PERKIN 2

The molecular structures of 2-, 3- and 4-chloropyridine and chloropyrazine in the gas phase by electron diffraction and *ab initio* calculations†

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The gas-phase molecular structures of chloropyrazine, 2-, 3- and 4-chloropyridine have been determined by *ab initio* calculations and by gas-phase electron diffraction (GED) supplemented with rotation constants and restraints based on *ab initio* calculations. Geometries are compared to those of their respective parent compounds and other related systems to demonstrate the effects of chlorination on ring geometry.

Introduction

Six-membered aromatic rings which contain one (pyridine) or two (pyrimidine, pyrazine and pyridazine) nitrogen atoms and their derivatives are key compounds in organic chemistry. Examples of each class of compound have been found in nature, most notably pyrimidine as a component part of the four bases in DNA, while pyrazines are responsible for flavouring in foodstuffs as diverse as cooked meats, cheese, tea and coffee. Many derivatives which possess biological activity have been synthesised, with applications including antibiotics and antihypertensive agents.

Reliable structural data for these rings are essential for use in molecular modelling programs. However, many important compounds contain oxygen or nitrogen substituents which distort the ring structure, but simple compounds with these substituents do not yield useful structural data for modelling because proton shifts give isomeric forms. Chloro derivatives are therefore particularly important, because the electronegativity of chlorine is as close to those of nitrogen and oxygen as can be obtained with a simple substituent, and electronegativity is the major influence on ring distortion.

We extend our earlier work on dichloro derivatives of pyrimidine, pyrazine and pyridazine to the monochloro derivatives of pyridine and pyrazine. The results are compared to both the parent compounds and other chlorinated derivatives of similar compounds,[1] thus illustrating the effects of the electron-withdrawing substituents on ring structure. Structures are derived experimentally from gas-phase electron diffraction (GED) supplemented with rotation constants,[2–5] and also calculated by *ab initio* methods using correlated wavefunctions. As insufficient structural information is available from the experiments to give complete structures the SARACEN method[6] has been employed, using theoretical data as restraints in the analysis of the experimental data and thereby making optimum use of all available information.

Experimental

Ab initio calculations

All calculations were performed on a Dec Alpha 1000 4/200 workstation using the Gaussian 94 program.[7] Geometry optimisations on all four molecules were undertaken at the SCF level using the standard 3-21G*,[8–10] 6-31G*[11–13] and 6-311G** basis sets, while the larger two basis sets were used for MP2 optimisations. For the smallest molecule in the series, chloropyrazine, we also investigated the effects of adding diffuse functions to the basis set and of including a larger polarisation set by performing calculations at the 6-31+G*/MP2 and 6-31G(df,p)/MP2 levels. The effects of including a more sophisticated treatment of electron correlation were investigated using the 6-31G* basis set at the MP3 and MP4SDQ levels of theory.

Vibrational frequency calculations undertaken at the 3-21G*/SCF, 6-31G*/SCF and 6-31G*/MP2 levels were used to verify overall C_s symmetry for chloropyrazine and 2- and 3-chloropyridine and overall C_{2v} symmetry for 4-chloropyridine. Predictions of the amplitudes of vibration used in GED refinements were obtained from the highest level frequency calculations by constructing a harmonic force field using the ASYM40 program.[14]

Sample preparation

All samples were purchased through the Aldrich catalogue (purity > 98%) and used in the GED analysis without further purification.

Gas-phase electron diffraction

Electron scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus operating at *ca.* 44.5 kV (electron wavelength *ca.* 5.6 pm).[15] Nozzle-to-plate distances for the metal inlet nozzle were *ca.* 95 and 259 mm yielding data in the *s* range 20–356 nm^{-1}; three plates were exposed at each camera distance. The sample and nozzle temperatures were maintained at *ca.* 373 and *ca.* 386 K respectively during the exposure periods.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analysed in exactly the same way as those for the target molecules so as to minimise systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors and electron wavelengths for the measurements are collected in Table 1.

