

1-butyl-2,3-bis(dicyclohexylamino)cyclopropeniminium chloride benzene solvate

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Abstract

1-butyl-2,3-bis(dicyclohexylamino)cyclopropenimine (**1**) crystallizes from benzene and hexanes in the presence of HCl as a monobenzene solvate of the hydrochloride salt, [1H]Cl·C₆H₆, in the $P2_1/n$ space group. The protonation of **1** results in the generation (of an aromatic structure based upon the delocalization of the cyclopropene double bond around the cyclopropene ring, giving three intermediate C—C bond lengths of ~1.41 Å, and the delocalization of imine-type C—N double bond, giving three intermediate C—N bond lengths of ~1.32 Å. Ion-ion and ion-benzene packing interactions are described and illustrated.

1. Chemical context

Pentasubstituted diaminopropenimines are a relatively new class of superbases that operate via the establishment of a stable aromatic electronic delocalization upon protonation. Originally reported as four-electron Lewis donors (Bruns, *et al.*, 2010), a more recently exploited application for the use of pentasubstitution is that of a superbase, with one of the six nitrogen coordination sites available for protonation, making these molecules facile initiators of stereoselective Michael (Bandar & Lambert, 2012) and Mannich reactions (Bandar & Lambert, 2013), hydroaminations (Mirabdolbaghi & Dudding, 2015), and ring-opening polymerization (Stukenbroeker *et al.*, 2015, Xu *et al.*, 2018). A number of examples of acid salts of these species have been structurally characterized, permitting direct observation of the aromatized cyclopropeniminium structures (Stukenbroeker *et al.*, 2015, Bruns *et al.*, 2010, Bandar *et al.*, 2015, Belding & Dudding, 2014, Guest *et al.*, 2020, Kozma *et al.*, 2015, Belding *et al.*, 2016, Bandar & Lambert, 2012, 2013, Mirabdolbaghi & Dudding, 2015). Examples of free-base pentasubstituted diaminopropenimines are uncommon, and these are typically only obtained with aromatic substituents at the imine position, which decreases the basicity of the imine by the delocalization of the nitrogen lone pair *p*-orbital into the aromatic group, facilitating isolation (Guest *et al.*, 2020, Kozma *et al.*, 2015, Bruns *et al.*, 2010). Some of these (Guest *et al.*, 2020, Kozma *et al.*, 2015, Belding & Dudding, 2014) are bis-(cyclopropenimine) variants of the famous "proton sponge", 1,8-Bis(dimethylamino)naphthalene and related classes of bifunctional Lewis superbases (Alder *et al.*, 1968). The only other example, to our knowledge, is an *N*-aminosubstituted example, which also decreases the basicity of the nitrogen lone pair by induction, a minor resonance structure delocalizing the double bond into the N—N contact, and, in the crystal structure, a nearby hydrogen bond with a water proton (Bruns *et al.*, 2010).

1-butyl-2,3-bis(dicyclohexylamino)cyclopropenimine (**1**) (see **Scheme 1**) is a newer version of superbase with improved basicity, which has been explored as a catalyst for ring-opening polymerization. Cyclopropenimines have a conjugate acid pK_a of about 27, an improvement over that of the superbase 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (BTMG) which has a pK_a of 23.56 (Bandar & Lambert, 2012). This allows **1** to deprotonate a lactide and initiate polymerization in the synthesis of polylactic acid, as shown in **Figure 1** (Stukenbroeker *et al.*, 2015). **1** can mediate the polymerization of lactic acid to 99% completion in 10 minutes or less. However, no X-ray crystal structure of the free base, nor an acid salt of this superbase is reported. In this report we provide the first X-ray crystallographic structure of a

benzene solvate of the hydrochloride salt $[1H]Cl \cdot C_6H_6$.

2. Structural commentary

$[1H]Cl$ crystallizes in the $P2_1/n$ space group on a general position as a closely associated ion pair, with the protonation site at the *n*-butyl imine as expected, and one formula unit in the asymmetric unit, as well as one benzene solvate, also on a general position (**Figure 2**). The molecule and solvate are generally well ordered, except for the δ methyl carbon of the *n*-butyl group, which shows a mild wagging disorder. This disorder was treated with a two-site disorder model.

Free-base **1** would be expected to have localized double bonds at the *n*-butylimine C=N position, and at the opposing cyclopropene position (**Scheme 1**). In the isolated free base of 1-mesityl-2,3-bis(diisopropylamino)cyclopropenimine (Bruns, *et al.*, 2010), the unprotonated C=N imine is 1.2951 (14) Å in length, while the C—N bonds to the tertiary amines are longer, at an average of 1.3494 (10) Å. The localized cyclopropene double bond is shorter, at 1.3712 (14) Å, than the single bonded C—C cyclopropene contacts at an average of 1.4155 (10) Å. Protonation of the *n*-butylimine position during crystal growth results in all nitrogen atoms being three-coordinate, leading to delocalization of the imine double bond character across all three C—N contacts. Correspondingly, the cyclopropene double bond is delocalized around the ring, giving a three-membered aromatic system. In $[1H]Cl$, the central C_3N_3 triangle is thus highly planar, with the six atoms exhibiting an RMS deviation of only 0.0052 Å from the best-fit plane of the six atoms. The three C—N bonds are approximately equal in length, with the two tertiary cyclohexylamine positions having C—N lengths of 1.3279 (13) Å on average. The C—N bond to the protonated butyl nitrogen is only slightly shorter at 1.319 (2) Å. The three cyclopropene C—C bonds exhibit lengths consistent with aromaticity; the unique C—C bond opposite the *n*-butyl group is 1.388 (2) Å, while the other two C—C bonds are similar or slightly shorter at 1.377 (2) and 1.383 (2) Å. Though these latter two bonds are equivalent under molecular point symmetry, their differences are attributed to the asymmetric crystal packing environment of the $P2_1/n$ space group. The comparable nature of the bond metrics of the three C—N bonds and the three cyclopropenyl C—C bonds is consistent with aromatization, and an analogous aromatization of the C_3N_3 core of 1-mesityl-2,3-bis(diisopropylamino)cyclopropeniminium tetrafluoroborate was observed in the crystal structure of this salt (Bruns, *et al.*, 2010). See **Table 1** for C_3N_3 bond metrics.

The comparison between free-base forms of cyclopropenimine (Bruns, *et al.*, 2010) and the protonated forms demonstrate aromatization upon protonation, and explain the behavior of **1** as a superbases. While alkylimines are typically weak bases (pK_a of conjugate acid ranges from about 2–5, (Fraser *et al.*, 1983), the pK_a of $1H^+$ is a staggering 27 (Bandar & Lambert, 2012), more on the scale of a C—H bond. The drastic difference in basicity between typical alkylimines and **1** is explainable by the observed aromatization upon protonation. As a result, the 1H resonance of the N—H hydrogen in $[1H]Cl$ is a sharp singlet at 7.4 ppm in deuterated chloroform, suggesting little to no exchange like that typically observed for broad N—H resonances. The stabilization of a molecule by aromatization is quantified by the Dewar Resonance Energy (DRE), which ranges from about 6–25 kJ/mol per π electron (Slayden & Liebman, 2001). Thus in the case of **1**, aromatic stabilization between 12 and 50 kJ/mol upon protonation explains the large reported basicity.

