142, 1042, 1026, 929, 851, 762, 714, 647; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.73 (*br*, 1H), 4.02 (*d*, 2H), 1.44 (*s*, 9H).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4.

References

Aakeröy, C. B., Spartz, C. L., Dembowski, S., Dwyre, S. & Desper, J. (2015). *IUCrJ*, **2**, 498–510.

Avtomonov, E. V., Grüning, R. & Lorberth, J. (1997). *Z. Naturforsch. Teil B*, **52**, 256–258.

Baillargeon, P., Caron-Duval, É., Pellerin, É., Gagné, S. & Dory, Y. L. (2016). *Crystals*, **6**, 37–49.

Bent, H. A. (1961). *Chem. Rev.* **61**, 275–311.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Bruker (2008). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G. & Terraneo, G. (2016). *Chem. Rev.* **116**, 2478–2601.

Cinčić, D., Friščić, T. & Jones, W. (2008). *Chem. Mater.* **20**, 6623–6626.

Dumele, O., Schreib, B., Warzok, U., Trapp, N., Schalley, C. A. & Diederich, F. (2017). *Angew. Chem. Int. Ed.* **56**, 1152–1157.

Dumele, O., Wu, D., Trapp, N., Goroff, N. & Diederich, F. (2014). *Org. Lett.* **16**, 4722–4725.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gilday, L. C., Robinson, S. W., Barendt, T. A., Langton, M. J., Mullaney, B. R. & Beer, P. D. (2015). *Chem. Rev.* **115**, 7118–7195.

Grabowski, S. J. (2016). *Crystals*, **6**, 59–63.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hoheisel, T. N., Schrettl, S., Marty, R., Todorova, T. K., Corminboeuf, C. & Sienkiewicz, A. (2013). *Nat. Chem.* **5**, 327–334.

Hou, Z.-K., Ren, Y.-G., Huang, M.-Z., Song, J. & Chen, L.-G. (2004). *Acta Cryst.* E**60**, o1336–o1337.

Jin, H., Plonka, A. M., Parise, J. B. & Goroff, N. S. (2013). *CrystEngComm*, **15**, 3106–3110.

Jin, H., Young, C. N., Halada, G. P., Phillips, B. L. & Goroff, N. S. (2015). *Angew. Chem. Int. Ed.* **54**, 14690–14695.

Kawai, H., Utamura, T., Motoi, E., Takahashi, T., Sugino, H., Tamura, M., Ohkita, M., Fujiwara, K., Saito, T., Tsuji, T. & Suzuki, T. (2013). *Chem. Eur. J.* **19**, 4513–4524.

Kratzer, P., Ramming, B., Römisch, S. & Maas, G. (2015). *CrystEngComm*, **17**, 4486–4494.

Li, Z., Fowler, F. W. & Lauher, J. W. (2009). *J. Am. Chem. Soc.* **131**, 634–643.

Luo, L., Wilhelm, C., Sun, A., Grey, C. P., Lauher, J. W. & Goroff, N. S. (2008). *J. Am. Chem. Soc.* **130**, 7702–7709.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Mukherjee, A., Teyssandier, J., Hennrich, G., De Feyter, S. & Mali, K. S. (2017). *Chem. Sci.* **8**, 3759–3769.

Mukherjee, A., Tothadi, S. & Desiraju, G. R. (2014). *Acc. Chem. Res.* **47**, 2514–2524.

Ouyang, X., Fowler, F. W. & Lauher, J. W. (2003). *J. Am. Chem. Soc.* **125**, 12400–12401.

Perkins, C., Libri, S., Adams, H. & Brammer, L. (2012). *CrystEngComm*, **14**, 3033–3038.

Priimagi, A., Cavallo, G., Metrangolo, P. & Restani, R. (2013). *Acc. Chem. Res.* **46**, 2686–2695.

Resnati, G., Boldyreva, E., Bombicz, P. & Kawano, M. (2015). *IUCrJ*, **2**, 675–690.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Shirman, T., Boterashvili, M., Orbach, M., Freeman, D., Shimon, L. J. W., Lahav, M. & van der Boom, M. E. (2015). *Cryst. Growth Des.* **15**, 4756–4759.