The electron-scattering patterns were converted into digital form using a computer-controlled Joyce Loebl MDM6 microdensitometer with a scanning program described elsewhere.[16] The programs used for data reduction[16] and least-squares

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† Supplementary material are available (SUPPL. NO. 57499, 13 pp.). For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors). The supplementary data is also available on the RSC's web server, http://www.rsc.org/suppdata/p2/1999/745/.

Table 1 Nozzle-to-plate distances (mm), weighting functions (nm^{-1}), correlation parameters, scale factors and electron wavelengths (pm) used in the electron diffraction study

Molecule	Nozzle-to-plate distance[a]	Δs	$s_{\min}$	s_{w1}	s_{w2}	$s_{\max}$	Correlation parameter	Scale factor[b]	Electron wavelength
Chloropyrazine	95.55	4	80	100	304	356	0.345	0.829(26)	5.699
	259.63	2	20	40	140	164	0.479	0.840(14)	5.696
2-Chloropyridine	95.46	4	100	120	304	356	0.343	0.810(26)	5.682
	260.06	2	20	40	140	164	0.456	0.824(10)	5.681
3-Chloropyridine	95.46	4	120	140	304	356	0.224	0.888(28)	5.611
	259.92	2	20	40	120	144	0.489	0.843(4)	5.688
4-Chloropyridine	94.56	4	80	100	304	356	0.340	0.752(23)	5.694
	258.63	2	20	40	122	144	0.484	0.874(6)	5.682

[a] Determined by reference to the scattering pattern of benzene vapour. [b] Values in parentheses are the estimated standard deviations.

Table 2 Calculated geometries for chloropyrazine (r_e/pm, ∠/°)

	3-21G*	6-31G*				6-31+G*	6-31G(df,p)	6-311G**	
	SCF	SCF	MP2	MP3	MP4	MP2	MP2	SCF	MP2[a]
*r*N(1)–C(2)	131.2	130.2	133.0	132.2	132.4	133.2	132.8	129.8	132.8
*r*N(1)–C(6)	133.6	132.4	134.7	134.3	134.5	134.8	134.3	132.3	134.5
*r*N(4)–C(3)	132.4	131.2	134.0	133.2	133.3	134.1	133.6	131.0	133.8
*r*N(4)–C(5)	133.5	132.3	134.6	134.2	134.4	134.8	134.2	132.2	134.5
*r*C(2)–C(3)	138.5	139.1	140.1	140.1	140.3	140.3	139.7	139.1	140.3
*r*C(5)–C(6)	137.6	138.1	139.3	139.1	139.2	139.5	139.0	137.9	139.6
*r*C(2)–Cl(7)	173.2	173.4	173.4	173.6	173.9	173.1	172.1	173.6	173.1
*r*C(3)–H(8)	106.7	107.3	108.7	108.5	108.8	108.7	108.4	107.3	108.6
*r*C(5)–H(9)	106.8	107.4	108.7	108.6	108.8	108.7	108.4	107.4	108.6
*r*C(6)–H(10)	106.8	107.4	108.7	106.6	108.8	108.8	108.4	107.4	108.7
∠N(1)–C(2)–C(3)	121.7	122.7	123.2	123.2	123.1	123.2	123.1	122.8	123.4
∠N(1)–C(6)–C(5)	120.6	121.6	122.2	122.2	122.1	122.2	122.3	121.6	122.4
∠N(4)–C(3)–C(2)	120.0	120.5	121.2	121.1	121.1	121.2	121.4	120.5	121.4
∠N(4)–C(5)–C(6)	120.6	121.3	122.0	121.9	121.9	121.9	122.0	121.3	122.1
∠C(2)–N(1)–C(6)	118.3	116.5	115.3	115.4	115.5	115.4	115.2	116.5	115.0
∠C(3)–N(4)–C(5)	118.7	117.4	116.1	116.2	116.3	116.2	115.9	117.4	115.8
∠N(1)–C(2)–Cl(7)	118.6	118.0	117.5	117.7	117.7	117.5	117.6	118.1	117.7
∠C(2)–C(3)–H(8)	121.2	121.1	121.2	121.0	121.0	121.3	120.9	121.2	120.9
∠C(6)–C(5)–H(9)	121.7	121.3	121.3	121.2	121.3	121.3	121.1	121.3	121.1
∠C(5)–C(6)–H(10)	122.1	121.5	121.5	121.4	121.5	121.6	121.3	121.5	121.3