3. Supramolecular features

Interionic/molecular interactions were examined using packing diagrams, and by the determination of partial atomic charge from Hirshfeld analysis. In the following discussion Hirshfeld charges are presented in parenthesis. The proton of the butylimine group (+0.121) interacts strongly with the chloride ion (−0.666) at a short $H \cdots Cl$ distance of 2.26 (2) Å. The chloride is positioned in a pocket surrounded by hydrogen atoms. In addition to the strong interaction with the acidic N—H proton, the chloride resides 2.8152 (7) Å from a benzene solvate proton, $H6A$ (+0.046), and 2.7169 (6) Å

from an intramolecular axial cyclohexyl proton, H29A (+0.050). The crystal packing demonstrates that the C_3N_3 planes of all molecules pack parallel to each other (as required by the space group symmetry), with a normal slightly oblique to the 101 plane (see **Figure 3**). The molecular planes stack in a staggered fashion via intervening inversion centers at the origin (**Figure 3**, red) and at the center of the a edge (**Figure 3**, teal). One face of the benzene solvate interacts distally with the cyclohexyl group of one $1H^+$ ion (closest atomic $C\cdots C$ distance: 3.829 (3) Å, **Figure 3**, green line), while the other face interacts distally with the disordered methyl group of the n -butyl chain (closest atomic $C\cdots C$ distance: 4.29 (3) Å, **Figure 4**, orange line). The benzene interacts weakly with two chloride ions approximately along its equatorial plane (**Figure 3**, blue lines), one via H6S (+0.069) with $H\cdots Cl = 2.8152$ (7) Å, also shown in **Figure 2**, and the other via H3S (+0.062) with $H\cdots Cl = 2.8365$ (7) Å. These benzene-chlorine interactions form a channel along the 101 plane, each channel situated 1/4 of the way along the b axis (**Figure 4**, top). Viewed from 90° along the [101] direction, the benzene solvates sit along a second channel, with the chloride ions sitting at the intersections of both channels, providing ionic bonds to the surrounding $1H^+$ cations (**Figure 4**, bottom). In this latter view, it is apparent that along the [101] direction, the chloride ions are positioned between the axial protons H26 (+0.058) and H29B (+0.059) of the flanking cyclohexyl groups. In summary, the $1H^+$ cations interact with each other and through the benzene solvate via their alkyl groups, and the chloride counterion is situated in a pocket of cyclohexyl and benzene $C-H$ contacts, with the proximal $N-H$ interaction on one side.

4. Database survey

In addition to the pentasubstituted examples discussed above, a survey of the CCDC Crystal Structure Database (Groom *et al.*, 2016) for cyclopropenimines reveals a number of other relevant structures. The parent (unsubstituted) diamino-propeniminium cation has been structurally characterized with chloride and iodide counteranions (UJAVEI, Mishiro *et al.*, 2016). Aprotic hexasubstituted examples are reported, and represent planar polyatomic cations (AHUVEH, Holthoff *et al.*, 2020, DOSRUB, Abdelbassit *et al.*, 2019, FURCIH, Clark *et al.*, 1995, GAXYEJ, Radhakrishnan *et al.*, 1987b, GERXUX02, Butchard *et al.*, 2012, GUNDUR, Curnow & Senthoooran, 2020, IFAGUU, Curnow *et al.*, 2018, LAYYOC01, Jin *et al.*, 2018, NUYBOB, Guest *et al.*, 2020, SERVIW, Kniep *et al.*, 2013, TUSDOD, Radhakrishnan *et al.*, 1987a, UGITIQ, Barthes *et al.*, 2020, XIKYAT01, ZABFUG, Wallace *et al.*, 2015, XOSTIL, XOSTOR, XOSTUX, XOSVAF, XOSVEJ, Abdelbassit & Curnow, 2019, YUVRAK, YUWJOR, Jungbauer *et al.*, 2015). Another class of variants includes cyclopropenimines tethered to ferrocene nuclei (TURNUQ, Bruns *et al.*, 2010, BEBPIK, BEBRAE, BEBREI, BEBRIM, BEBROS, Jess *et al.*, 2017). There are a few structural studies of Lewis complexes with metal ions (BEBRIM, Jess *et al.*, 2017, UGITOW, UGITUC, Barthes *et al.*, 2020, YOQPOM, Chen *et al.*, 2019, TURNOK, Bruns *et al.*, 2010) or other boron-based Lewis acids (NUYBOB, Guest *et al.*, 2020, TURPOM, Bruns *et al.*, 2010). One structural report of a trisubstituted cyclopropenimine is noted (XEXGEP, Xu *et al.*, 2018), as well as several types of oligomeric versions (OGOLUT, OGORAF, OGOWOY, OGOWUE, OGOXAL, OGOXEP, OGOXIT, OGOXOZ, OGOXUF, OGOYAM, Kozma *et al.*, 2015, SUSWAG, SUSWOU, Nacsa & Lambert, 2015).

5. Synthesis and crystallization

Initially, crystals of $[1H]Cl \cdot C_6H_6$ were obtained from the commercial sample of **1** via a double-vial apparatus by dissolution of 1-butyl-2,3-bis(dicyclohexylamino)cyclopropenimine (**1**) in benzene in an inner vial, and charging the outer vial with hexanes. After diffusion for a few days at room temperature, powdery solid and a few colorless crystals of $[1H]Cl \cdot C_6H_6$ were observed inside. The yield of crystalline $[1H]Cl \cdot C_6H_6$ was significantly improved by the addition of HCl. To a glass shell vial containing 7.2 mg of 1-butyl-2,3-bis(dicyclohexylamino)cyclopropenimine, 2 mL of benzene was added. A drop of dilute HCl (0.730 M) was added. This was diffused with 3 mL hexanes in the outer vial for 2-3

days. Crystallization works best when the drop is not in contact with the walls of the vial where the crystals grow. Crystals were isolated by decanting the liquid from the inner vial using a disposable pipette, and taking care to remove the visible aqueous HCl droplet with the first pipette draw. After removing the mother liquor, the crystals were rinsed with hexanes. Yield 6.3 mg (70%). Yields in this small-scale preparation ranged from 22% to 70% across multiple attempts. ^1H NMR [ppm] (400 MHz, CDCl_3): δ (ppm): 0.97 (t, 3H, Me), 1.62-1.82 (m, 14H, Cy and Bu), 1.62-1.76 (m, 14H, Cy and Bu), 1.80 (d, 8H, Cy- β -H), 1.96 (d, 8H, Cy- β -H), 3.34 (tt, 4H, Cy- α -H), 3.56 (t, 2H, Bu- α -H), 7.4 (s, 1H, NH). ^{13}C NMR [ppm] (400 MHz, CDCl_3): δ (ppm): 13.97, 19.94, 24.58, 25.84, 32.34, 33.79, 46.15, 59.55, 114.01, 128.35. FTIR (cm^{-1}): 2926 (m), 2851 (m), 1503 (s), 1445 (m), 1383 (w), 1374 (w), 1345 (w), 1324 (w), 1253 (w), 1188 (w), 1180 (w), 1102 (w), 1092 (w), 1004 (w), 895 (w), 696 (m). Anal. Calcd for $\text{C}_{31}\text{H}_{53}\text{N}_3 \cdot 0.5 \text{C}_6\text{H}_6$ (%): C, 76.31; H, 10.38; N, 7.22. Found: C, 75.873; H, 10.83; N, 7.24. MP: 80-83 (decomposes).

