

Poli- and isomorphism in halogen-substituted 4-(phenylamino)pent-3-en-2-one compounds

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A range of halogen-substituted phenyl β -enaminoketonato compounds (N,O-donor atoms) as ligand models is presented. The influence of halogen substitution on the phenyl ring on solid state parameters was investigated by X-ray structures of 4-(4-fluorophenylamino)pent-3-en-2-one (4-F-PhonyH), 4-(4-chlorophenylamino)pent-3-en-2-one (4-Cl-PhonyH), and 4-(4-bromophenyl-amino)pent-3-en-2-one (4-Br-PhonyH), which are reported. Although structurally very similar, 4-F-PhonyH and its chloro- and bromo-substituted counterparts differ significantly with regard to dihedral angles and intermolecular interactions. All three compounds show polymorphism in two different crystal systems, with 4-F-PhonyH crystallising in $P2_1/c$, both 4-Cl-PhonyH and 4-Br-PhonyH crystallising in Cc , and all three crystallising in $P\bar{1}$.

Keywords: enaminoketone, polymorphism, isomorphism

Poli- en isomorfisme in halogeengesubstitueerde 4-(fenielamino)pent-3-en-2-oon verbindings: 'n Reeks halogeengesubstitueerde feniel- β -enaminoketonaat verbindings (N,O-skenkeratome) word voorgelê. Die invloed van halogeensubstitusie aan die fenielring op vastetoestand parameters is ondersoek. X-straal strukture van 4-(4-fluorofenielamino)pent-3-en-2-oon (4-F-PhonyH), 4-(4-chlorofenielamino)pent-3-en-2-oon (4-Cl-PhonyH), en 4-(4-bromofeniel-amino)pent-3-en-2-oon (4-Br-PhonyH) is gerapporteer. Alhoewel 4-F-PhonyH en die chloro- en bromo-eweknieë struktureel soortgelyk is, is daar daadwerklike verskille in terme van dihedriese hoeke en intermolekulêre interaksies. Al drie verbindings vertoon polimorfisme in twee verskillende kristalstelsels, met 4-F-PhonyH wat in $P2_1/c$, beide 4-Cl-PhonyH en 4-Br-PhonyH in Cc , en al drie in $P\bar{1}$ kristalliseer.

Sleutelwoorde: Enaminoketoon, polimorfisme, isomorfisme.

Introduction

A well-known system in organometallic and general coordination chemistry is the β -diketone compound AcacH (acetylacetonate). A multitude of derivatives have been synthesised to date (Groom et al. 2016), and include nitrogen-substituted enaminoketones, also known as ketoimines. Electron-rich enaminoketones contain nitrogen and oxygen atoms as well as an alkene, and have application possibilities in various fields including liquid crystals (Pyżuk et al. 1993), fluorescence studies (Xia et al. 2008), catalysis (Nair et al. 2002) and medicine (Tan et al. 2008; Chen and Rhodes 1996). Although enaminoketones vary in design, they generally act as mono-anionic, bidentate ligands. Halogens are ever-present in both inorganic and organic chemistry, serving as monodentate, bridging ligands or substituents in organic compounds. In supramolecular chemistry and crystal engineering, wherein the halogen atoms are directly involved in forming intermolecular interactions, the steric impact of halogens has potential applications (Fox et al. 2004; Csöregi et al. 2001).

This study focuses on halogen-substituted 4-(phenylamino)pent-3-en-2-one (PhonyH, Shaheen, et al., 2006; Figure 1) type compounds and the effect that different halogens in the same position on the phenyl ring has on geometry and packing effects, as observed from solid state single crystal X-ray studies.

The marked difference in Van der Waals radii between halogens (1.47 Å for F, 1.75 Å for Cl and 1.83 Å for Br; Bondi 1964; Mantina et al. 1987) leads to the question of what the impact of the steric properties of the substituents on the phenyl ring is on the geometric parameters of isostructural compounds and their respective packing modes. This query is of vital importance

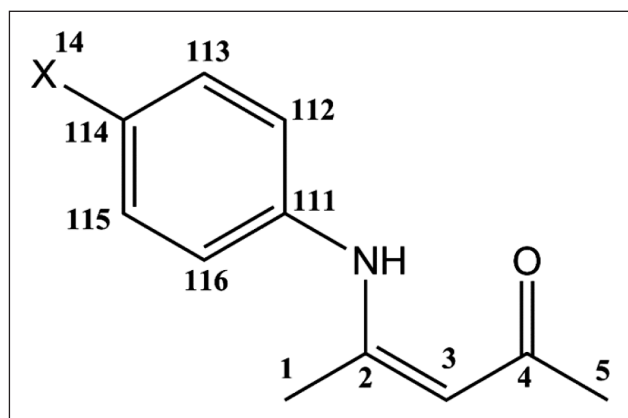


FIGURE 1: Schematic representation of 4-(X-phenylamino)pent-3-en-2-one (4-X-PhonyH, where X = F, Cl, Br), illustrating the numbering used throughout this paper. For the C atoms in the phenyl ring, the first digit indicates molecule number, the second digit indicates ring number and the third digit indicates the position of the atom in the ring. For halogen substitutions on the phenyl ring, designated by X, the first digit indicates the molecule number while the second digit indicates position on the phenyl ring.

when considering the design of complexes utilising these compounds as ligand systems in appropriate applications.

Polymorphs of the structures for 4-Cl-PhonyH and 4-Br-PhonyH were reported previously (Olejník et al. 2012; Sergienko et al. 1987) and are contained in the Cambridge Crystal Structure Database (CSD) under the codes WUQDOD and GEZSEJ. Other published structures similar to PhonyH include the following, with X-substituents: methyl (Venter et al. 2010a; 2010b; 2012a; 2014), fluoride (Gordon et al. 2002), chloride (Venter et al. 2012b; 2013), bromide (Venter et al. 2011), hydroxyl (Parekh et al. 2007) and nitro (Da Silva et al. 1993) containing compounds. However, no systematic *halogen* variation has been done.

