Halogen-bonded zigzag molecular network based upon 1,2-diiodoperchlorobenzene and the photoproduct \textit{rctt}-1,3-bis(pyridin-4-yl)-2,4-diphenylcyclobutane

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The formation and crystal structure of a zigzag molecular network held together by I···N halogen bonds is reported. In particular, the halogen-bond donor is 1,2-diiodoperchlorobenzene (\textit{1,2-C$_6$I$_2$Cl$_4$}) while the acceptor is a head-to-tail photoproduct, namely \textit{rctt}-1,3-bis(pyridin-4-yl)-2,4-diphenylcyclobutane (\textit{ht-PP}). In this co-crystal (\textit{1,2-C$_6$I$_2$Cl$_4$}/\textit{ht-PP}), the donor acts as a bent two-connected node while the acceptor behaves as a linear linker to form the extended solid. Neighbouring chains pack in a tongue-and-groove-like pattern resulting in a supramolecular two-dimensional sheet.

1. Chemical context

A continued area of research within crystal engineering is the design and formation of supramolecular networks that have specific and targeted structures (Yang \textit{et al.}, 2015; Vantomme & Meijer, 2019). While the field is diverse and interdisciplinary, the self-assembly of small molecules to yield purely organic materials continues to be a main focus for materials scientists as well as solid-state chemists (Zhang \textit{et al.}, 2019). Controlling the overall topology of these assembled supramolecular networks can easily be achieved by the careful selection of both the node and linker groups typified by metal–organic and supramolecular coordination frameworks (Jiang \textit{et al.}, 2018) as well as flexible organic frameworks (Huang \textit{et al.}, 2019). Halogen bonding continues to be a well-established and reliable non-covalent interaction in the formation of these supramolecular networks (Gilday \textit{et al.}, 2015). A continued goal within our research groups has been the design and construction of halogen-bonded molecular solids containing nodes generated by the [2 + 2] cycloaddition reaction (Dunning \textit{et al.}, 2021; Oburn \textit{et al.}, 2020; Sinnwell \textit{et al.}, 2020). In each example, the cyclobutane-based photoproduct accepts I···N halogen bonds to form these extended solids. These functionalized photoproducts are ideal components, in the formation of these networks, due to the ability to control the number and position of halogen-bond accepting groups coming off the central cyclobutane ring (Gan \textit{et al.}, 2018). Recently, we reported the ability to vary the topology within a pair of halogen-bonded networks by controlling the regiochemistry of the pendant groups (Dunning \textit{et al.}, 2021). In that contribution, the resulting topology was dictated by the regiochemical position of the 4-pyridyl groups around the...
cyclobutane ring. In particular, the incorporation of the head-to-tail photoproduct \textit{rcrr}-1,3-bis(pyridin-4-yl)-2,4-diphenyl-cyclobutane \textit{ht-PP} or the head-to-head photoproduct \textit{rcrr}-1,2-bis(pyridin-4-yl)-3,4-diphenyl-cyclobutane resulted in either a linear or zigzag molecular topology, respectively. In both networks, the halogen-bond donor was 1,4-diiodo-perchlorobenzene, which acted as a linear linker due to the \textit{para}-position of the two I-atoms.

Using this as inspiration, a research project was undertaken to exploit the ability of 1,2-diiodoperchlorobenzene \textit{1,2-C6I2Cl4} to act as a halogen-bond donor (Bosch \textit{et al.}, 2020) that would result in a similar zigzag structure when combined with \textit{ht-PP}, a linear node-based photoproduct. To this end, we report here the synthesis and crystal structure of the co-crystal \textit{1,2-C6I2Cl4/ht-PP} that has a zigzag topology due to the \textit{ortho}-position of the I atoms on the halogen-bond donor. This co-crystal is sustained by I···N halogen bonds with the 4-pyridyl rings on \textit{ht-PP} (Fig. 2). The I1···N1 and I2···N2' bond distances are 2.809 (6) and 2.927 (6) Å along with bond angles for C27—I1···N1 and C28—I2···N2' of 177.8 (2) and 175.6 (2)°, respectively [symmetry code: (i) \(-x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}\)]. Since the I atoms are in an \textit{ortho}-position, \textit{1,2-C6I2Cl4/ht-PP} acts as a bent halogen-bond donor with a bond angle of 65.8 (1)° measured between the centroid of the donor and the two N atoms (Fig. 2), forming zigzag chains.