6. Refinement

Single-crystal X-ray crystallographic data were obtained on a Bruker D8 Quest PHOTON 100 diffractometer with an Oxford Cryostream 700 low-temperature device. The radiation was from a sealed-tube molybdenum $\text{K}\alpha$ source with a TRIUMPH monochromator. Crystals were typically multiple, and a single piece was cut away with a razor blade, mounted on a MiTeGen loop with paratone-N oil, and collected at 100K in ω/ϕ scansets. Integration was performed using SAINT, and data were reduced and absorption-corrected using SADABS (Bruker, 2008). Space group determination was performed using XPREP (Sheldrick, 2008), and the structure was solved using intrinsic phasing using SHELXT (Sheldrick, 2015b). The structural model of $[\text{1H}]\text{Cl} \cdot \text{C}_6\text{H}_6$ was refined using the least-squares approach with the ShelX package (Sheldrick, 2015a) with Olex2 as a GUI (Dolomanov *et al.*, 2009). A disordered methyl group was treated with a two-site disorder model, with atom positions freely refined, and relative occupancies refined using Free Variable 2 with a final ratio of 0.71 (3): 0.29 (3). RIGU/SIMU restraints were applied to the wagging methyl group. C-H hydrogen atoms were treated using a standard riding model. The imine proton was located as a peak in the Fourier difference map and was freely refined. Crystal data, data collection and structure refinement details are summarized in Table 2. Hirshfeld charge was determined at the 3-21-g/B3LYP level of theory by iterative computation of electronic structure of $[\text{1H}]\text{Cl} \cdot \text{C}_6\text{H}_6$ using ORCA (Neese, 2018) followed by re-refinement of the structure using non-spherical formfactors computed using NoSpherA2 (Kleemiss, 2021), and repeating the process until the structure converged. Hirshfeld charges resulting from this approach are given in Table 3.

Table 1

Comparative Bond Lengths (Å) for 1-mesityl-2,3-bis(diisopropylamino)cyclopropenimine, 1-mesityl-2,3-bis(diisopropylamino)cyclopropeniminium (Bruns, *et al.*, 2010), and 1-*n*-butyl-2,3-bis(dicyclohexyl)cyclopropeniminium.

	$\text{Mes}(\text{C}_3\text{N}_3)\text{Pr}_4$	$[\text{Mes}(\text{C}_3\text{N}_3\text{H})\text{Pr}_4]\text{BF}_4$	$[\text{Bu}(\text{C}_3\text{N}_3\text{H})\text{Cy}_4]\text{Cl}([\text{1H}]\text{Cl})$
C-N(imine)	1.2951 (14)	1.3342 (16)	1.319 (2)
C-N(amine)	1.3450 (14)/1.3539 (14)	1.3205 (15)/1.3286 (16)	1.3248 (17)/1.331 (2)
C-C(para)	1.3712 (14)	1.3984 (17)	1.388 (2)
C-C(meta)	1.4202 (14)/1.4108 (14)	1.3792 (16)/1.3827 (16)	1.377 (2)/1.3831 (19)

Divided entries refer to separate, related pairs of atoms and their associated metrics, e.g., 1.3450 (14)/1.3539 (14) denotes 2 distances for the two C-N(amine) contacts.

Table 2

Experimental details

Crystal data	
Chemical formula	Cl·C ₃₁ H ₅₄ N ₃ ·C ₆ H ₆
M_r	582.33
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	12.253 (3), 22.699 (7), 12.884 (3)
β (°)	104.164 (7)
V (Å ³)	3474.6 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.14
Crystal size (mm)	0.55 × 0.53 × 0.16
Data collection	
Diffractometer	Bruker D8 Quest Photon 100 Diffractometer
Absorption correction	Multi-scan 54471 Corrected reflections written to file z162_4_0m.hkl Estimated minimum and maximum transmission: 0.6619 0.7459 The ratio of these values is more reliable than their absolute values! Additional spherical absorption correction applied with $\mu^*r = 0.2000$
$T_{\min}, T_{\max}$	0.662, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	48756, 8072, 6516
R_{int}	0.044
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.055, 0.136, 1.02
No. of reflections	8072
No. of parameters	385
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.55, -0.40

Computer programs: COSMO (BrukerAXS), SAINT V8.40A (Bruker, 2019), XS (Sheldrick, 2015a), XL (Sheldrick, 2015a), Olex2 1.5 (Dolomanov *et al.*, 2009).

Table 3

Hirshfeld Charges of Atoms in [1H]Cl $\hat{\text{A}}$ ·C₆H₆.

Cl1	-0.666
N1	-0.048
N2	-0.027
N3	-0.018
C1	0.026
C2	0.014
C3	0.024

C4	-0.036
C5	-0.102
C6	-0.095
C7	-0.133
C8	-0.011
C9	-0.103
C10	-0.093
C11	-0.097
C12	-0.088
C13	-0.093
C14	-0.008
C15	-0.097
C16	-0.094
C17	-0.098
C18	-0.098
C19	-0.101
C20	-0.005
C21	-0.094
C22	-0.093
C23	-0.093
C24	-0.091
C25	-0.093
C26	-0.002
C27	-0.096
C28	-0.094
C29	-0.099
C30	-0.093
C31	-0.097
C1S	-0.058
C2S	-0.071
C3S	-0.078
C4S	-0.084
C5S	-0.082
C6S	-0.064
H1S	0.071
H6S	0.069
H5S	0.065
H4S	0.062
H3S	0.062
H2S	0.056
H4a	0.051
H4b	0.075
H5a	0.061
H5b	0.042
H6aa	0.046
H6ab	0.055
H7a	0.05
H7b	0.039
H7c	0.051
H8	0.072
H9a	0.05

H9b	0.06
H10a	0.061
H10b	0.061
H11a	0.061
H11b	0.049
H12a	0.057
H12b	0.053
H13a	0.059
H13b	0.049
H14	0.066
H15a	0.057
H15b	0.062
H16a	0.051
H16b	0.052
H17a	0.055
H17b	0.051
H18a	0.056
H18b	0.062
H19a	0.055
H19b	0.065
H20	0.06
H21a	0.055
H21b	0.055
H22a	0.05
H22b	0.056
H23a	0.056
H23b	0.052
H24a	0.051
H24b	0.056
H25a	0.057
H25b	0.057
H26	0.058
H27a	0.049
H27b	0.062
H28a	0.044
H28b	0.057
H29a	0.05
H29b	0.059
H30a	0.061
H30b	0.039
H31a	0.047
H31b	0.064
H1	0.121

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Figure 1

Catalytic ring opening polymerization mediated by **1**.

Figure 2

Thermal ellipsoid plot of the asymmetric unit of $[1\text{H}]\text{Cl}\cdot\text{C}_6\text{H}_6$ with ellipsoids set at 50% probability. Hydrogen atoms shown as small spheres.

Figure 3

Partially packed thermal ellipsoid plot of $[1\text{H}]\text{Cl}\cdot\text{C}_6\text{H}_6$ showing neighboring intermolecular/interionic nearest-neighbor interactions.