Thus, reported in this study is a systematic expansion of the fluoro, chloro and bromo analogs by single crystal X-Ray analyses of halogen-containing structures and polymorphs of 4-(4-fluorophenylamino)pent-3-en-2-one (4-F-PhonyH, **I** and **II**), 4-(4-chlorophenylamino)pent-3-en-2-one (4-Cl-PhonyH, **III** and **IV**) as well as 4-(4-bromophenylamino)pent-3-en-2-one (4-Br-PhonyH, **V** and **VI**). It specifically focuses on investigating the possible effect of systematic electronic influences on geometric parameters and packing styles in these model ligand systems.

Materials and methods

Synthesis

All reagents were used as purchased. Preparation of 4-Cl-PhonyH is reported as an example of a typical synthesis procedure for these enaminketones.

A solution of acetylacetone (11.07 g, 0.1106 mol), 4-chloroaniline (12.77 g, 0.1001 mol) and 2 drops of H_2SO_4 (conc.) in 150 ml benzene was refluxed for 24 hours in a Dean-Stark trap, filtered and left to crystallise. Crystals suitable for X-ray diffraction were obtained (17.14 g, 81.67% yield). All N,O-bidentate compounds were prepared using the same procedure. These products are stable in air and light over a period of several years.

Single-crystal X-ray crystallography

The data collection was done on a Bruker Apex II 4K CCD diffractometer using Mo $K\alpha$ (0.71073 Å) and ϕ and ω -scans at 100(2) K. All reflections were merged and integrated with SAINT-PLUS (Bruker 2004) and were corrected for Lorentz, polarisation and absorption effects using SADABS (Bruker 1998). The structures were solved by direct methods and refined through full-matrix least-squares cycles using SHELX-97 (Sheldrick 2008) as part of the WinGX (Farrugia 2012) package with $\Sigma(|F_o| - |F_c|)^2$ being minimised. All non-H atoms were refined with anisotropic displacement parameters, while H atoms were constrained to parent atom sites using a riding model (aromatic C–H = 0.95 Å; aliphatic C–H = 0.98 Å). The graphics were done with the DIAMOND (Putz and Brandenburg 2018) Visual Crystal Structure Information System software. Crystallographic data for the structures are available on the Cambridge Structural database under CCDC 1910214-1910217.

Results

The starting reagents easily react to yield the target N,O-bidentate compounds which crystallise as follows: Triclinic: $P\bar{1}$ 4-F-PhonyH (**I**), Monoclinic: $P2_1/c$ 4-F-PhonyH (**II**), Monoclinic: Cc 4-Cl-PhonyH (**III**), and Monoclinic: Cc 4-Br-PhonyH (**V**) that are shown in Figure 2. The triclinic P polymorphs of 4-Cl-PhonyH (**IV**) and 4-Br-PhonyH (**VI**) are included for comparative purposes.

Compound **I** crystallised with two independent molecules in the asymmetric unit in the triclinic space group $P\bar{1}$, while compounds **III** and **IV** crystallised with four independent molecules in the monoclinic space group Cc . All other polymorphs crystallise with only one independent molecule. All compounds are stable under ambient conditions. Table 1 contains the basic data collection and refinement parameters for the crystal structures mentioned above. Important bond distances and angles for each set of polymorphs are provided in Tables 2 to 4.