3. Supramolecular features

These zigzag chains interact with nearest neighbours by various Cl···\(\pi\) interactions (Fig. 3). In particular, all the chlorine atoms on \textit{1,2-C6I2Cl4} are found to interact via Cl···\(\pi\) interactions with either 4-pyridyl rings [3.466 (4) and 3.865 (3) Å] or phenyl rings [3.288 (4) and 3.842 (4) Å]. These distances were measured from the chlorine atom to the centroid of the aromatic ring (Youn \textit{et al.}, 2016). The combination of I···N halogen bonds along with the various Cl···\(\pi\) interactions generates a supramolecular two-dimensional sheet within \textit{1,2-C6I2Cl4/ht-PP}. The polymeric chain is sustained by I···N halogen bonds between \textit{1,2-C6I2Cl4} and the photoproduct \textit{ht-PP}.

The various non-covalent interactions were also investigated and visualized by using a Hirshfeld surface analysis (Spackman \textit{et al.}, 2021) mapped over \textit{d}$_{norm}$ (Fig. 4). The darkest red spots on the surface represent the I···N halogen bonds while the lighter red spots are the Cl···\(\pi\) interactions. The \textit{ortho}-position of the I atoms on the halogen-bond donor makes this molecule behave as a bent two-connecting node, which is required for the formation of a zigzag network.
4. Database survey

A search of the Cambridge Crystallographic Database (CSD, Version 5.43, November 2021; Groom et al., 2016) using Conquest (Bruno et al., 2002) for structures containing 1,2-C₆I₂Cl₄ revealed only one from our earlier study, refcode SUZFUR (Bosch et al., 2020). A similar search for structures including h₄-PP with a halobenzene that is within the sum of the van der Waals radii of one of the pyridine N atoms yielded two structures, refcodes EQOVUC and EQOWEN (Mondal et al., 2011). Each of these structures describes a halogen-bonding interaction within a single molecule, viz. 4,4'-bis(2,4-bromophenyl)cyclobutane-1,3-diyl)dipyridine and 4,4'-bis(4-iodophenyl)cyclobutane-1,3-diyl)dipyridine, respectively.

5. Synthesis and crystallization

Materials and general methods. The solvents reagent grade ethanol (95%), methylene chloride, and toluene were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. In addition, 4,6-dichlororesorcinol (4,6-diCl res), 4-stilbazole (SB), and sodium hydroxide pellets were also purchased from Sigma-Aldrich and were used as received. The [2 + 2] cycloaddition reaction was conducted in an ACE Glass photochemistry cabinet using UV radiation from a 450 W medium-pressure mercury lamp. The occurrence and yield of the [2 + 2] cycloaddition reaction was determined by using ¹H Nuclear Magnetic Resonance Spectroscopy on a Bruker Avance 400 MHz spectrometer with dimethyl sulfoxide (DMSO-d₆) as the solvent. The halogen-bond donor 1,2-diiodoperchlorobenzene (1,2-C₆I₂Cl₄) was synthesized utilizing a previously published method (Reddy et al., 2006).

Synthesis and crystallization. The formation of the photo-reactive co-crystal (4,6-diCl res)-(SB) was achieved using a previously published approach (Grobelny et al., 2018). In particular, co-crystals of (4,6-diCl res)-(SB) were formed by dissolving 50.0 mg of SB in 2.0 mL of ethanol, which was then combined with a separate 2.0 mL ethanol solution containing 24.7 mg of 4,6-diCl res (2:1 molar equivalent). Then the resulting solution was allowed to slowly evaporate. After evaporation of the solvent, the remaining solid was removed and placed between Pyrex glass plates for irradiation. After 20 h of UV exposure, the [2 + 2] cycloaddition reaction occurred with a 100% yield. The formation of h₄-PP was confirmed by ¹H NMR (Grobelny et al., 2018) by the complete loss of the olefin peak on SB at 7.57 ppm along with the appearance of a cyclobutane peak at 4.59 ppm (Fig. S1 in the supporting information). The 4,6-diCl res template was then removed by a base extraction with a 5.0 mL of a 0.2 M sodium hydroxide solution that was heated and stirred on a hot plate for 10 minutes. Afterwards, h₄-PP was extracted by using three 10 mL aliquots of methylene chloride as the solvent. Then the methylene chloride was removed under vacuum to yield pure h₄-PP. The formation of (1,2-C₆I₂Cl₄)-(h₄-PP) was achieved by dissolving 25.0 mg of 1,2-C₆I₂Cl₄ in 2.0 mL of toluene and then combined with a 3.0 mL toluene solution containing 19.4 mg of h₄-PP (1:1 molar equivalent). Within two days, single crystals suitable for X-ray diffraction were formed upon loss of some of the solvent by slow evaporation.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Data collection at low temperature, namely 100 K, was facilitated using a Kryoflex system with an accuracy of 1 K. H atoms were included in the refinement at calculated positions.