[a] Coordinates and energies are given in Table 1 of the electronic supplementary data.

refinement[17] have been described previously; the complex scattering factors were those listed by Ross *et al.*[18]

Results

Ab initio calculations

A graded series of *ab initio* molecular orbital calculations was undertaken to investigate the structure of chloropyrazine (see Table 2). In general, the variation in the values of structural parameters was found to be rather small with variations in bond lengths and angles typically being in the region of 2–3 pm and 1–2°, respectively. The largest structural changes resulted from the inclusion of electron correlation, which led to a lengthening of ring bonds by 2–3 pm. Improving the theoretical treatment beyond 6-31G*/MP2 led to only minor changes in the values of bond lengths. For example, improving the correlation treatment from MP2 to MP4SDQ led to changes in ring bond lengths of around 0.5 pm when the 6-31G* basis set was employed. Similarly, the addition of diffuse functions or adopting a larger polarisation set led to only minor changes in parameter values. In general, improving either the basis set or the treatment of electron correlation beyond MP2 had little impact upon the values of bond angles.

In view of the relative insensitivity of the predicted molecular geometry for chloropyrazine, a smaller set of geometry optimisations was undertaken for 2-, 3- and 4-chloropyrazine (Table 3). Geometric changes were broadly similar to those observed for chloropyrazine. For example, adding a description of electron correlation into the calculation led to elongation of ring bonds by 2–3 pm, while improving the basis from 6-31G* to 6-311G** led to changes in bond lengths of a few tenths of a picometer. Most bond angle parameters varied across a range of less than 1° in the set of calculations.

Gas-phase electron diffraction analysis

GED Models. The geometric parameters used to describe chloropyrazine, 2-chloropyridine, 3-chloropyridine (all in C_s symmetry) and 4-chloropyridine (C_{2v} symmetry) are documented in Tables 4–7; the atom numbering systems are shown in Fig. 1. The starting parameters for the r_α° refinements were taken from the theoretical geometries optimised at the 6-311G**/MP2 level. Theoretical (6-31G*/MP2) Cartesian force fields were obtained for all four molecules and converted into force fields described by a set of symmetry coordinates using the program ASYM40.[14] The *ab initio* force constants were then scaled by 0.95, 0.90 and 0.85 for bond stretches, angle bends and torsions, respectively, with values chosen falling within acceptable guidelines as suggested by Rauhut and Pulay.[19] The resulting force field was then used to calculate both parallel (u) and perpendicular (k) amplitudes of vibration, which were taken as starting values for all refinements. The rotation constant values (corresponding to the ^{35}Cl and ^{37}Cl isotopomers for each compound, see Table 8) used to supplement the GED data sets were obtained from the literature.[2–5] Vibrational corrections required to convert the rotation constants from the experimental structure type B_0 to B_z (equivalent

Table 3 Calculated geometries for *n*-chloropyridine (*n* = 2, 3 or 4) (r_e/pm, ∠/°)