Sun, A., Lauher, J. W. & Goroff, N. S. (2006). *Science*, **312**, 1030–1034.

Takemura, A., McAllister, L. J., Hart, S., Pridmore, N. E., Karadakov, P. B., Whitwood, A. C. & Bruce, D. W. (2014). *Chem. Eur. J.* **20**, 6721–6732.

Voth, A. R., Khuu, P., Oishi, K. & Ho, P. S. (2009). *Nat. Chem.* **1**, 74–79.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Wilcken, R., Zimmermann, M. O., Lange, A., Joerger, A. C. & Boeckler, F. M. (2013). *J. Med. Chem.* **56**, 1363–1388.

supporting information

Isomorphous crystal structures of chlorodiacetylene and iododiacetylene derivatives: simultaneous hydrogen and halogen bonds on carbonyl

Pierre Baillargeon, Tarik Rahem, Édouard Caron-Duval, Jacob Tremblay, Cloé Fortin, Étienne Blais, Victor Fan, Daniel Fortin and Yves L. Dory

Computing details

For both structures, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

tert-**Butyl (5-chloropenta-2,4-diyn-1-yl)carbamate (II)**

Crystal data

$C_{10}H_{12}ClNO_2$	$F(000) = 448$
$M_r = 213.66$	$D_x = 1.283$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8841 reflections
$a = 10.336$ (3) Å	$\theta = 2.8–26.4°$
$b = 9.171$ (3) Å	$\mu = 0.32$ mm^{-1}
$c = 11.870$ (3) Å	$T = 173$ K
$\beta = 100.656$ (5)°	Plate, orange
$V = 1105.8$ (5) Å^3	$0.34 \times 0.22 \times 0.02$ mm
$Z = 4$	

Data collection

Bruker APEXII diffractometer	16132 measured reflections
Radiation source: sealed x-ray tube	2249 independent reflections
Graphite monochromator	1755 reflections with $I > 2\sigma(I)$
φ or ω oscillation scans	$R_{int} = 0.045$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$\theta_{max} = 26.4°$, $\theta_{min} = 2.0°$
	$h = -12 \rightarrow 12$
	$k = -11 \rightarrow 11$
$T_{min} = 0.66$, $T_{max} = 0.745$	$l = -9 \rightarrow 14$

Refinement

Refinement on F^2	130 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.036$	0 constraints
$wR(F^2) = 0.089$	Hydrogen site location: inferred from neighbouring sites
$S = 1.06$	
2249 reflections	H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.2863P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.40035 (19)	0.0211 (2)	0.15762 (16)	0.0343 (4)
C2	0.50716 (18)	−0.0266 (2)	0.15615 (16)	0.0336 (4)
C3	0.63096 (19)	−0.0798 (2)	0.15309 (16)	0.0336 (4)
C4	0.73990 (19)	−0.1223 (2)	0.15037 (16)	0.0334 (4)
C5	0.87519 (17)	−0.1687 (2)	0.14761 (17)	0.0339 (4)
H5A	0.882935	−0.274828	0.16243	0.041*
H5B	0.894345	−0.150569	0.070125	0.041*
C6	1.04144 (17)	−0.15939 (19)	0.32333 (15)	0.0271 (4)
C7	1.22986 (18)	−0.11065 (19)	0.47967 (15)	0.0304 (4)
C8	1.1748 (2)	−0.1841 (2)	0.57483 (17)	0.0439 (5)
H8A	1.106364	−0.122368	0.597047	0.066*
H8B	1.245644	−0.198955	0.641132	0.066*
H8C	1.136913	−0.278618	0.547923	0.066*
C9	1.32333 (19)	−0.2075 (2)	0.42986 (18)	0.0408 (5)
H9A	1.278745	−0.298815	0.40299	0.061*
H9B	1.400577	−0.228971	0.488902	0.061*
H9C	1.351283	−0.15766	0.365371	0.061*
C10	1.2953 (2)	0.0332 (2)	0.52078 (19)	0.0449 (5)
H10A	1.324136	0.082715	0.456527	0.067*
H10B	1.371735	0.014414	0.581378	0.067*
H10C	1.232365	0.095115	0.550916	0.067*
Cl1	0.24981 (4)	0.08590 (5)	0.15756 (4)	0.03061 (14)
N1	0.97160 (14)	−0.09282 (16)	0.23144 (13)	0.0314 (4)
H1	0.984766	0.000739	0.221551	0.038*
O1	1.03225 (13)	−0.28874 (13)	0.34594 (11)	0.0361 (3)
O2	1.12149 (12)	−0.06256 (12)	0.38708 (11)	0.0311 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0342 (11)	0.0349 (11)	0.0334 (11)	−0.0009 (9)	0.0055 (8)	0.0009 (8)
C2	0.0337 (11)	0.0333 (10)	0.0323 (11)	−0.0036 (8)	0.0019 (8)	0.0007 (8)
C3	0.0333 (11)	0.0300 (10)	0.0346 (11)	−0.0005 (8)	−0.0011 (8)	0.0016 (8)
C4	0.0339 (11)	0.0279 (10)	0.0350 (11)	−0.0023 (8)	−0.0028 (8)	−0.0006 (8)
C5	0.0309 (10)	0.0311 (10)	0.0368 (11)	0.0013 (8)	−0.0014 (8)	−0.0030 (8)
C6	0.0264 (9)	0.0222 (9)	0.0323 (10)	−0.0014 (7)	0.0045 (7)	−0.0023 (7)