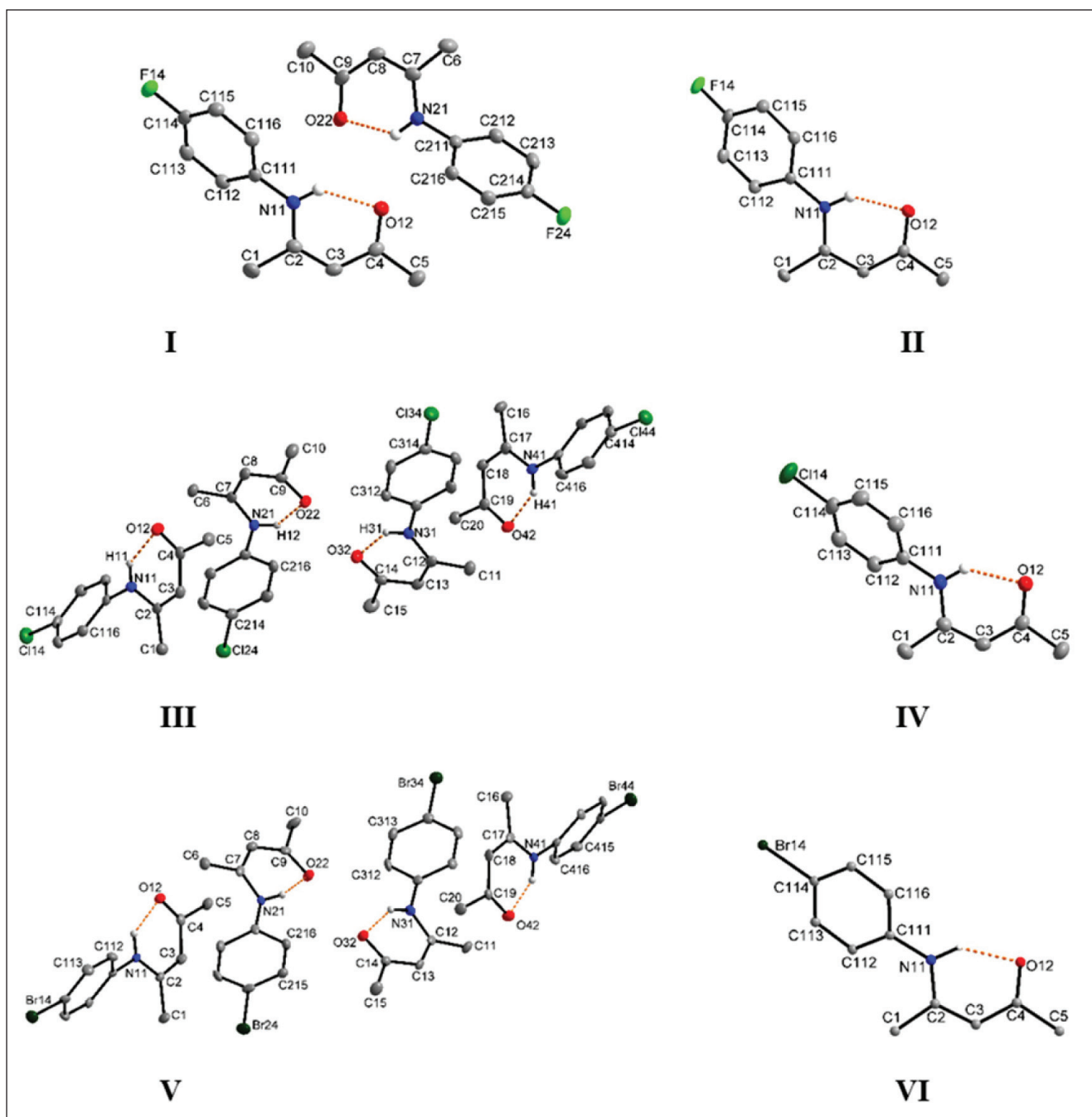


FIGURE 2: DIAMOND views of $P\bar{1}$ 4-F-PhonyH (I), $P2_1/c$ 4-F-PhonyH (II), Cc 4-Cl-PhonyH (III), $P\bar{1}$ 4-Cl-PhonyH (IV), Cc 4-Br-PhonyH (V), and $P\bar{1}$ 4-Br-PhonyH (VI) (50% probability displacement ellipsoids), where PhonyH = 4-(phenylamino)pent-3-en-2-one. Phenyl and alkyl hydrogen atoms are omitted for clarity. For the C atoms in the phenyl ring, the first digit indicates the molecule number, the second digit the ring number and the third digit the position of the atom in the ring. Some labels have been omitted for clarity, but all rings are numbered in the same consistent way. For the halogen atoms, the first digit indicates molecule number while the second digit indicates the position on the phenyl ring.

TABLE 1: Structural information on the halogen derivatives of PhonyH

Compound	4-F-PhonyH (I)	4-F-PhonyH polymorph (II)	4-Cl-PhonyH (III)	4-Cl-PhonyH polymorph (IV) ^a	4-Br-PhonyH (V)	4-Br-PhonyH polymorph (VI) ^b
Crystal colour	Colourless	Colourless	Yellow	Colourless	Yellow	Colourless
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	Cc	$P\bar{1}$	Cc	$P\bar{1}$
Temperature (K)	100(2)	100(2)	100(2)	150(1)	100(2)	295
<i>a</i> (Å)	8.9561(2)	9.2410(8)	14.1370(7)	6.9730(5)	14.2020(2)	6.977(2)
<i>b</i> (Å)	10.8218(2)	10.8140(9)	14.5370(6)	7.9481(4)	14.6910(2)	8.154(2)
<i>c</i> (Å)	12.3640(3)	10.1670(9)	20.4780(8)	10.5520(4)	20.8920(3)	10.821(3)
α (°)	111.429(1)	90	90	99.767(4)	90	100.11(2)
β (°)	97.691(1)	107.468(4)	100.516(1)	100.433(5)	101.244(1)	100.73(2)
γ (°)	108.876(1)	90	90	109.868(4)	90	108.67(2)
<i>V</i> (Å ³)	1011.37(4)	969.2(2)	4137.7(3)	523.74(5)	4275.3(1)	554.435
<i>Z</i>	4	4	16	2	16	2
<i>D</i> _{calc} (g.cm ⁻³)	1.269	1.3242	1.3462	1.33	1.5792	1.418
Crystal size (mm ³)	0.35 × 0.29 × 0.24	0.71 × 0.56 × 0.28	0.17 × 0.13 × 0.1	0.32 × 0.19 × 0.17	0.50 × 0.48 × 0.45	
μ (mm ⁻¹)	0.094	0.098	0.334	0.33	3.812	
Reflections measured	11052	36822	23579	10122	24956	
unique, <i>R</i> _{int}	4405, 0.0222	2418, 0.0507	8986, 0.0311	2265, 0.0794	9849, 0.0513	
No. of parameters	265	133	513	135	513	
<i>R</i> 1 [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0384	0.0406	0.0335	0.0433	0.0357	
<i>wR</i> ₂ (all data, <i>F</i> ²)	0.1081	0.1337	0.0785	0.1133	0.0712	
GOF on <i>F</i> ²	1.053	1.061	1.038	1.075	0.936	
$\Delta\rho$ min/max (e.Å ⁻³)	0.23/-0.21	0.37/-0.43	0.25/-0.29	0.275/-0.391	0.51/-0.80	

^a Adapted from Olejnik et al. 1987. Copyright: IUCr, with permission. ^b Adapted from Sergienko et al. 1987. Copyright: IUCr, with permission.

TABLE 2: Selected bond lengths (Å) and angles (°) in 4-F-PhonyH polymorphs

	I		II
	1	2	
N ₁₁ -C ₁₁₁	1.424(2)	1.424(2)	1.412(2)
N ₁₁ -C ₂	1.340(2)	1.347(2)	1.354(1)
O ₁₂ -C ₄	1.247(2)	1.247(2)	1.254(1)
N ₁₁ ...O ₁₂	2.668(1)	2.709(2)	2.641(1)
C ₂ -C ₃	1.382(2)	1.375(2)	1.383(2)
C ₃ -C ₄	1.426(2)	1.427(2)	1.428(2)
N ₁₁ -H ₁₁ ...O ₁₂	136(2)	134(2)	142(2)
N ₁₁ -C ₂ -C ₄ -O ₁₂	-0.5(1)	-1.0(1)	1.72(9)
Dihedral angle ^c	58.99(4)	31.67(6)	31.97(4)

^c Defined as the angle between the N-C-C-C-O plane and the phenyl ring.