Figure 4

Top: Packed unit cell viewed along the 101 plane. Bottom: Packed unit cell viewed along the $[101]$ direction.

supporting information

1-butyl-2,3-bis(dicyclohexylamino)cyclopropeniminium chloride benzene solvate

Gaby Muñoz Sánchez and Michael J. Zdilla*

Computing details

Data collection: COSMO (BrukerAXS); cell refinement: *SAINT* V8.40A (Bruker, 2019); data reduction: *SAINT* V8.40A (Bruker, 2019); program(s) used to solve structure: XS (Sheldrick, 2015a); program(s) used to refine structure: XL (Sheldrick, 2015a); molecular graphics: Olex2 1.5 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 1.5 (Dolomanov *et al.*, 2009).

1-butyl-2,3-bis(dicyclohexylamino)cyclopropenimine*Crystal data*

Cl·C₃₁H₅₄N₃·C₆H₆
 $M_r = 582.33$
 Monoclinic, $P2_1/n$
 $a = 12.253 (3) \text{ \AA}$
 $b = 22.699 (7) \text{ \AA}$
 $c = 12.884 (3) \text{ \AA}$
 $\beta = 104.164 (7)^\circ$
 $V = 3474.6 (16) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 1280$

$D_x = 1.113 \text{ Mg m}^{-3}$
 Melting point: 356 K
 Mo $K\alpha$ radiation, $\lambda = 0.71076 \text{ \AA}$
 Cell parameters from 9959 reflections
 $\theta = 2.6\text{--}29.6^\circ$
 $\mu = 0.14 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Chunk, colourless
 $0.55 \times 0.53 \times 0.16 \text{ mm}$

Data collection

Bruker D8 Quest Photon 100 Diffractometer
 Radiation source: sealed tube
 Detector resolution: $10.417 \text{ pixels mm}^{-1}$
 ϕ and ω scans

Absorption correction: multi-scan
 54471 Corrected reflections written to file
 z162_4_0m.hkl Estimated minimum and maximum
 transmission: 0.6619 0.7459 The ratio of these values
 is more reliable than their absolute values! Additional
 spherical absorption correction applied with $\mu^*r =$
 0.2000
 $T_{\min} = 0.662$, $T_{\max} = 0.746$
 48756 measured reflections
 8072 independent reflections
 6516 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 2.6^\circ$
 $h = -16 \rightarrow 14$
 $k = -29 \rightarrow 29$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.136$

$S = 1.02$
 8072 reflections
 385 parameters
 6 restraints

Primary atom site location: dual
 Secondary atom site location: difference Fourier map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent and
 constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 2.3777P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL2018/3* (Sheldrick
 2018), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0081 (7)

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 ($\text{\AA}^2$) for (I)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C11	0.44296 (4)	0.74552 (2)	0.69373 (3)	0.03152 (13)	
N1	0.36809 (13)	0.61997 (7)	0.64021 (11)	0.0287 (3)	
N2	0.28059 (11)	0.47671 (6)	0.52228 (11)	0.0214 (3)	
N3	0.16710 (10)	0.61804 (5)	0.38294 (10)	0.0153 (3)	
C1	0.30625 (12)	0.58844 (7)	0.56140 (12)	0.0187 (3)	
C2	0.27226 (12)	0.53505 (7)	0.51360 (11)	0.0161 (3)	
C3	0.23000 (12)	0.58703 (6)	0.46257 (11)	0.0152 (3)	
C4	0.42658 (14)	0.59655 (8)	0.74386 (13)	0.0258 (4)	
H4A	0.482194	0.625847	0.781488	0.031*	
H4B	0.468020	0.560497	0.733256	0.031*	
C5	0.34533 (15)	0.58187 (9)	0.81298 (14)	0.0297 (4)	
H5A	0.299691	0.617193	0.818508	0.036*	
H5B	0.293374	0.550454	0.777551	0.036*	
C6	0.40470 (18)	0.56176 (11)	0.92421 (15)	0.0417 (5)	
H6AA	0.453690	0.528001	0.917569	0.050*	0.71 (3)
H6AB	0.454139	0.594103	0.959793	0.050*	0.71 (3)
H6BC	0.463745	0.589993	0.959547	0.050*	0.29 (3)
H6BD	0.438414	0.522186	0.923334	0.050*	0.29 (3)
C7	0.3303 (10)	0.5437 (7)	0.9956 (7)	0.053 (2)	0.71 (3)
H7A	0.376946	0.531504	1.065397	0.079*	0.71 (3)
H7B	0.282871	0.577033	1.005181	0.079*	0.71 (3)
H7C	0.282420	0.510733	0.962831	0.079*	0.71 (3)
C7A	0.302 (2)	0.5607 (13)	0.980 (2)	0.052 (3)	0.29 (3)
H7AA	0.329164	0.548113	1.055049	0.079*	0.29 (3)
H7AB	0.269538	0.600292	0.978288	0.079*	0.29 (3)
H7AC	0.244456	0.533150	0.942430	0.079*	0.29 (3)
C8	0.36221 (13)	0.45256 (7)	0.61774 (12)	0.0217 (3)	
H8	0.381382	0.485489	0.670631	0.026*	
C9	0.47084 (15)	0.43290 (10)	0.59447 (16)	0.0353 (4)	
H9A	0.502862	0.465328	0.559880	0.042*	
H9B	0.456679	0.398984	0.544653	0.042*	
C10	0.55473 (15)	0.41505 (11)	0.69901 (17)	0.0402 (5)	
H10A	0.624144	0.399694	0.682382	0.048*	
H10B	0.575268	0.450269	0.744965	0.048*	
C11	0.50711 (16)	0.36903 (8)	0.75884 (15)	0.0304 (4)	