Figure 3
Space-filling model of (1,2-C₆I₂Cl₄)-(h₄-PP) illustrating the various Cl···π interactions.

Figure 4
Hirshfeld surface of (1,2-C₆I₂Cl₄)-(h₄-PP) mapped over Δνₚₑₚₚ illustrating the I···N halogen bonds and Cl···π interactions.

Figure 5
Hirshfeld surface of (1,2-C₆I₂Cl₄)-(h₄-PP) mapped over Δνₚₑₚₚ illustrating the I···N halogen bonds and Cl···π interactions.
Table 1
Experimental details.

| Crystal data                        | Chemical formula C_{26}H_{22}N_{2}C_{6}Cl_{4}I_{2} |
|-------------------------------------|--------------------------------------------------|
| Mass (g/mol)                        | 830.11                                           |
| Crystal system, space group         | Monoclinic, P_{2}/n                               |
| Temperature (K)                     | 100                                              |
| a, b, c (Å)                         | 9.6519 (6), 28.3120 (16), 11.1909 (6)             |
| β (°)                               | 92.154 (1)                                       |
| V (Å^3)                             | 3055.9 (3)                                       |
| Z                                    | 4                                                |
| Radiation type                      | Mo Kα                                            |
| μ (mm^-1)                           | 2.43                                             |
| Crystal size (mm)                   | 0.55 × 0.23 × 0.17                               |

Data collection

| Diffractometer                      | Bruker APEXII CCD                                 |
|-------------------------------------|--------------------------------------------------|
| Absorption correction              | Multi-scan (SADABS, Bruker, 2014)                 |
| T_{min}, T_{max}                    | 0.690, 0.746                                      |
| No. of measured, independent and    | 39572, 6730, 6601                                 |
| observed [I > 2σ(I)] reflections    | 0.024                                            |
| \(\sin(\theta)\)_{max} (Å^-1)      | 0.641                                            |

Refinement

| \(R(F^2 > 2\sigma(F^2))\), wR(F^2), S | 0.056, 0.118, 1.39                               |
| No. of reflections                  | 6730                                             |
| No. of parameters                   | 361                                              |
| H-atom treatment                    | H-atom parameters constrained                    |
| \(\Delta R_{max}, \Delta P_{max} (e \ Å^-3)\) | 1.85, −1.11                                      |

Computer programs: SMART and SAINT (Bruker, 2014), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and X-SEED (Barbour, 2020).

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Halogen-bonded zigzag molecular network based upon 1,2-diodoperchloro-benzene and the photoproduct rctt-1,3-bis(pyridin-4-yl)-2,4-diphenylcyclobutane

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**Computing details**

Data collection: SMART (Bruker, 2014); cell refinement: SMART (Bruker, 2014); data reduction: SAINT (Bruker, 2014); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: X-SEED (Barbour, 2020).