		3-21G*	6-31G*		6-311G**	
n		SCF	SCF	MP2	SCF	MP2[a]
2	*r*N(1)–C(2)	131.1	130.4	132.9	130.0	132.7
	*r*N(1)–C(6)	133.5	132.5	134.7	132.5	134.6
	*r*C(2)–C(3)	138.3	138.7	139.8	138.6	139.9
	*r*C(3)–C(4)	138.0	138.0	139.2	137.9	139.4
	*r*C(4)–C(5)	138.7	138.7	139.6	138.7	139.8
	*r*C(5)–C(6)	137.8	138.0	139.3	137.9	139.5
	*r*C(2)–Cl(7)	174.3	174.2	174.3	174.4	174.0
	*r*C(3)–H(8)	106.8	107.2	108.5	107.2	108.4
	*r*C(4)–H(9)	107.1	107.5	108.7	107.5	108.6
	*r*C(5)–H(9)	107.0	107.4	108.6	107.4	108.5
	*r*C(6)–H(11)	106.9	107.5	108.7	107.5	108.7
	∠C(2)–N(1)–C(6)	118.9	117.6	116.7	117.5	116.6
	∠N(1)–C(2)–C(3)	123.5	124.7	124.9	124.9	125.0
	∠N(1)–C(6)–C(5)	122.2	123.4	123.6	123.4	123.8
	∠C(2)–C(3)–C(4)	117.7	117.1	117.5	117.0	117.6
	∠C(3)–C(4)–C(5)	119.4	119.2	119.0	119.2	118.8
	∠C(4)–C(5)–C(6)	118.3	118.0	118.4	118.0	118.4
	∠N(1)–C(2)–Cl(7)	117.5	116.7	116.5	116.7	116.7
	∠C(2)–C(3)–H(8)	120.3	120.7	120.6	120.8	120.5
	∠C(3)–C(4)–H(9)	120.0	120.1	120.1	120.1	120.3
	∠C(4)–C(5)–H(10)	121.2	121.5	121.3	121.5	121.4
	∠C(5)–C(6)–H(11)	121.5	120.8	121.0	120.8	120.8
3	*r*N(1)–C(2)	132.7	131.8	134.2	131.7	134.0
	*r*N(1)–C(6)	133.1	132.1	134.5	131.9	134.3
	*r*C(2)–C(3)	138.1	138.5	139.7	138.3	140.0
	*r*C(3)–C(4)	137.9	138.1	139.3	137.9	139.4
	*r*C(4)–C(5)	138.4	138.3	139.4	138.2	139.6
	*r*C(5)–C(6)	138.2	138.4	139.5	138.4	139.8
	*r*C(3)–Cl(8)	174.1	173.9	173.5	174.0	173.1
	*r*C(2)–H(7)	106.9	107.4	108.8	107.5	108.7
	*r*C(4)–H(9)	107.0	107.4	108.6	107.4	108.5
	*r*C(5)–H(10)	107.0	107.4	108.6	107.4	108.6
	*r*C(6)–H(11)	107.0	107.5	108.8	107.6	108.7
	∠C(2)–N(1)–C(6)	119.3	118.4	117.5	118.4	117.4
	∠N(1)–C(2)–C(3)	121.7	122.5	122.7	122.5	122.9
	∠N(1)–C(6)–C(5)	122.3	123.3	123.4	123.3	123.5
	∠C(2)–C(3)–C(4)	119.6	119.4	119.7	119.5	119.6
	∠C(3)–C(4)–C(5)	118.4	117.9	117.6	117.8	117.5
	∠C(4)–C(5)–C(6)	118.8	118.6	119.0	118.6	119.1
	∠C(2)–C(3)–Cl(8)	119.9	119.9	119.7	119.8	119.8
	∠C(3)–C(2)–H(7)	120.6	120.3	120.3	120.2	120.0
	∠C(3)–C(4)–H(9)	120.3	120.6	120.6	120.6	120.6
	∠C(4)–C(5)–H(10)	120.7	120.9	120.6	120.9	120.6
	∠C(5)–C(6)–H(11)	121.0	120.5	120.8	120.4	120.6
4	*r*N(1)–C(2)	133.0	132.0	134.5	131.9	134.3
	*r*C(3)–C(4)	137.9	138.1	139.3	137.9	139.4
	*r*C(2)–C(3)	138.3	138.5	139.5	138.4	139.8
	*r*C(4)–Cl(9)	174.2	173.6	173.6	173.7	173.1
	*r*C(3)–H(8)	106.9	107.3	108.6	107.2	108.5
	*r*C(2)–H(7)	107.0	107.5	108.8	107.6	108.8
	∠C(3)–C(4)–C(5)	120.0	119.8	119.5	119.9	119.2
	∠C(4)–C(3)–C(2)	117.9	117.4	117.8	117.3	117.9
	∠N(1)–C(2)–C(3)	122.8	123.9	124.2	123.9	124.3
	∠C(2)–N(1)–C(6)	118.7	117.6	116.5	117.6	116.4
	∠C(3)–C(4)–Cl(9)	120.0	120.1	120.2	120.1	120.4
	∠C(4)–C(3)–H(8)	121.0	121.4	121.1	121.5	121.0
	∠C(3)–C(2)–H(7)	120.3	119.7	119.9	119.7	119.7