C7	0.0311 (10)	0.0269 (10)	0.0299 (10)	0.0017 (8)	−0.0026 (8)	0.0021 (8)
C8	0.0524 (13)	0.0429 (12)	0.0369 (12)	0.0014 (10)	0.0091 (10)	0.0049 (9)
C9	0.0344 (11)	0.0415 (12)	0.0451 (13)	0.0056 (9)	0.0037 (9)	0.0019 (9)
C10	0.0468 (13)	0.0339 (11)	0.0462 (13)	−0.0041 (10)	−0.0121 (10)	−0.0007 (9)
Cl1	0.0268 (2)	0.0320 (3)	0.0337 (3)	0.00451 (19)	0.00733 (18)	0.00090 (19)
N1	0.0303 (8)	0.0220 (8)	0.0381 (9)	−0.0024 (7)	−0.0036 (7)	0.0013 (7)
O1	0.0409 (8)	0.0217 (7)	0.0427 (8)	−0.0034 (6)	0.0003 (6)	0.0014 (6)
O2	0.0314 (7)	0.0220 (7)	0.0358 (8)	−0.0009 (5)	−0.0049 (6)	−0.0006 (5)

Geometric parameters (Å, º)

C1—C2	1.191 (3)	C6—N1	1.339 (2)
C1—Cl1	1.666 (2)	C6—O2	1.347 (2)
C2—C3	1.376 (3)	C7—O2	1.484 (2)
C3—C4	1.198 (3)	C7—C9	1.511 (3)
C4—C5	1.468 (3)	C7—C8	1.513 (3)
C5—N1	1.449 (2)	C7—C10	1.521 (3)
C6—O1	1.224 (2)		
C2—C1—Cl1	178.9 (2)	O2—C7—C9	109.55 (15)
C1—C2—C3	179.0 (2)	O2—C7—C8	110.41 (15)
C4—C3—C2	178.2 (2)	C9—C7—C8	112.70 (16)
C3—C4—C5	177.8 (2)	O2—C7—C10	102.12 (14)
N1—C5—C4	112.49 (16)	C9—C7—C10	110.89 (17)
O1—C6—N1	124.66 (17)	C8—C7—C10	110.67 (17)
O1—C6—O2	125.48 (17)	C6—N1—C5	122.64 (16)
N1—C6—O2	109.86 (15)	C6—O2—C7	121.42 (13)
O1—C6—N1—C5	0.3 (3)	N1—C6—O2—C7	−166.78 (14)
O2—C6—N1—C5	−178.98 (15)	C9—C7—O2—C6	59.3 (2)
C4—C5—N1—C6	111.1 (2)	C8—C7—O2—C6	−65.4 (2)
O1—C6—O2—C7	13.9 (3)	C10—C7—O2—C6	176.85 (16)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1[i]	0.88	2.09	2.935	162
C1—Cl1···O1[ii]	1.67	3.13	4.793	179