H11A	0.560159	0.362242	0.829220	0.036*
H11B	0.499093	0.331562	0.718347	0.036*
C12	0.39465 (16)	0.38660 (12)	0.77577 (17)	0.0443 (6)
H12A	0.404691	0.420050	0.826542	0.053*
H12B	0.362632	0.353219	0.807993	0.053*
C13	0.31273 (15)	0.40433 (13)	0.67130 (17)	0.0502 (7)
H13A	0.295939	0.369777	0.623135	0.060*
H13B	0.241307	0.418020	0.686061	0.060*
C14	0.22900 (14)	0.43733 (7)	0.43423 (12)	0.0228 (3)
H14	0.251060	0.396403	0.459615	0.027*
C15	0.10137 (15)	0.43961 (8)	0.40904 (14)	0.0294 (4)
H15A	0.075663	0.480402	0.389687	0.035*
H15B	0.075736	0.428155	0.473345	0.035*
C16	0.04928 (19)	0.39800 (10)	0.31628 (16)	0.0421 (5)
H16A	0.065028	0.356690	0.339859	0.051*
H16B	−0.033395	0.403439	0.296143	0.051*
C17	0.09633 (19)	0.40960 (8)	0.21891 (15)	0.0388 (5)
H17A	0.064423	0.380550	0.162311	0.047*
H17B	0.073038	0.449374	0.190386	0.047*
C18	0.2230 (2)	0.40551 (9)	0.24633 (15)	0.0404 (5)
H18A	0.250416	0.415061	0.182158	0.048*
H18B	0.246121	0.364657	0.268072	0.048*
C19	0.27602 (15)	0.44745 (8)	0.33640 (13)	0.0281 (4)
H19A	0.261060	0.488590	0.311459	0.034*
H19B	0.358567	0.441498	0.356404	0.034*
C20	0.10054 (12)	0.59000 (6)	0.28437 (11)	0.0154 (3)
H20	0.121932	0.547404	0.287367	0.018*
C21	−0.02557 (12)	0.59316 (7)	0.27777 (12)	0.0208 (3)
H21A	−0.048940	0.634910	0.277906	0.025*
H21B	−0.041475	0.573704	0.341256	0.025*
C22	−0.09312 (14)	0.56299 (8)	0.17598 (14)	0.0270 (4)
H22A	−0.076043	0.520300	0.179794	0.032*
H22B	−0.174555	0.567825	0.170890	0.032*
C23	−0.06516 (14)	0.58893 (8)	0.07659 (13)	0.0273 (4)
H23A	−0.106868	0.567204	0.012491	0.033*
H23B	−0.089479	0.630630	0.068675	0.033*
C24	0.06045 (14)	0.58532 (8)	0.08384 (12)	0.0232 (3)
H24A	0.076785	0.604027	0.019878	0.028*
H24B	0.083535	0.543480	0.085098	0.028*
C25	0.12775 (12)	0.61616 (7)	0.18448 (12)	0.0188 (3)
H25A	0.109634	0.658734	0.180255	0.023*
H25B	0.209217	0.611798	0.189237	0.023*
C26	0.15551 (12)	0.68225 (6)	0.39646 (12)	0.0155 (3)
H26	0.099398	0.696644	0.331400	0.019*
C27	0.10861 (13)	0.69733 (7)	0.49275 (12)	0.0198 (3)
H27A	0.037198	0.675821	0.487607	0.024*
H27B	0.162771	0.684987	0.559541	0.024*
C28	0.08784 (14)	0.76347 (7)	0.49579 (14)	0.0235 (3)
H28A	0.028444	0.774989	0.432041	0.028*
H28B	0.060970	0.773161	0.560235	0.028*
C29	0.19481 (14)	0.79815 (7)	0.49779 (14)	0.0258 (3)

H29A	0.251074	0.790334	0.565857	0.031*
H29B	0.177627	0.840825	0.494357	0.031*
C30	0.24396 (14)	0.78122 (7)	0.40405 (14)	0.0236 (3)
H30A	0.315816	0.802469	0.410204	0.028*
H30B	0.191359	0.793486	0.336272	0.028*
C31	0.26484 (12)	0.71506 (7)	0.40078 (12)	0.0190 (3)
H31A	0.292722	0.705234	0.336957	0.023*
H31B	0.322722	0.703020	0.465293	0.023*
C1S	0.68908 (19)	0.74647 (9)	0.54411 (18)	0.0396 (5)
H1S	0.696225	0.738475	0.617844	0.048*
C2S	0.78338 (18)	0.74472 (10)	0.5024 (2)	0.0445 (5)
H2S	0.855070	0.735644	0.547561	0.053*
C3S	0.77266 (19)	0.75618 (10)	0.3953 (2)	0.0430 (5)
H3S	0.836697	0.754721	0.366155	0.052*
C4S	0.6681 (2)	0.76980 (9)	0.33078 (18)	0.0414 (5)
H4S	0.660378	0.777832	0.256966	0.050*
C5S	0.57486 (18)	0.77183 (9)	0.37275 (18)	0.0390 (5)
H5S	0.503360	0.781612	0.327955	0.047*
C6S	0.58513 (17)	0.75981 (8)	0.47859 (18)	0.0367 (4)
H6S	0.520582	0.760638	0.507068	0.044*
H1	0.3710 (18)	0.6567 (11)	0.6337 (18)	0.035 (6)*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0369 (2)	0.0277 (2)	0.0232 (2)	−0.01656 (17)	−0.00559 (16)	−0.00049 (16)
N1	0.0371 (8)	0.0193 (7)	0.0193 (7)	−0.0048 (6)	−0.0128 (6)	0.0002 (6)
N2	0.0270 (7)	0.0164 (6)	0.0174 (6)	0.0060 (5)	−0.0013 (5)	−0.0020 (5)
N3	0.0169 (6)	0.0138 (6)	0.0123 (6)	0.0014 (5)	−0.0021 (5)	−0.0010 (5)
C1	0.0179 (7)	0.0185 (7)	0.0166 (7)	0.0012 (6)	−0.0017 (6)	0.0013 (6)
C2	0.0153 (6)	0.0185 (7)	0.0129 (6)	0.0028 (5)	0.0003 (5)	−0.0009 (5)
C3	0.0142 (6)	0.0168 (7)	0.0138 (7)	−0.0005 (5)	0.0017 (5)	−0.0023 (5)
C4	0.0286 (8)	0.0260 (8)	0.0159 (7)	−0.0020 (7)	−0.0081 (6)	0.0003 (6)
C5	0.0251 (8)	0.0343 (10)	0.0262 (9)	0.0035 (7)	−0.0007 (7)	−0.0116 (7)
C6	0.0414 (11)	0.0616 (14)	0.0217 (9)	−0.0093 (10)	0.0068 (8)	−0.0050 (9)
C7	0.044 (4)	0.091 (6)	0.026 (3)	−0.019 (3)	0.012 (2)	−0.012 (3)
C7A	0.047 (7)	0.085 (8)	0.029 (5)	−0.024 (5)	0.016 (5)	−0.017 (5)
C8	0.0245 (8)	0.0200 (7)	0.0167 (7)	0.0071 (6)	−0.0023 (6)	−0.0010 (6)
C9	0.0238 (8)	0.0507 (12)	0.0337 (10)	0.0075 (8)	0.0112 (7)	0.0191 (9)
C10	0.0218 (8)	0.0586 (13)	0.0395 (11)	0.0113 (8)	0.0063 (8)	0.0230 (10)
C11	0.0353 (9)	0.0249 (9)	0.0254 (9)	0.0039 (7)	−0.0033 (7)	0.0046 (7)
C12	0.0296 (9)	0.0728 (16)	0.0298 (10)	0.0027 (10)	0.0060 (8)	0.0271 (10)
C13	0.0189 (8)	0.102 (2)	0.0284 (10)	−0.0030 (10)	0.0027 (7)	0.0339 (12)
C14	0.0334 (8)	0.0158 (7)	0.0166 (7)	−0.0001 (6)	0.0011 (6)	−0.0021 (6)
C15	0.0323 (9)	0.0330 (9)	0.0198 (8)	−0.0072 (7)	0.0003 (7)	0.0049 (7)
C16	0.0522 (12)	0.0348 (10)	0.0292 (10)	−0.0185 (9)	−0.0096 (9)	0.0069 (8)
C17	0.0635 (13)	0.0220 (9)	0.0205 (8)	−0.0053 (9)	−0.0096 (8)	−0.0035 (7)
C18	0.0667 (14)	0.0304 (10)	0.0201 (8)	0.0127 (9)	0.0030 (9)	−0.0075 (7)
C19	0.0349 (9)	0.0287 (9)	0.0205 (8)	0.0107 (7)	0.0063 (7)	−0.0022 (7)
C20	0.0157 (6)	0.0151 (7)	0.0127 (6)	0.0023 (5)	−0.0013 (5)	−0.0021 (5)
C21	0.0162 (7)	0.0268 (8)	0.0178 (7)	−0.0023 (6)	0.0007 (6)	−0.0062 (6)