TABLE 3: Selected bond lengths (Å) and angles (°) in 4-Cl-PhonyH polymorphs

	III				IV
	1	2	3	4	
N ₁₁ -C ₁₁₁	1.423(3)	1.419(3)	1.410(3)	1.419(3)	1.417(2)
N ₁₁ -C ₂	1.352(3)	1.344(3)	1.350(3)	1.353(3)	1.348(2)
O ₁₂ -C ₄	1.247(3)	1.252(3)	1.250(3)	1.246(3)	1.243(2)
N ₁₁ ...O ₁₂	2.676(3)	2.620(3)	2.634(3)	2.678(3)	2.705(2)
C ₂ -C ₃	1.378(3)	1.378(3)	1.380(3)	1.376(3)	1.375(3)
C ₃ -C ₄	1.427(3)	1.422(3)	1.421(3)	1.434(3)	1.434(3)
N ₁₁ -H ₁₁ ...O ₁₂	134.8(1)	137.5(2)	139.4(2)	134.7(2)	137(2)
N ₁₁ -C ₂ -C ₄ -O ₁₂	1.5(2)	1.7(2)	-3.0(2)	-1.7(2)	0.7(1)
Dihedral angle ^c	51.71(8)	-41.30(8)	38.36(9)	-52.71(7)	45.45(5)

^c Defined as angle between the N-C-C-C-O plane and the phenyl ring.

TABLE 4: Selected bond lengths (Å) and angles (°) in 4-Br-PhonyH polymorphs.

	V				VI
	1	2	3	4	
N ₁₁ -C ₁₁₁	1.430(4)	1.392(4)	1.417(4)	1.413(4)	1.44(1)
N ₁₁ -C ₂	1.360(4)	1.341(4)	1.359(4)	1.370(4)	1.34(1)
O ₁₂ -C ₄	1.244(4)	1.251(4)	1.252(4)	1.247(4)	1.25(1)
N ₁₁ ...O ₁₂	2.675(4)	2.635(4)	2.629(4)	2.664(4)	2.70(1)
C ₂ -C ₃	1.368(5)	1.372(5)	1.379(5)	1.373(4)	1.37(1)
C ₃ -C ₄	1.431(5)	1.432(5)	1.430(4)	1.427(5)	1.41(1)
N ₁₁ -H ₁₁ ...O ₁₂	131.5(1)	152.9(2)	145.5(2)	139.3(2)	139(6)
N ₁₁ -C ₂ -C ₄ -O ₁₂ ^c	-1.8(3)	-3.4(3)	2.3(3)	1.0(3)	0.7(7)
Dihedral angle ^c	51.54(8)	-37.0(1)	39.5(1)	-51.61(9)	47.9(3)

^c Defined as the angle between the N-C-C-O plane and the phenyl ring.

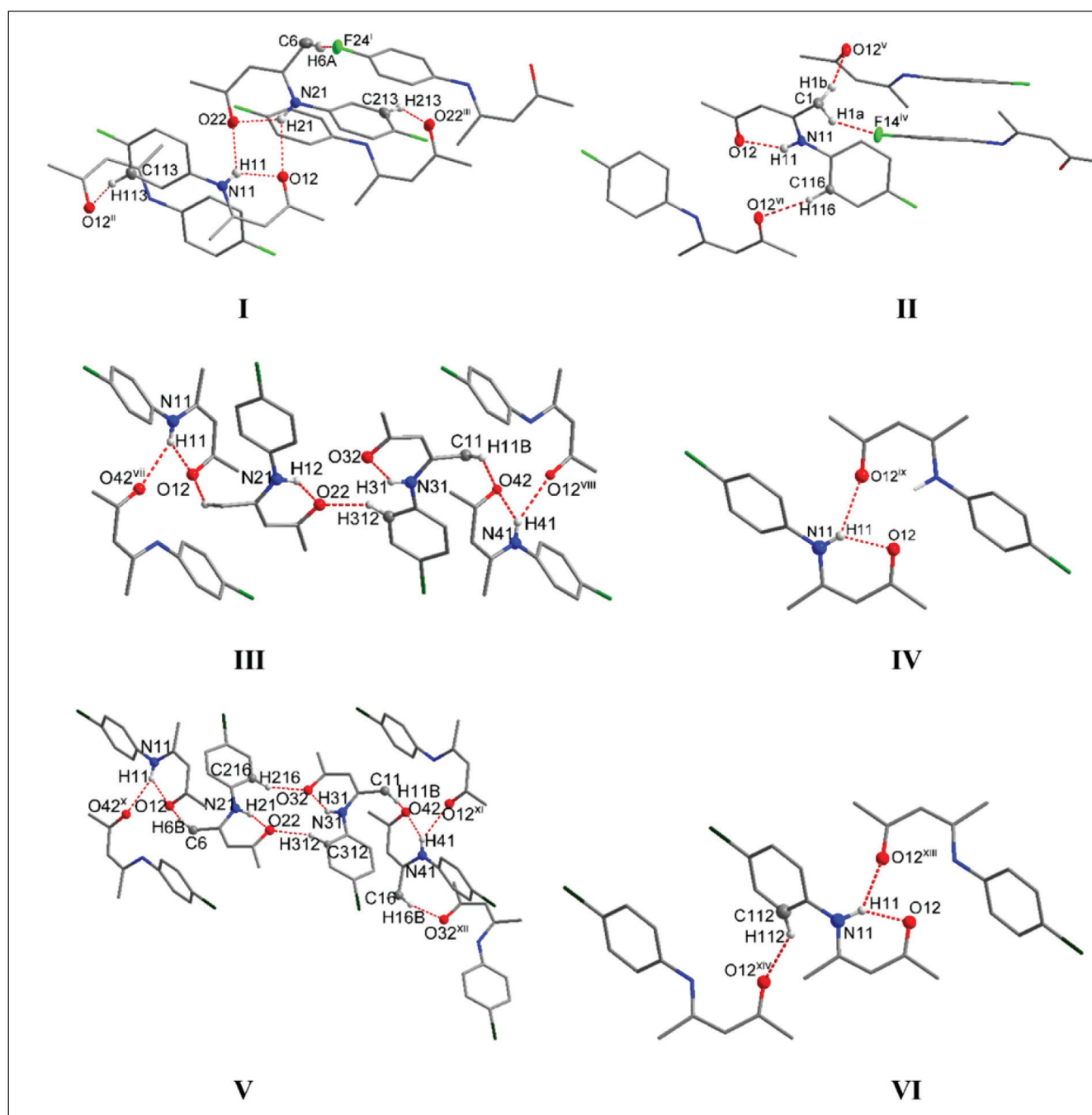


FIGURE 3: DIAMOND views of intra- and intermolecular interactions in $P\bar{1}$ 4-F-PhonyH (I), $P2_1/c$ 4-F-PhonyH (II), Cc 4-Cl-PhonyH (III), $P\bar{1}$ 4-Cl-PhonyH (IV), Cc 4-Br-PhonyH (V), and $P\bar{1}$ 4-Br-PhonyH (VI), where PhonyH = 4-(phenylamino)pent-3-en-2-one. Phenyl and alkyl hydrogen atoms are omitted for clarity.