1,2,3,4-Tetrachloro-5,6-diiodobenzene–4-[2,4-diphenyl-3-(pyridin-4-yl)cyclobutyl]pyridine (1/1)

**Crystal data**

C₃₀H₂₂N₂·C₆Cl₄I₂

F(000) = 1608

Dₐ = 1.804 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 9788 reflections

θ = 2.2–27.1°

µ = 2.43 mm⁻¹

T = 100 K

Cut block, gold

0.55 × 0.23 × 0.17 mm

**Data collection**

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3660 pixels mm⁻¹

phi and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

Tmin = 0.690, Tmax = 0.746

39572 measured reflections

6730 independent reflections

6601 reflections with I > 2σ(I)

Rint = 0.024

θmax = 27.1°, θmin = 1.4°

h = −12→12

k = −36→36

l = −14→14

**Refinement**

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.056

wR(F²) = 0.118

S = 1.39

6730 reflections

361 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(Fo) + 34.6345P]

where P = (Fo² + 2Fc²)/3

(Δ/σ)max = 0.001

Δρmax = 1.85 e Å⁻³

Δρmin = −1.11 e Å⁻³
**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

|    | x    | y    | z    | Uiso*Ueq |
|----|------|------|------|----------|
| I1 | 0.42402 (5) | 0.67570 (2) | 0.76670 (4) | 0.01997 (11) |
| Cl1 | 0.32159 (16) | 0.50027 (5) | 1.01755 (15) | 0.0205 (3) |
| N1 | 0.4404 (7) | 0.7347 (2) | 0.5659 (5) | 0.0289 (14) |
| C1 | 0.5615 (9) | 0.7937 (3) | 0.4624 (7) | 0.0366 (19) |
| H1 | 0.643186 | 0.812241 | 0.457280 | 0.044* |
| I2 | 0.33844 (4) | 0.55063 (2) | 0.75026 (4) | 0.01986 (11) |
| Cl2 | 0.36316 (19) | 0.54909 (6) | 1.26078 (14) | 0.0278 (4) |
| N2 | 0.2232 (7) | 0.9965 (2) | −0.0317 (5) | 0.0284 (14) |
| C2 | 0.5502 (8) | 0.7620 (3) | 0.5512 (7) | 0.0346 (18) |
| H2 | 0.626199 | 0.758897 | 0.607178 | 0.041* |
| Cl3 | 0.45076 (19) | 0.65490 (7) | 1.27684 (15) | 0.0277 (4) |
| C3 | 0.3349 (8) | 0.7400 (2) | 0.4888 (6) | 0.0265 (15) |
| H3 | 0.255056 | 0.720864 | 0.497785 | 0.032* |
| Cl4 | 0.4745 (2) | 0.71377 (6) | 1.04655 (16) | 0.0308 (4) |
| C4 | 0.3349 (8) | 0.7723 (2) | 0.3944 (6) | 0.0291 (16) |
| Cl5 | 0.255937 | 0.775788 | 0.341925 | 0.035* |
| Cl6 | 0.4541 (9) | 0.7993 (2) | 0.3794 (6) | 0.0290 (16) |
| C6 | 0.4776 (8) | 0.8351 (3) | 0.2821 (7) | 0.0307 (16) |
| C7 | 0.575422 | 0.833443 | 0.255902 | 0.037* |
| Cl7 | 0.3761 (9) | 0.8370 (3) | 0.1726 (7) | 0.0319 (17) |
| C8 | 0.307057 | 0.810670 | 0.173423 | 0.038* |
| C9 | 0.4407 (9) | 0.8410 (3) | 0.0559 (7) | 0.0328 (18) |
| C10 | 0.3756 (10) | 0.8186 (3) | −0.0507 (9) | 0.041 (2) |
| H11 | 0.289941 | 0.802314 | −0.045522 | 0.049* |
| C12 | 0.4405 (12) | 0.8214 (3) | −0.1583 (7) | 0.045 (2) |
| H12 | 0.398415 | 0.806288 | −0.226264 | 0.054* |
| C13 | 0.5575 (12) | 0.8439 (3) | −0.1709 (9) | 0.052 (3) |
| H13 | 0.597664 | 0.845191 | −0.247032 | 0.062* |
| C14 | 0.6206 (11) | 0.8650 (3) | −0.0772 (8) | 0.045 (2) |
| H14 | 0.704995 | 0.881530 | −0.087581 | 0.054* |
| C15 | 0.5657 (8) | 0.8634 (2) | 0.0336 (7) | 0.0286 (16) |
| H15 | 0.615099 | 0.878176 | 0.098356 | 0.034* |
| C16 | 0.3151 (8) | 0.8844 (3) | 0.2236 (7) | 0.0317 (16) |
| H16 | 0.229183 | 0.877278 | 0.267459 | 0.038* |
| C17 | 0.2863 (9) | 0.9255 (3) | 0.1365 (7) | 0.0345 (19) |
| H17 | 0.1784 (10) | 0.9223 (4) | 0.0598 (11) | 0.063 (3) |
| C18 | 0.120838 | 0.895069 | 0.060582 | 0.075* |
| H18 | 0.1494 (10) | 0.9574 (4) | −0.0196 (11) | 0.062 (3) |
| H19 | 0.069486 | 0.953656 | −0.070986 | 0.074* |
### Atomic displacement parameters (Å²)