C22	0.0175 (7)	0.0349 (9)	0.0251 (8)	−0.0024 (7)	−0.0015 (6)	−0.0099 (7)
C23	0.0243 (8)	0.0332 (9)	0.0182 (8)	0.0062 (7)	−0.0069 (6)	−0.0058 (7)
C24	0.0270 (8)	0.0277 (8)	0.0129 (7)	0.0058 (7)	0.0010 (6)	−0.0021 (6)
C25	0.0172 (7)	0.0231 (8)	0.0151 (7)	0.0043 (6)	0.0019 (6)	0.0003 (6)
C26	0.0170 (6)	0.0125 (7)	0.0152 (7)	0.0013 (5)	0.0005 (5)	−0.0006 (5)
C27	0.0213 (7)	0.0195 (7)	0.0185 (7)	−0.0010 (6)	0.0046 (6)	−0.0036 (6)
C28	0.0232 (8)	0.0216 (8)	0.0248 (8)	0.0012 (6)	0.0042 (6)	−0.0067 (6)
C29	0.0271 (8)	0.0170 (7)	0.0295 (9)	−0.0017 (6)	−0.0001 (7)	−0.0053 (6)
C30	0.0243 (8)	0.0164 (7)	0.0281 (8)	−0.0035 (6)	0.0024 (6)	0.0031 (6)
C31	0.0188 (7)	0.0183 (7)	0.0191 (7)	−0.0014 (6)	0.0032 (6)	0.0014 (6)
C1S	0.0548 (12)	0.0281 (10)	0.0371 (11)	−0.0012 (9)	0.0135 (9)	0.0017 (8)
C2S	0.0348 (10)	0.0405 (12)	0.0554 (14)	0.0020 (9)	0.0056 (10)	0.0035 (10)
C3S	0.0394 (11)	0.0378 (11)	0.0574 (14)	−0.0094 (9)	0.0229 (10)	−0.0042 (10)
C4S	0.0584 (13)	0.0277 (10)	0.0389 (11)	−0.0127 (9)	0.0137 (10)	−0.0011 (8)
C5S	0.0381 (10)	0.0241 (9)	0.0500 (12)	−0.0007 (8)	0.0010 (9)	−0.0026 (9)
C6S	0.0341 (10)	0.0261 (9)	0.0532 (13)	−0.0018 (7)	0.0171 (9)	−0.0077 (8)

Geometric parameters (Å, °) for (I)

N1—C1	1.319 (2)	C16—C17	1.526 (3)
N1—C4	1.453 (2)	C17—H17A	0.9900
N1—H1	0.84 (2)	C17—H17B	0.9900
N2—C2	1.331 (2)	C17—C18	1.507 (3)
N2—C8	1.4872 (19)	C18—H18A	0.9900
N2—C14	1.461 (2)	C18—H18B	0.9900
N3—C3	1.3247 (19)	C18—C19	1.519 (3)
N3—C20	1.4752 (18)	C19—H19A	0.9900
N3—C26	1.4789 (19)	C19—H19B	0.9900
C1—C2	1.377 (2)	C20—H20	1.0000
C1—C3	1.383 (2)	C20—C21	1.528 (2)
C2—C3	1.388 (2)	C20—C25	1.527 (2)
C4—H4A	0.9900	C21—H21A	0.9900
C4—H4B	0.9900	C21—H21B	0.9900
C4—C5	1.526 (3)	C21—C22	1.531 (2)
C5—H5A	0.9900	C22—H22A	0.9900
C5—H5B	0.9900	C22—H22B	0.9900
C5—C6	1.510 (3)	C22—C23	1.523 (3)
C6—H6AA	0.9900	C23—H23A	0.9900
C6—H6AB	0.9900	C23—H23B	0.9900
C6—H6BC	0.9900	C23—C24	1.521 (2)
C6—H6BD	0.9900	C24—H24A	0.9900
C6—C7	1.502 (9)	C24—H24B	0.9900
C6—C7A	1.60 (2)	C24—C25	1.526 (2)
C7—H7A	0.9800	C25—H25A	0.9900
C7—H7B	0.9800	C25—H25B	0.9900
C7—H7C	0.9800	C26—H26	1.0000
C7A—H7AA	0.9800	C26—C27	1.528 (2)
C7A—H7AB	0.9800	C26—C31	1.522 (2)
C7A—H7AC	0.9800	C27—H27A	0.9900
C8—H8	1.0000	C27—H27B	0.9900
C8—C9	1.502 (2)	C27—C28	1.525 (2)

C8—C13	1.499 (3)	C28—H28A	0.9900
C9—H9A	0.9900	C28—H28B	0.9900
C9—H9B	0.9900	C28—C29	1.524 (2)
C9—C10	1.535 (3)	C29—H29A	0.9900
C10—H10A	0.9900	C29—H29B	0.9900
C10—H10B	0.9900	C29—C30	1.525 (2)
C10—C11	1.499 (3)	C30—H30A	0.9900
C11—H11A	0.9900	C30—H30B	0.9900
C11—H11B	0.9900	C30—C31	1.526 (2)
C11—C12	1.501 (3)	C31—H31A	0.9900
C12—H12A	0.9900	C31—H31B	0.9900
C12—H12B	0.9900	C1S—H1S	0.9500
C12—C13	1.523 (3)	C1S—C2S	1.389 (3)
C13—H13A	0.9900	C1S—C6S	1.379 (3)
C13—H13B	0.9900	C2S—H2S	0.9500
C14—H14	1.0000	C2S—C3S	1.378 (4)
C14—C15	1.518 (2)	C3S—H3S	0.9500
C14—C19	1.526 (2)	C3S—C4S	1.381 (3)
C15—H15A	0.9900	C4S—H4S	0.9500
C15—H15B	0.9900	C4S—C5S	1.379 (3)
C15—C16	1.535 (3)	C5S—H5S	0.9500
C16—H16A	0.9900	C5S—C6S	1.366 (3)
C16—H16B	0.9900	C6S—H6S	0.9500
C1—N1—C4	124.75 (15)	C16—C17—H17A	109.3
C1—N1—H1	119.5 (16)	C16—C17—H17B	109.3
C4—N1—H1	115.5 (16)	H17A—C17—H17B	107.9
C2—N2—C8	117.30 (13)	C18—C17—C16	111.77 (16)
C2—N2—C14	122.26 (13)	C18—C17—H17A	109.3
C14—N2—C8	119.49 (13)	C18—C17—H17B	109.3
C3—N3—C20	122.13 (12)	C17—C18—H18A	109.4
C3—N3—C26	119.14 (12)	C17—C18—H18B	109.4
C20—N3—C26	118.54 (11)	C17—C18—C19	111.36 (16)
N1—C1—C2	151.11 (15)	H18A—C18—H18B	108.0
N1—C1—C3	148.47 (15)	C19—C18—H18A	109.4
C2—C1—C3	60.37 (11)	C19—C18—H18B	109.4
N2—C2—C1	146.06 (14)	C14—C19—H19A	109.4
N2—C2—C3	153.88 (14)	C14—C19—H19B	109.4
C1—C2—C3	60.04 (11)	C18—C19—C14	111.05 (16)
N3—C3—C1	146.57 (14)	C18—C19—H19A	109.4
N3—C3—C2	153.84 (14)	C18—C19—H19B	109.4
C1—C3—C2	59.59 (11)	H19A—C19—H19B	108.0
N1—C4—H4A	109.3	N3—C20—H20	107.4
N1—C4—H4B	109.3	N3—C20—C21	111.47 (12)
N1—C4—C5	111.76 (15)	N3—C20—C25	111.67 (12)
H4A—C4—H4B	107.9	C21—C20—H20	107.4
C5—C4—H4A	109.3	C25—C20—H20	107.4
C5—C4—H4B	109.3	C25—C20—C21	111.18 (12)
C4—C5—H5A	109.0	C20—C21—H21A	109.5
C4—C5—H5B	109.0	C20—C21—H21B	109.5
H5A—C5—H5B	107.8	C20—C21—C22	110.73 (13)