All the compounds under discussion display intramolecular N-H...O interactions; intermolecular N-H...O and C-H...O interactions are also common. The interactions are illustrated in Figure 3, with the parameters summarised in Table A.1 in the supplementary material.

Discussion

4-X-PhonyH derivatives show a clear tendency to crystallise in multiple crystal systems and space groups as indicated in Table 1. The impression that temperature may play a role as indicated by the different temperature collections for 4-Cl-PhonyH and 4-Br-PhonyH in literature is negated by the fact that polymorphs of 4-F-PhonyH are observed regardless of identical temperatures. In all cases 4-F-PhonyH display marked differences from its Cl and Br counterparts; even though all compounds under discussion crystallise in at least $P\bar{1}$, the unit cell parameters of 4-F-PhonyH are significantly different from 4-Cl-PhonyH and 4-Br-PhonyH while those of 4-Cl-PhonyH and 4-Br-PhonyH are closer to each other. While the radius of F is much smaller than that of Cl and Br, two 4-F-PhonyH molecules in the asymmetric unit as opposed to one increases the unit cell parameters to such an extent that the unit cell volume virtually doubles. All the structures crystallising in $P\bar{1}$ share one property which is intra- and intermolecular N-H...O bonds with bifurcated H_{11} (or H_{21} , where present) hydrogens which manifests as crystallographic dimerism. Since hydrogen bonds are long-range interactions, more than one acceptor A can bond to a donor group D-H. When there are two acceptors A_1 and A_2 , the interaction is classified as a bifurcated hydrogen bond D-H...(A_1, A_2) (Francl et al. 1982), as was observed in these compounds. This dimeric arrangement is not present in the $P2_1/c$ polymorph of 4-F-PhonyH but again manifests in the Cc polymorphs of 4-Cl-PhonyH and 4-Br-PhonyH. Crystallographic polymerism displayed by **III** and **V** can clearly be seen from Figure 3, with bifurcated hydrogen bonds present for H_{11} and H_{41} . This type of polymerism is enabled by the intermolecular N-H...O interactions between adjacent molecules.

The largest difference between the geometric parameters of the polymorphs of 4-F-PhonyH, compounds **I** and **II**, is in the $N_{11}\cdots O_{12}$ distances which are 2.668(1) Å and 2.709(2) Å for **I** and 2.641(1) Å for **II**. This indicates an opening in the 'bite' of the ligand for polymorph **I**, but is in contrast with the $N_{11}\cdots H_{11}\cdots O_{12}$ angles which are 136(2)° and 134(2)° for **I** and 142(1)° for **II** and the $N_{11}\cdots C_2\cdots C_4\cdots O_{12}$ torsion angles of -0.5(1)° and -1.0(1)° versus 1.72(9)°. It is noted that the dihedral angle of one of the molecules in polymorph **I** [31.67(6)°] is close to that of the molecule in polymorph **II** [31.97(4)°] while the other is 58.99(4)°. Surprisingly 4-F-PhonyH is the only compound to display a hydrogen...halogen interaction, and in both polymorphs. This is an anomaly in terms of electronegativity ($H < Br <$

$Cl < F$; Little and Jones 1960), electron affinity ($H < Br < F < Cl$; Meyers 1990), and atom radius ($H < F < Cl < Br$; Mantina et al. 2009) also when taking unsubstituted PhonyH into account which also does not display a hydrogen...hydrogen interaction at the *para* position of the phenyl ring.

As with 4-F-PhonyH, the triclinic $P\bar{1}$ polymorphs of both 4-Cl-PhonyH (**IV**) and 4-Br-PhonyH (**VI**) exhibit a larger 'bite' than their monoclinic Cc polymorphic counterparts. For **IV** the $N_{11}\cdots O_{12}$ distance is 2.705(2) Å and for **VI** it is 2.70(1) Å, thus a 0.029(4) Å to 0.085(4) Å range difference between **IV** and **III** and a 0.03(1) Å and 0.07(1) Å range between **VI** and **V**, respectively. Differences in intermolecular interactions could also account for the fact that the polymorphs are distinguishable by colour: the monoclinic Cc polymorphs for both 4-Cl-PhonyH and 4-Br-PhonyH are yellow whereas the triclinic $P\bar{1}$ polymorphs are colourless.

The first indication of isomorphism between 4-Cl-PhonyH and 4-Br-PhonyH are the comparable unit cell parameters, and although it is rare for complexes to crystallise with four independent molecules in the asymmetric unit, both compounds **III** and **V** display this property. Isomorphism is also observed for compounds **IV** and **VI**. The overlays of the two sets of molecules for compounds **III** and **V**, and **IV** and **VI** are shown in Figure 4.