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| I1  | 0.0268 (2) | 0.01597 (19) | 0.0172 (2) | 0.00231 (16) | 0.00253 (15) | 0.00356 (15) |
| Cl1 | 0.0182 (7) | 0.0156 (7) | 0.0277 (8) | −0.0016 (6) | 0.0019 (6) | 0.0031 (6) |
| N1  | 0.046 (4)  | 0.017 (3)  | 0.024 (3)  | 0.005 (3)  | 0.001 (3)  | 0.006 (2)  |
| C1  | 0.038 (4)  | 0.042 (5)  | 0.030 (4)  | −0.015 (4) | 0.011 (3)  | −0.003 (3) |
| I2  | 0.0240 (2) | 0.0190 (2) | 0.0166 (2) | −0.00125 (16) | 0.00060 (15) | −0.00368 (15) |
| Cl2 | 0.0359 (9) | 0.0298 (9) | 0.0178 (7) | 0.0041 (7)  | 0.0029 (7)  | 0.0089 (6)  |
| N2  | 0.039 (4)  | 0.029 (3)  | 0.017 (3)  | 0.012 (3)  | 0.004 (3)  | 0.008 (2)  |
| C2  | 0.030 (4)  | 0.038 (4)  | 0.036 (4)  | 0.008 (3)  | −0.001 (3) | 0.000 (3)  |
| Cl3 | 0.0316 (9) | 0.0345 (9) | 0.0170 (7) | −0.0033 (7) | 0.0026 (6) | −0.0080 (7) |
| C3  | 0.037 (4)  | 0.021 (3)  | 0.022 (3)  | −0.011 (3) | 0.005 (3)  | 0.003 (3)  |
| Cl4 | 0.0479 (11) | 0.0180 (8) | 0.0268 (8) | −0.0092 (7) | 0.0075 (8) | −0.0041 (6) |
| C4  | 0.042 (4)  | 0.020 (3)  | 0.024 (4)  | 0.003 (3)  | −0.012 (3) | 0.001 (3)  |
| C5  | 0.050 (5)  | 0.018 (3)  | 0.019 (3)  | −0.006 (3) | 0.007 (3)  | 0.001 (3)  |
| C6  | 0.032 (4)  | 0.030 (4)  | 0.030 (4)  | 0.002 (3)  | −0.002 (3) | −0.002 (3) |
| C7  | 0.040 (4)  | 0.027 (4)  | 0.028 (4)  | −0.002 (3) | 0.003 (3)  | 0.007 (3)  |
| C8  | 0.042 (4)  | 0.025 (4)  | 0.032 (4)  | 0.018 (3)  | 0.018 (3)  | 0.019 (3)  |
| C9  | 0.047 (5)  | 0.021 (4)  | 0.055 (5)  | −0.002 (3) | 0.004 (4)  | 0.008 (4)  |
| C10 | 0.086 (8)  | 0.032 (4)  | 0.016 (3)  | 0.023 (5)  | −0.004 (4) | −0.002 (3) |
| C11 | 0.081 (8)  | 0.038 (5)  | 0.038 (5)  | 0.025 (5)  | 0.015 (5)  | 0.005 (4)  |
| C12 | 0.063 (6)  | 0.040 (5)  | 0.034 (5)  | 0.022 (4)  | 0.029 (4)  | 0.013 (4)  |
| C13 | 0.041 (4)  | 0.020 (3)  | 0.025 (4)  | −0.002 (3) | 0.001 (3)  | 0.006 (3)  |
### Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°) |
|-----------------------|--------------|-----------|
| I1—C27                | 2.110 (6)    |           |
| C11—C29               | 1.725 (6)    |           |
| N1—C3                 | 1.318 (10)   |           |
| N1—C2                 | 1.327 (11)   |           |
| C1—C2                 | 1.348 (11)   |           |
| C1—C5                 | 1.375 (12)   |           |
| C1—H1                 | 0.9500       |           |
| I2—C28                | 2.115 (6)    |           |
| C12—C30               | 1.718 (6)    |           |
| N2—C18                | 1.314 (11)   |           |
| N2—C17                | 1.327 (12)   |           |
| C2—H2                 | 0.9500       |           |
| C13—C31               | 1.725 (6)    |           |
| C3—C4                 | 1.397 (10)   |           |
| C3—H3                 | 0.9500       |           |
| C14—C32               | 1.725 (7)    |           |
| C4—C5                 | 1.397 (11)   |           |
| C4—H4                 | 0.9500       |           |
| C5—C6                 | 1.513 (10)   |           |
| C6—C7                 | 1.541 (11)   |           |
| C6—C20                | 1.588 (10)   |           |
| C6—H6                 | 1.0000       |           |
| C7—C8                 | 1.472 (10)   |           |
| C7—C14                | 1.583 (11)   |           |
| C7—H7                 | 1.0000       |           |
| C8—C13                | 1.393 (11)   |           |