C6—C5—C4	112.84 (15)	H21A—C21—H21B	108.1
C6—C5—H5A	109.0	C22—C21—H21A	109.5
C6—C5—H5B	109.0	C22—C21—H21B	109.5
C5—C6—H6AA	108.3	C21—C22—H22A	109.4
C5—C6—H6AB	108.3	C21—C22—H22B	109.4
C5—C6—H6BC	111.6	H22A—C22—H22B	108.0
C5—C6—H6BD	111.6	C23—C22—C21	111.21 (14)
C5—C6—C7A	100.6 (11)	C23—C22—H22A	109.4
H6AA—C6—H6AB	107.4	C23—C22—H22B	109.4
H6BC—C6—H6BD	109.4	C22—C23—H23A	109.4
C7—C6—C5	116.1 (5)	C22—C23—H23B	109.4
C7—C6—H6AA	108.3	H23A—C23—H23B	108.0
C7—C6—H6AB	108.3	C24—C23—C22	111.10 (13)
C7A—C6—H6BC	111.6	C24—C23—H23A	109.4
C7A—C6—H6BD	111.6	C24—C23—H23B	109.4
C6—C7—H7A	109.5	C23—C24—H24A	109.5
C6—C7—H7B	109.5	C23—C24—H24B	109.5
C6—C7—H7C	109.5	C23—C24—C25	110.84 (13)
H7A—C7—H7B	109.5	H24A—C24—H24B	108.1
H7A—C7—H7C	109.5	C25—C24—H24A	109.5
H7B—C7—H7C	109.5	C25—C24—H24B	109.5
C6—C7A—H7AA	109.5	C20—C25—H25A	109.5
C6—C7A—H7AB	109.5	C20—C25—H25B	109.5
C6—C7A—H7AC	109.5	C24—C25—C20	110.73 (13)
H7AA—C7A—H7AB	109.5	C24—C25—H25A	109.5
H7AA—C7A—H7AC	109.5	C24—C25—H25B	109.5
H7AB—C7A—H7AC	109.5	H25A—C25—H25B	108.1
N2—C8—H8	106.6	N3—C26—H26	106.8
N2—C8—C9	113.20 (14)	N3—C26—C27	112.48 (12)
N2—C8—C13	112.58 (14)	N3—C26—C31	112.18 (12)
C9—C8—H8	106.6	C27—C26—H26	106.8
C13—C8—H8	106.6	C31—C26—H26	106.8
C13—C8—C9	110.67 (16)	C31—C26—C27	111.30 (12)
C8—C9—H9A	109.7	C26—C27—H27A	109.7
C8—C9—H9B	109.7	C26—C27—H27B	109.7
C8—C9—C10	109.82 (15)	H27A—C27—H27B	108.2
H9A—C9—H9B	108.2	C28—C27—C26	109.86 (13)
C10—C9—H9A	109.7	C28—C27—H27A	109.7
C10—C9—H9B	109.7	C28—C27—H27B	109.7
C9—C10—H10A	109.2	C27—C28—H28A	109.4
C9—C10—H10B	109.2	C27—C28—H28B	109.4
H10A—C10—H10B	107.9	H28A—C28—H28B	108.0
C11—C10—C9	111.95 (16)	C29—C28—C27	111.15 (13)
C11—C10—H10A	109.2	C29—C28—H28A	109.4
C11—C10—H10B	109.2	C29—C28—H28B	109.4
C10—C11—H11A	109.2	C28—C29—H29A	109.4
C10—C11—H11B	109.2	C28—C29—H29B	109.4
C10—C11—C12	112.11 (16)	C28—C29—C30	111.18 (13)
H11A—C11—H11B	107.9	H29A—C29—H29B	108.0
C12—C11—H11A	109.2	C30—C29—H29A	109.4
C12—C11—H11B	109.2	C30—C29—H29B	109.4

C11—C12—H12A	109.3	C29—C30—H30A	109.3
C11—C12—H12B	109.3	C29—C30—H30B	109.3
C11—C12—C13	111.82 (17)	C29—C30—C31	111.80 (13)
H12A—C12—H12B	107.9	H30A—C30—H30B	107.9
C13—C12—H12A	109.3	C31—C30—H30A	109.3
C13—C12—H12B	109.3	C31—C30—H30B	109.3
C8—C13—C12	110.27 (17)	C26—C31—C30	109.30 (12)
C8—C13—H13A	109.6	C26—C31—H31A	109.8
C8—C13—H13B	109.6	C26—C31—H31B	109.8
C12—C13—H13A	109.6	C30—C31—H31A	109.8
C12—C13—H13B	109.6	C30—C31—H31B	109.8
H13A—C13—H13B	108.1	H31A—C31—H31B	108.3
N2—C14—H14	106.5	C2S—C1S—H1S	120.0
N2—C14—C15	111.86 (14)	C6S—C1S—H1S	120.0
N2—C14—C19	111.73 (14)	C6S—C1S—C2S	120.1 (2)
C15—C14—H14	106.5	C1S—C2S—H2S	120.1
C15—C14—C19	113.31 (14)	C3S—C2S—C1S	119.8 (2)
C19—C14—H14	106.5	C3S—C2S—H2S	120.1
C14—C15—H15A	109.5	C2S—C3S—H3S	120.3
C14—C15—H15B	109.5	C2S—C3S—C4S	119.5 (2)
C14—C15—C16	110.85 (17)	C4S—C3S—H3S	120.3
H15A—C15—H15B	108.1	C3S—C4S—H4S	119.8
C16—C15—H15A	109.5	C5S—C4S—C3S	120.4 (2)
C16—C15—H15B	109.5	C5S—C4S—H4S	119.8
C15—C16—H16A	109.3	C4S—C5S—H5S	119.9
C15—C16—H16B	109.3	C6S—C5S—C4S	120.1 (2)
H16A—C16—H16B	108.0	C6S—C5S—H5S	119.9
C17—C16—C15	111.41 (16)	C1S—C6S—H6S	120.0
C17—C16—H16A	109.3	C5S—C6S—C1S	120.05 (19)
C17—C16—H16B	109.3	C5S—C6S—H6S	120.0
N1—C1—C2—N2	4.0 (5)	C11—C12—C13—C8	−55.7 (3)
N1—C1—C2—C3	−177.3 (3)	C13—C8—C9—C10	−58.7 (2)
N1—C1—C3—N3	−2.2 (5)	C14—N2—C2—C1	−173.4 (2)
N1—C1—C3—C2	177.5 (3)	C14—N2—C2—C3	9.2 (4)
N1—C4—C5—C6	−175.67 (16)	C14—N2—C8—C9	68.4 (2)
N2—C2—C3—N3	−2.0 (6)	C14—N2—C8—C13	−58.1 (2)
N2—C2—C3—C1	178.3 (4)	C14—C15—C16—C17	−52.9 (2)
N2—C8—C9—C10	173.80 (16)	C15—C14—C19—C18	−53.5 (2)
N2—C8—C13—C12	−172.96 (18)	C15—C16—C17—C18	55.6 (2)
N2—C14—C15—C16	179.90 (14)	C16—C17—C18—C19	−56.5 (2)
N2—C14—C19—C18	179.06 (14)	C17—C18—C19—C14	54.6 (2)
N3—C20—C21—C22	−179.07 (13)	C19—C14—C15—C16	52.51 (19)
N3—C20—C25—C24	178.39 (12)	C20—N3—C3—C1	175.9 (2)
N3—C26—C27—C28	−174.43 (12)	C20—N3—C3—C2	−3.7 (4)
N3—C26—C31—C30	174.66 (12)	C20—N3—C26—C27	117.46 (14)
C1—N1—C4—C5	−73.7 (2)	C20—N3—C26—C31	−116.15 (14)
C1—C2—C3—N3	179.7 (3)	C20—C21—C22—C23	−55.36 (18)
C2—N2—C8—C9	−100.70 (18)	C21—C20—C25—C24	−56.42 (16)
C2—N2—C8—C13	132.84 (18)	C21—C22—C23—C24	56.07 (19)
C2—N2—C14—C15	−67.2 (2)	C22—C23—C24—C25	−56.65 (19)