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

***tert*-Butyl (5-iodopenta-2,4-diyn-1-yl)carbamate (IV)**

Crystal data

$C_{10}H_{12}INO_2$	c = 12.9899 (18) Å
M_r = 305.11	β = 108.731 (2)°
Monoclinic, $P2_1/n$	V = 1239.4 (3) Å³
Hall symbol: -P 2yn	Z = 4
a = 11.1587 (16) Å	$F(000)$ = 592
b = 9.0288 (13) Å	D_x = 1.635 Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9940 reflections
$\theta = 2.3$–$26.4°$
$\mu = 2.56$ mm^{-1}

$T = 173$ K
Prism, yellow
$0.36 \times 0.3 \times 0.28$ mm

Data collection

Bruker APEXII
  diffractometer
Radiation source: sealed x-ray tube
Graphite monochromator
φ or ω oscillation scans
Absorption correction: multi-scan
  (SADABS; Bruker, 2008)
$T_{min} = 0.675$, $T_{max} = 0.745$

17970 measured reflections
2532 independent reflections
2342 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.1°$
$h = -12 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.054$
$S = 1.08$
2532 reflections
130 parameters
0 restraints
0 constraints

Hydrogen site location: inferred from
  neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 1.7447P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.32$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.2157 (2)	1.0340 (3)	0.3437 (2)	0.0328 (6)
C2	0.3210 (2)	1.0012 (3)	0.34873 (19)	0.0304 (5)
C3	0.4425 (2)	0.9623 (3)	0.35280 (19)	0.0279 (5)
C4	0.5465 (2)	0.9286 (3)	0.35525 (19)	0.0275 (5)
C5	0.6760 (2)	0.8938 (3)	0.35692 (19)	0.0282 (5)
H5A	0.736704	0.927089	0.42691	0.034*
H5B	0.684833	0.785076	0.352172	0.034*
C6	0.7111 (2)	0.8882 (2)	0.18051 (19)	0.0219 (4)
C7	0.7579 (3)	0.9226 (3)	0.0094 (2)	0.0344 (6)
C8	0.7976 (4)	1.0622 (3)	−0.0367 (3)	0.0511 (8)
H8A	0.730469	1.136625	−0.049832	0.077*
H8B	0.812386	1.038609	−0.105307	0.077*
H8C	0.875616	1.101212	0.015278	0.077*
C9	0.6338 (4)	0.8624 (4)	−0.0654 (3)	0.0559 (9)
H9A	0.611252	0.772368	−0.033698	0.084*
H9B	0.642508	0.839113	−0.136337	0.084*
H9C	0.567195	0.936832	−0.074587	0.084*

C10	0.8637 (3)	0.8100 (4)	0.0377 (3)	0.0506 (8)
H10A	0.936443	0.849222	0.095807	0.076*
H10B	0.888703	0.789497	−0.02666	0.076*
H10C	0.834626	0.718248	0.062297	0.076*
N1	0.7077 (2)	0.9636 (2)	0.26832 (16)	0.0263 (4)
H1	0.725256	1.058913	0.272455	0.032*
O1	0.73962 (17)	0.97953 (18)	0.11063 (13)	0.0272 (4)
O2	0.69111 (17)	0.75519 (18)	0.16743 (14)	0.0289 (4)
I1	0.04221 (2)	1.09875 (2)	0.33737 (2)	0.03907 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0294 (14)	0.0398 (14)	0.0301 (13)	0.0020 (11)	0.0106 (10)	0.0027 (11)
C2	0.0333 (14)	0.0328 (13)	0.0263 (12)	−0.0012 (11)	0.0110 (10)	0.0031 (10)
C3	0.0312 (14)	0.0309 (13)	0.0250 (11)	−0.0015 (10)	0.0139 (10)	0.0011 (10)
C4	0.0337 (14)	0.0284 (12)	0.0236 (11)	−0.0036 (10)	0.0135 (10)	0.0005 (9)
C5	0.0298 (13)	0.0321 (13)	0.0259 (12)	0.0007 (10)	0.0132 (10)	0.0032 (10)
C6	0.0180 (11)	0.0216 (11)	0.0271 (11)	0.0013 (8)	0.0087 (9)	0.0020 (9)
C7	0.0490 (17)	0.0323 (13)	0.0293 (13)	−0.0017 (12)	0.0229 (12)	−0.0034 (10)
C8	0.085 (3)	0.0407 (17)	0.0437 (17)	−0.0055 (16)	0.0430 (18)	0.0016 (13)
C9	0.067 (2)	0.065 (2)	0.0325 (15)	−0.0141 (18)	0.0106 (15)	−0.0046 (15)
C10	0.065 (2)	0.0415 (17)	0.063 (2)	0.0074 (15)	0.0446 (18)	−0.0051 (15)
N1	0.0334 (11)	0.0215 (10)	0.0304 (10)	−0.0039 (8)	0.0191 (9)	−0.0015 (8)
O1	0.0396 (10)	0.0196 (8)	0.0293 (9)	0.0004 (7)	0.0209 (7)	0.0004 (7)
O2	0.0348 (10)	0.0197 (8)	0.0352 (9)	−0.0030 (7)	0.0157 (8)	−0.0001 (7)
I1	0.02499 (10)	0.04928 (12)	0.04157 (11)	0.00657 (8)	0.00878 (7)	0.00614 (8)