In general the bond parameters of the two sets of molecules compare quite well. Although differences are observed between molecules of the same compound, these variations are repeated in both the Cl and Br variants. Differences are observed between the geometric parameters of the various molecules in each of the Cc polymorphs but these differences do not follow a trend with regard to molecule position (*i.e.* comparing molecules 1 and 3, or 1 and 2, or 2 and 3). Molecules 1 and 3 both display a positive dihedral angle, while molecules 2 and 4 are orientated towards a negative dihedral angle. Despite the resemblance in this regard, dihedral angles differ for molecules with similar orientations of the dihedral angles [13.4(1)° and 11.4(1)° for **III**, and 12.0(1)° and 14.6(1)° for **V** for molecules 1 and 3, and 2 and 4, respectively]. The $N_{11}\cdots C_2\cdots C_3\cdots C_4\cdots O_{12}$ moieties of all molecules are only slightly distorted, as confirmed by the relatively small $N_{11}\cdots C_2\cdots C_4\cdots O_{12}$ torsion angles [smaller than 3.4(3)°]. Both compounds contain intermolecular interactions to such an extent that they may be viewed as crystallographic polymers, as demonstrated in Figure 3. The differences between compounds **IV** and **VI** can be considered as negligible within experimental error, but the low quality of the crystal data for **VI** has to be taken into account. As a result these compounds are included for completeness but a recollection should be undertaken in order to fully compare the isomorphs.

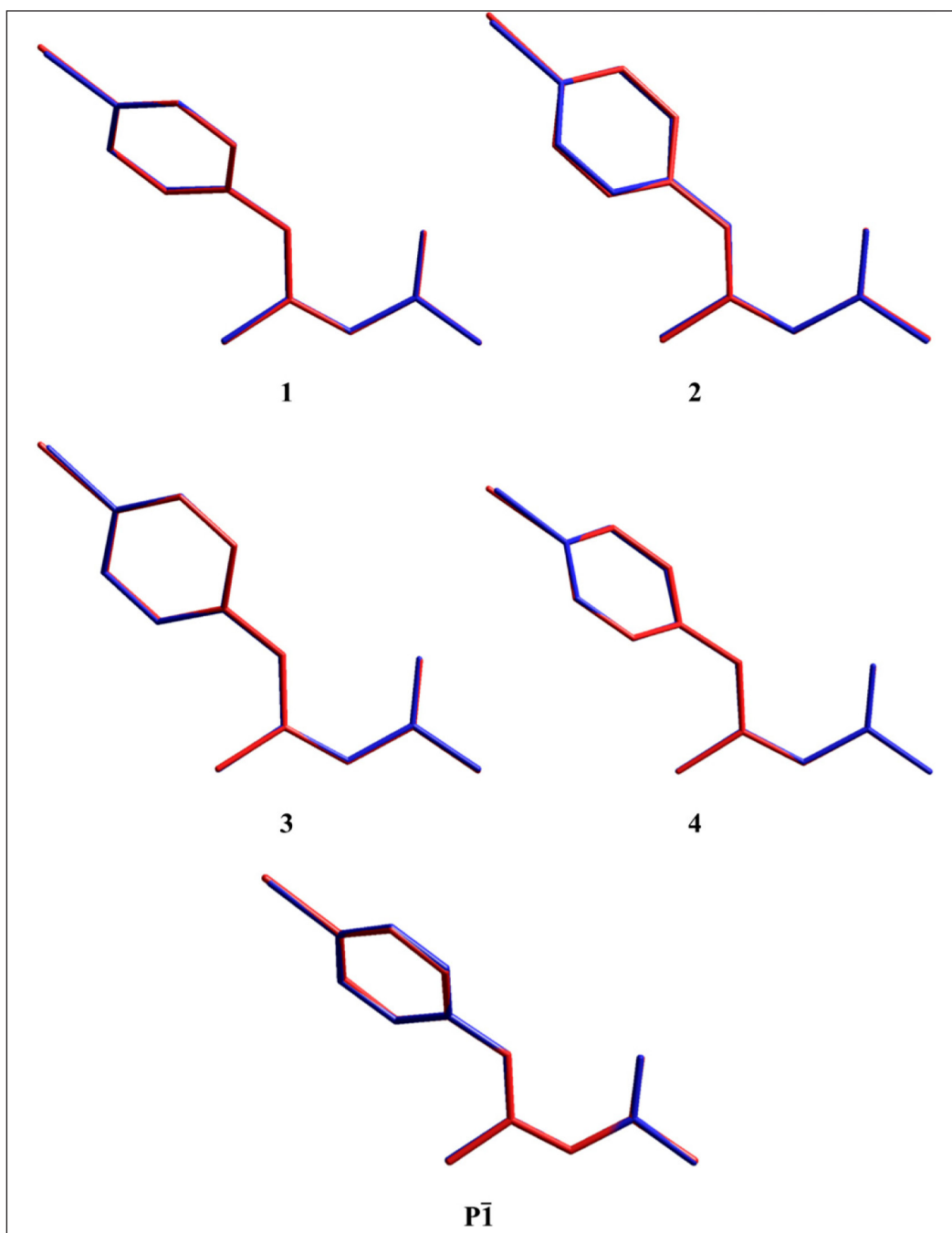


FIGURE 4: HyperChem overlay of the four molecules of monoclinic *Cc* 4-Cl-PhonyH (III) with the four equivalent molecules of monoclinic *Cc* 4-Br-PhonyH (V), and triclinic *P1* 4-Cl-PhonyH (IV) with triclinic *P1* 4-Br-PhonyH (VI). 1: RMS = 0.0573 Å; 2: RMS = 0.00855 Å; 3: RMS = 0.00542 Å; 4: RMS = 0.0793 Å; *P1*: RMS = 0.0488 Å. The overlay fit includes all non-hydrogen atoms. The blue structures denote 4-Cl-PhonyH, while the red structures refer to 4-Br-PhonyH.

Conclusion

Knowing the physical properties of ligand systems is important for applications in industrial processes, and large differences were observed not only between polymorphs of the same type of 4-X-PhonyH compounds but also between 4-F-PhonyH and its Cl and Br counterparts. For both iterations of 4-Cl-PhonyH and 4-Br-PhonyH isomorphism was observed between like space groups. Polymorphs of 4-Cl-PhonyH and 4-Br-PhonyH are visibly distinguishable through colour differences.

Despite differences in the electronic and steric properties of the halogens F, Cl, and Br, these differences do not appear to display a clear trend in terms of the geometric properties of the solid-state properties of the 4-X-PhonyH compounds. Further studies are therefore needed where these compounds are implemented as ligand systems.

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Contribution of each author

The project was planned and executed by GJSV, and the article was written and translated. ZGM did the synthesis of some compounds as well as the refinement of some crystal data.