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| Bond        | Distance (Å) | Bond        | Distance (Å) | Comment |
|-------------|--------------|-------------|--------------|---------|
| C8—C9       | 1.472 (13)   | C26—H26    | 0.9500       |         |
| C9—C10      | 1.381 (13)   | C27—C28    | 1.406 (9)    |         |
| C9—H9       | 0.9500       | C27—C32    | 1.414 (9)    |         |
| C10—C11     | 1.309 (15)   | C28—C29    | 1.400 (9)    |         |
| C10—H10     | 0.9500       | C29—C30    | 1.396 (9)    |         |
| C11—C12     | 1.335 (15)   | C30—C31    | 1.389 (9)    |         |
| C11—H11     | 0.9500       | C31—C32    | 1.389 (9)    |         |
| C3—N1—C2    | 117.0 (6)    | C19—C15—C14| 124.7 (8)    |         |
| C2—C1—C5    | 119.6 (8)    | C15—C16—C17| 120.8 (10)   |         |
| C2—C1—H1    | 120.2        | C15—C16—H16| 119.6        |         |
| C5—C1—H1    | 120.2        | C17—C16—H16| 119.6        |         |
| C18—N2—C17  | 114.8 (7)    | N2—C17—C16| 125.5 (9)    |         |
| N1—C2—C1    | 124.5 (8)    | N2—C17—H17| 117.2        |         |
| N1—C2—H2    | 117.7        | C16—C17—H17| 117.2        |         |
| C1—C2—H2    | 117.7        | N2—C18—C19 | 122.2 (9)    |         |
| N1—C3—C4    | 123.2 (7)    | N2—C18—H18 | 118.9        |         |
| N1—C3—H3    | 118.4        | C19—C18—H18| 118.9        |         |
| C4—C3—H3    | 118.4        | C15—C19—C18| 119.9 (8)    |         |
| C5—C4—C3    | 118.2 (7)    | C15—C19—H19| 120.1        |         |
| C5—C4—H4    | 120.9        | C18—C19—H19| 120.1        |         |
| C3—C4—H4    | 120.9        | C14—C20—C21| 118.6 (6)    |         |
| C1—C5—C4    | 117.4 (7)    | C14—C20—C6 | 89.1 (6)     |         |
| C1—C5—C6    | 115.7 (7)    | C21—C20—C6 | 120.3 (6)    |         |
| C4—C5—C6    | 126.9 (7)    | C14—C20—C6 | 124.4 (7)    |         |
| C5—C6—C7    | 119.1 (7)    | C21—C20—C6 | 118.1 (7)    |         |
| C5—C6—C20   | 115.8 (6)    | C6—C20—H20 | 122.8 (7)    |         |
| C7—C6—C20   | 89.3 (6)     | C6—C20—C21 | 109.1        |         |
| C5—C6—H6    | 110.3        | C26—C21—C22| 117.4 (7)    |         |
| C7—C6—H6    | 110.3        | C26—C21—C20| 124.4 (7)    |         |
| C20—C6—H6   | 110.3        | C22—C21—C20| 118.1 (7)    |         |
| C8—C7—C6    | 115.5 (7)    | C23—C22—C21| 122.8 (7)    |         |