Geometric parameters (Å, º)

C1—C2	1.193 (4)	C7—C9	1.514 (4)
C1—I1	1.999 (3)	C7—C8	1.521 (4)
C2—C3	1.385 (4)	C8—H8A	0.98
C3—C4	1.191 (4)	C8—H8B	0.98
C4—C5	1.472 (3)	C8—H8C	0.98
C5—N1	1.452 (3)	C9—H9A	0.98
C5—H5A	0.99	C9—H9B	0.98
C5—H5B	0.99	C9—H9C	0.98
C6—O2	1.223 (3)	C10—H10A	0.98
C6—O1	1.338 (3)	C10—H10B	0.98
C6—N1	1.340 (3)	C10—H10C	0.98
C7—O1	1.486 (3)	N1—H1	0.88
C7—C10	1.512 (4)		
C2—C1—I1	177.3 (3)	H8A—C8—H8B	109.5
C1—C2—C3	179.1 (3)	C7—C8—H8C	109.5
C4—C3—C2	179.4 (3)	H8A—C8—H8C	109.5
C3—C4—C5	177.4 (3)	H8B—C8—H8C	109.5

N1—C5—C4	112.5 (2)	C7—C9—H9A	109.5
N1—C5—H5A	109.1	C7—C9—H9B	109.5
C4—C5—H5A	109.1	H9A—C9—H9B	109.5
N1—C5—H5B	109.1	C7—C9—H9C	109.5
C4—C5—H5B	109.1	H9A—C9—H9C	109.5
H5A—C5—H5B	107.8	H9B—C9—H9C	109.5
O2—C6—O1	125.7 (2)	C7—C10—H10A	109.5
O2—C6—N1	124.3 (2)	C7—C10—H10B	109.5
O1—C6—N1	110.00 (19)	H10A—C10—H10B	109.5
O1—C7—C10	109.6 (2)	C7—C10—H10C	109.5
O1—C7—C9	109.6 (2)	H10A—C10—H10C	109.5
C10—C7—C9	113.4 (3)	H10B—C10—H10C	109.5
O1—C7—C8	101.7 (2)	C6—N1—C5	122.3 (2)
C10—C7—C8	110.5 (3)	C6—N1—H1	118.8
C9—C7—C8	111.5 (3)	C5—N1—H1	118.8
C7—C8—H8A	109.5	C6—O1—C7	121.17 (18)
C7—C8—H8B	109.5		
O2—C6—N1—C5	−1.7 (4)	N1—C6—O1—C7	175.9 (2)
O1—C6—N1—C5	178.5 (2)	C10—C7—O1—C6	−58.9 (3)
C4—C5—N1—C6	−103.9 (3)	C9—C7—O1—C6	66.1 (3)
O2—C6—O1—C7	−3.9 (4)	C8—C7—O1—C6	−175.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2[i]	0.88	2.04	2.881	160
C1—I1···O2[ii]	2.00	2.95	4.919	168

Symmetry codes: (i) −*x*+3/2, *y*+3/2, −*z*+3/2; (ii) −*x*+1/2, *y*+3/2, −*z*+3/2.