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Supporting material

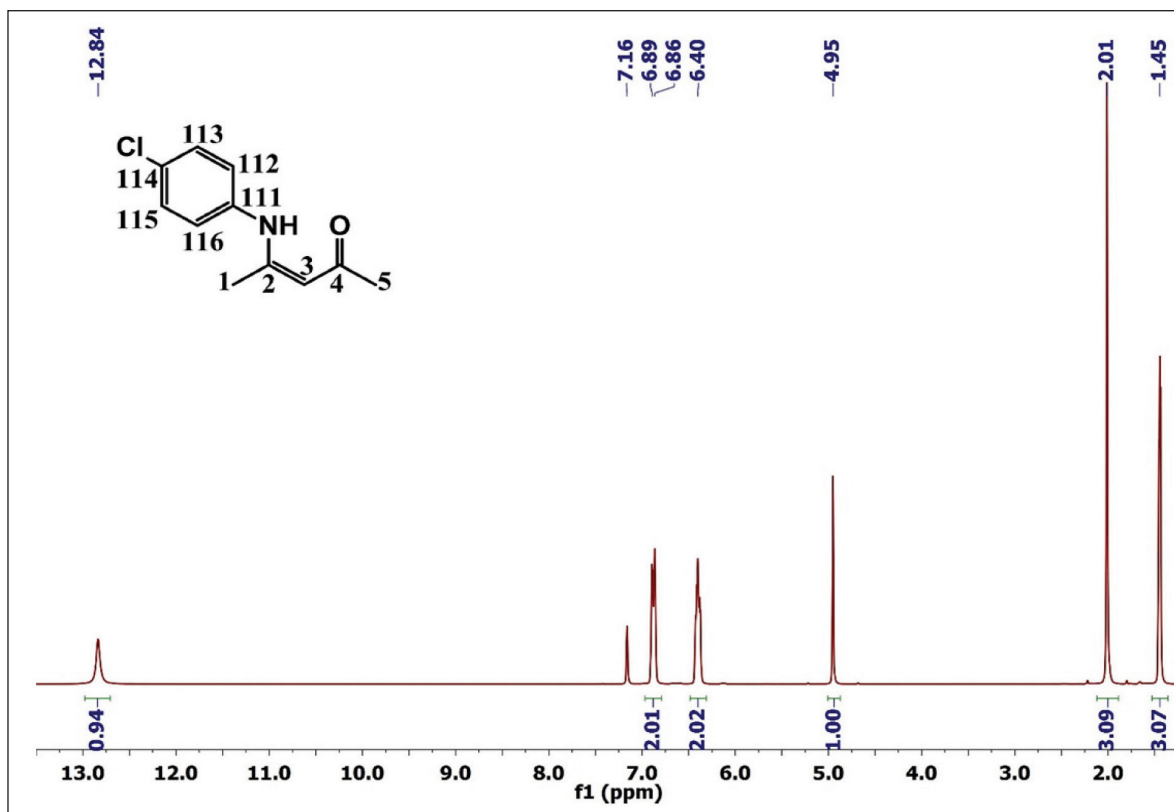


FIGURE A.1: ^1H (300.13 MHz) NMR spectrum of 4-Cl-PhonyH in C_6D_6 at 25°C .

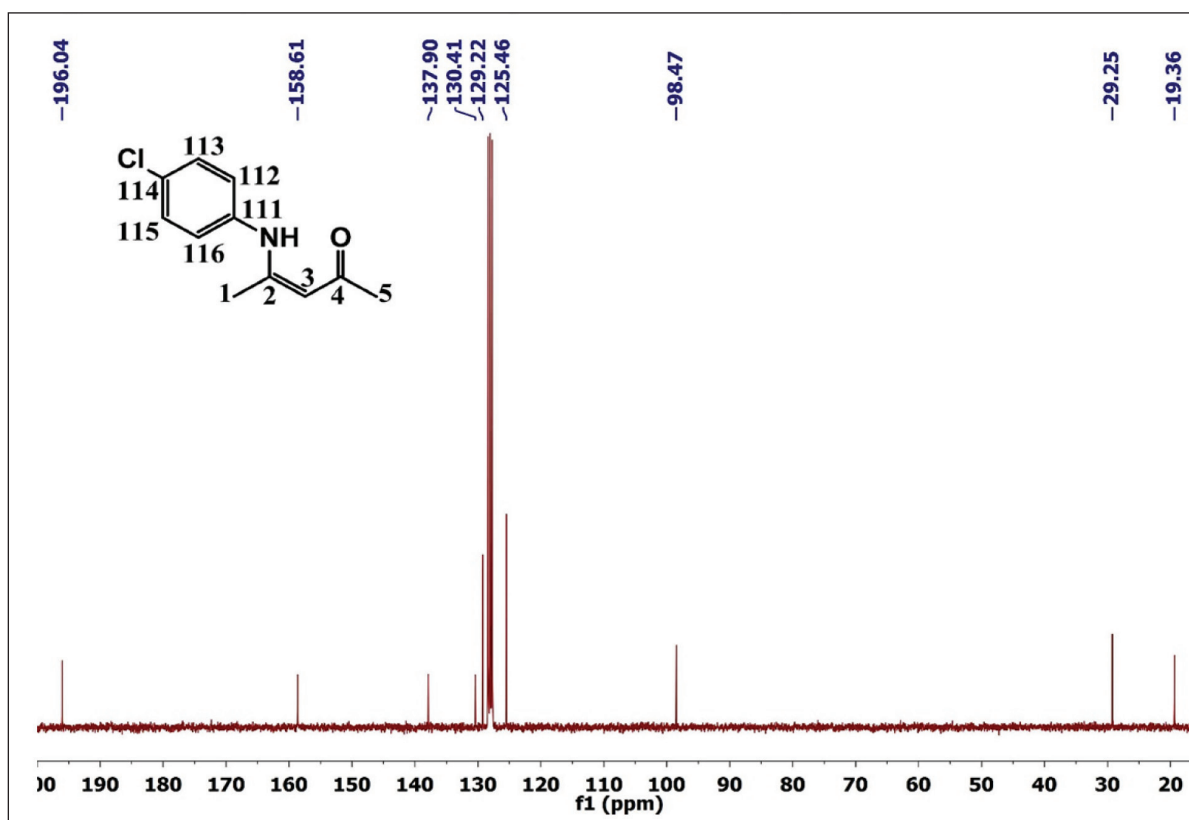


FIGURE A.2: ^{13}C (75.48 MHz) NMR spectrum of 4-Cl-PhonyH in C_6D_6 at 25°C .