| C8—C7—H7    | 115.4 (6)    | C23—C22—H22| 118.6        |         |
| C6—C7—C14   | 88.6 (6)     | C22—C23—C24| 119.9 (7)    |         |
| C8—C7—H7    | 111.8        | C22—C23—H23| 120.0        |         |
| C6—C7—H7    | 111.8        | C24—C23—H23| 120.0        |         |
| C14—C7—H7   | 111.8        | C23—C24—C25| 117.5 (8)    |         |
| C13—C8—C7   | 126.4 (8)    | C23—C24—H24| 121.3        |         |
| C13—C8—C9   | 113.4 (7)    | C25—C24—H24| 121.3        |         |
| C7—C8—C9    | 120.2 (8)    | C26—C25—C24| 121.0 (8)    |         |
| C10—C9—C8   | 119.2 (8)    | C26—C25—H25| 119.5        |         |
| C10—C9—H9   | 120.4        | C24—C25—H25| 119.5        |         |
| C8—C9—H9    | 120.4        | C21—C26—C25| 121.3 (7)    |         |
| C11—C10—C9  | 122.9 (9)    | C21—C26—H26| 119.3        |         |
| C11—C10—H10 | 118.5        | C25—C26—H26| 119.3        |         |
| C9—C10—H10  | 118.5        | C28—C27—C32| 118.6 (6)    |         |
| C10—C11—C12 | 120.3 (9)    | C28—C27—I1 | 122.2 (5)    |         |
| C10—C11—H11 | 119.9        | C32—C27—I1 | 119.2 (5)    |         |
C12—C11—H11  119.9  C12—C13—C1  121.1 (10)  C29—C28—C27  119.8 (6)
C11—C12—C13  119.5  C29—C28—C12  118.6 (4)  C27—C28—I2  121.6 (4)
C11—C12—H12  119.5  C28—C27—C2  120.6 (6)  C28—C27—I2  121.0 (4)
C13—C12—H12  119.5  C30—C29—C27  118.6 (4)  C30—C29—C28  121.6 (4)
C12—C13—C8  123.1 (8)  C30—C29—C31  118.4 (5)  C30—C29—Cl1  120.1 (6)
C12—C13—H13  118.4  C28—C27—C30  120.6 (6)  C28—C27—I2  121.0 (4)
C8—C13—H13  118.4  C31—C30—C28  120.1 (6)  C31—C30—C29  120.3 (5)
C20—C14—C15  118.8 (7)  C31—C30—Cl1  120.3 (5)  C31—C30—Cl2  120.3 (5)
C20—C14—C7  90.1 (6)  C29—C30—Cl2  119.6 (5)  C29—C30—C12  118.0 (5)
C15—C14—C7  118.3 (6)  C30—C31—C32  119.8 (6)  C30—C31—C32  120.2 (5)
C20—C14—H14  109.4  C30—C31—Cl3  120.0 (5)  C30—C31—Cl3  121.1 (6)
C15—C14—H14  109.4  C32—C31—Cl3  120.2 (5)  C31—C32—C27  118.7 (5)
C7—C14—H14  109.4  C31—C32—Cl4  121.1 (6)  C31—C32—Cl4  118.7 (5)
C16—C15—C19  116.8 (8)  C31—C32—Cl4  120.2 (5)  C31—C32—Cl4  120.2 (5)
C16—C15—C14  118.5 (9)  C27—C32—Cl4  120.2 (5)  C27—C32—Cl4  120.2 (5)

Hydrogen-bond geometry (Å, º)

| D—H···A  | D—H | H···A | D···A | D—H···A |
|---------|-----|------|------|---------|
| C17—H17···Cl2i | 0.95 | 2.69 | 3.632 (10) | 172 |

Symmetry code: (i) x−1/2, −y+3/2, z−3/2.