C2—N2—C14—C19	61.1 (2)	C23—C24—C25—C20	56.72 (17)
C2—C1—C3—N3	−179.8 (3)	C25—C20—C21—C22	55.63 (18)
C3—N3—C20—C21	109.43 (15)	C26—N3—C3—C1	−9.3 (3)
C3—N3—C20—C25	−125.54 (14)	C26—N3—C3—C2	171.2 (3)
C3—N3—C26—C27	−57.58 (17)	C26—N3—C20—C21	−65.46 (17)
C3—N3—C26—C31	68.81 (17)	C26—N3—C20—C25	59.57 (16)
C3—C1—C2—N2	−178.7 (3)	C26—C27—C28—C29	−56.36 (17)
C4—N1—C1—C2	−15.3 (4)	C27—C26—C31—C30	−58.31 (16)
C4—N1—C1—C3	169.1 (2)	C27—C28—C29—C30	54.94 (18)
C4—C5—C6—C7	−177.2 (6)	C28—C29—C30—C31	−55.23 (18)
C4—C5—C6—C7A	170.9 (10)	C29—C30—C31—C26	56.37 (17)
C8—N2—C2—C1	−4.6 (3)	C31—C26—C27—C28	58.71 (16)
C8—N2—C2—C3	178.0 (3)	C1S—C2S—C3S—C4S	0.5 (3)
C8—N2—C14—C15	124.29 (15)	C2S—C1S—C6S—C5S	−0.6 (3)
C8—N2—C14—C19	−107.48 (16)	C2S—C3S—C4S—C5S	−0.2 (3)
C8—C9—C10—C11	55.2 (2)	C3S—C4S—C5S—C6S	−0.6 (3)
C9—C8—C13—C12	59.2 (3)	C4S—C5S—C6S—C1S	1.0 (3)
C9—C10—C11—C12	−52.4 (3)	C6S—C1S—C2S—C3S	−0.2 (3)
C10—C11—C12—C13	52.5 (3)		

Comparative Bond Lengths (Å) for 1-mesityl-2,3-bis(diisopropylamino)cyclopropenimine, 1-mesityl-2,3-bis(diisopropylamino)cyclopropeniminium (Bruns, et al., 2010), and 1-n-butyl-2,3-bis(dicyclohexyl)cyclopropeniminium.

	Mes(C₃N₃)⁺Pr₄	[Mes(C₃N₃H)⁺Pr₄]BF₄	[Bu(C₃N₃H)Cy₄]Cl([1H]Cl)
C-N(imine)	1.2951 (14)	1.3342 (16)	1.319 (2)
C-N(amine)	1.3450 (14)/1.3539 (14)	1.3205 (15)/1.3286 (16)	1.3248 (17)/1.331 (2)
C-C(para)	1.3712 (14)	1.3984 (17)	1.388 (2)
C-C(meta)	1.4202 (14)/1.4108 (14)	1.3792 (16)/1.3827 (16)	1.377 (2)/1.3831 (19)

Divided entries refer to separate, related pairs of atoms and their associated metrics, e.g., 1.3450 (14)/1.3539 (14) denotes 2 distances for the two C-N(amine) contacts.

Hirshfeld Charges of Atoms in [1H]ClA·C₆H₆.

C11	−0.666
N1	−0.048
N2	−0.027
N3	−0.018
C1	0.026
C2	0.014
C3	0.024
C4	−0.036
C5	−0.102
C6	−0.095
C7	−0.133
C8	−0.011
C9	−0.103
C10	−0.093
C11	−0.097
C12	−0.088
C13	−0.093

C14	-0.008
C15	-0.097
C16	-0.094
C17	-0.098
C18	-0.098
C19	-0.101
C20	-0.005
C21	-0.094
C22	-0.093
C23	-0.093
C24	-0.091
C25	-0.093
C26	-0.002
C27	-0.096
C28	-0.094
C29	-0.099
C30	-0.093
C31	-0.097
C1S	-0.058
C2S	-0.071
C3S	-0.078
C4S	-0.084
C5S	-0.082
C6S	-0.064
H1S	0.071
H6S	0.069
H5S	0.065
H4S	0.062
H3S	0.062
H2S	0.056
H4a	0.051
H4b	0.075
H5a	0.061
H5b	0.042
H6aa	0.046
H6ab	0.055
H7a	0.05
H7b	0.039
H7c	0.051
H8	0.072
H9a	0.05
H9b	0.06
H10a	0.061
H10b	0.061
H11a	0.061
H11b	0.049
H12a	0.057
H12b	0.053
H13a	0.059
H13b	0.049
H14	0.066

H15a	0.057
H15b	0.062
H16a	0.051
H16b	0.052
H17a	0.055
H17b	0.051
H18a	0.056
H18b	0.062
H19a	0.055
H19b	0.065
H20	0.06
H21a	0.055
H21b	0.055
H22a	0.05
H22b	0.056
H23a	0.056
H23b	0.052
H24a	0.051
H24b	0.056
H25a	0.057
H25b	0.057
H26	0.058
H27a	0.049
H27b	0.062
H28a	0.044
H28b	0.057
H29a	0.05
H29b	0.059
H30a	0.061
H30b	0.039
H31a	0.047
H31b	0.064
H1	0.121