TABLE A.1: Hydrogen bonds for 4-X-PhonyH compounds (Å and °).

Compound	D-H...A	d_{D-H} (Å)	$d_{H...A}$ (Å)	$d_{D...A}$ (Å)	\angle_{DHA} (°)	Symmetry code
I	$N_{11}-H_{11}\cdots O_{12}$	0.86(2)	1.98(2)	2.668(1)	136(2)	
	$N_{21}-H_{21}\cdots O_{22}$	0.89(2)	2.01(2)	2.709(2)	134(2)	
	$N_{11}-H_{11}\cdots O_{22}$	0.86(2)	2.31(2)	2.971(2)	133(2)	
	$N_{21}-H_{21}\cdots O_{12}$	0.89(2)	2.33(2)	3.041(2)	137(1)	
	$C_6-H_{6A}\cdots F_{24}^i$	0.98	2.5	3.420(2)	156.8	2-x, 1-y, 1-z
	$C_{113}-H_{113}\cdots O_{12}^{ii}$	0.95	2.54	3.349(2)	142.8	1-x, 2-y, 2-z
	$C_{213}-H_{213}\cdots O_{22}^{iii}$	0.95	2.43	3.273(1)	148.1	1-x, 1-y, 1-z
II	$N_{11}-H_{11}\cdots O_{12}$	0.88(2)	1.89(2)	2.641(2)	142(2)	
	$C_1-H_{1A}\cdots F_{14}^{iv}$	0.98	2.48	3.326(2)	144.9	2-x, $\frac{1}{2}$ -y, $\frac{1}{2}$ -z
	$C_1-H_{1B}\cdots O_{12}^v$	0.98	2.63	3.534(1)	143.6	x, $1\frac{1}{2}$ -y, $-\frac{1}{2}$ +z
	$C_{116}-H_{116}\cdots O_{12}^{vi}$	0.95	2.53	3.407(2)	153.6	1-x, 1-y, 1-z
III	$N_{11}-H_{11}\cdots O_{12}$	0.81(2)	2.02(3)	2.673(3)	138(2)	
	$N_{21}-H_{12}\cdots O_{22}$	0.83(2)	1.92(3)	2.624(2)	142(2)	
	$N_{31}-H_{31}\cdots O_{32}$	0.89(3)	1.89(3)	2.631(2)	140(2)	
	$N_{41}-H_{41}\cdots O_{42}$	0.89(3)	1.99(3)	2.682(2)	134(2)	
	$C_6-H_{6C}\cdots O_{12}$	0.98	2.51	3.341(3)	142	
	$C_{11}-H_{11B}\cdots O_{42}$	0.98	2.42	3.266(3)	143.9	
	$C_{312}-H_{312}\cdots O_{22}$	0.95	2.54	3.287(3)	135.2	
	$N_{11}-H_{11}\cdots O_{42}^{vii}$	0.81(2)	2.49(2)	3.136(2)	138(2)	$-\frac{1}{2}$ +x, $-\frac{1}{2}$ +y, z
	$N_{41}-H_{41}\cdots O_{12}^{viii}$	0.89(3)	2.44(3)	3.166(2)	139(2)	$\frac{1}{2}$ +x, $\frac{1}{2}$ +y, z
	IV	$N_{11}-H_{11}\cdots O_{12}$	0.87(3)	2.00(2)	2.705(2)	137(2)
$N_{11}-H_{11}\cdots O_{12}^{ix}$		0.87(3)	2.48(3)	3.316(2)	130(2)	-x, 2-y, 1-z
V	$N_{11}-H_{11}\cdots O_{12}$	0.886(3)	2.003(2)	2.675(4)	131.50(18)	
	$N_{21}-H_{21}\cdots O_{22}$	0.899(3)	1.802(2)	2.635(3)	152.98(19)	
	$N_{31}-H_{31}\cdots O_{32}$	0.906(3)	1.832(2)	2.629(3)	145.5(2)	
	$N_{41}-H_{41}\cdots O_{42}$	0.840(3)	1.972(2)	2.665(4)	139.24(19)	
	$C_6-H_{6B}\cdots O_{12}$	0.98	2.43	3.291(4)	146.2	
	$C_{11}-H_{11B}\cdots O_{42}$	0.98	2.53	3.325(4)	138.6	
	$C_{216}-H_{216}\cdots O_{32}$	0.95	2.52	3.312(4)	141.1	
	$C_{312}-H_{312}\cdots O_{22}$	0.95	2.61	3.396(4)	139.7	
	$N_{11}-H_{11}\cdots O_{42}^x$	0.886(3)	2.473(2)	3.217(4)	141.92(18)	$-\frac{1}{2}$ +x, $\frac{1}{2}$ +y, z
	$N_{41}-H_{41}\cdots O_{12}^{xi}$	0.840(3)	2.527(2)	3.180(4)	135.41(19)	$\frac{1}{2}$ +x, $-\frac{1}{2}$ +y, z
	$C_{16}-H_{16B}\cdots O_{32}^{xii}$	0.98	2.59	3.555(4)	166.5	$-\frac{1}{2}$ +x, $-\frac{1}{2}$ +y, z
VI	$N_{11}-H_{11}\cdots O_{12}$	0.97(8)	1.89(8)	2.70(1)	139(6)	
	$N_{11}-H_{11}\cdots O_{12}^{xiii}$	0.97(8)	2.46(7)	3.16(1)	129(5)	1-x, 1-y, 1-z
	$N_{11}-H_{11}\cdots O_{12}^{xiv}$	1.07(7)	2.44(7)	3.35(1)	141(6)	1+x, y, z