[a] Coordinates and energies are given in Table 1 of the electronic supplementary data.

to the r_α° structural type derived from the GED data) were obtained from the scaled *ab initio* force fields. Note that no attempt was made to account for the change in C–Cl bond distance due to isotopic substitution as inclusion of this effect in an earlier structural refinement was negligible.[1]

Discussion

The presence of a large number of similar interatomic distances and of parameters involving hydrogen (which is a poor scatterer of electrons) prevented complete structure determinations for chloropyrazine, 2-, 3- and 4-chloropyridine using just experimental data. In such cases it is our practice to include information obtained theoretically to allow complete structural determination using the SARACEN method.[6] The essential feature of this method is that information calculated by *ab initio* methods is introduced into the refinement procedure as additional observations (or restraints), the weight of any observation being assigned according to the level of convergence achieved in a series of graded *ab initio* calculations. By employ-

Table 4 Refined and calculated geometric parameters for chloropyrazine (r_α°/pm, ∠/°) from the SARACEN study[a,b,c]

No.	Parameter	GED (r_α°)	6-311G**/MP2 (r_e)
Independent parameters			
p_1	r[C(2)–N(1) + C(3)–N(4) + C(5)–N(4)]/3	133.1(2)	133.7
p_2	rC(2)–N(1) − rC(3)–N(4)	−1.1(4)	−1.0
p_3	rC(2)–N(1) − rC(5)–N(4)	−1.8(5)	−1.7
p_4	rC(2)–Cl(7)	173.6(2)	173.1
p_5	rC–C$_{\text{av}}$	139.0(3)	139.9
p_6	rC(2)–C(3) − rC(5)–C(6)	0.3(5)	0.7
p_7	rC–H$_{\text{av}}$	108.0(7)	108.7
p_8	rC(3)–H(5) − rC(5)–H(9)	0.0(5)	0.0
p_9	rC(3)–H(8) − rC(6)–H(10)	0.0(5)	−0.1
p_{10}	∠N(1)–C(2)–Cl(7)	118.2(3)	117.7
p_{11}	[∠C(2)–C(3)–H(8) + ∠C(5)–C(6)–H(10) + ∠N(4)–C(5)–H(9)]/3	120.6(8)	119.7
p_{12}	∠C(2)–C(3)–H(8) − ∠N(4)–C(5)–H(9)	4.6(5)	4.1
p_{13}	∠C(2)–C(3)–H(8) − ∠C(5)–C(6)–H(10)	0.1(5)	−0.4
p_{14}	[∠N(1)–C(2)–C(3) + ∠C(2)–C(3)–N(4) + ∠C(3)–N(4)–C(5) + ∠N(4)–C(5)–C(6)]/4	120.8(1)	120.7
p_{15}	∠N(1)–C(2)–C(3) − ∠C(2)–C(3)–N(4)	2.8(4)	2.0
p_{16}	∠N(1)–C(2)–C(3) − ∠C(3)–N(4)–C(5)	7.6(4)	7.6
p_{17}	∠N(1)–C(2)–C(3) − ∠N(4)–C(5)–C(6)	1.7(4)	1.3
Dependent parameters			
p_{18}	rN(1)–C(2)	132.2(3)	132.8
p_{19}	rN(1)–C(6)	135.1(3)	134.5
p_{20}	rN(4)–C(3)	133.2(4)	133.8
p_{21}	rN(4)–C(5)	134.0(3)	134.5
p_{22}	rC(2)–C(3)	139.2(4)	140.3
p_{23}	rC(5)–C(6)	138.9(4)	139.6
p_{24}	rC(3)–H(8)	108.0(7)	108.6
p_{25}	rC(5)–H(9)	108.0(8)	108.6
p_{26}	rC(6)–H(10)	108.1(8)	108.7
p_{27}	∠N(1)–C(2)–C(3)	123.8(2)	123.4
p_{28}	∠N(1)–C(6)–C(5)	121.8(4)	122.4
p_{29}	∠N(4)–C(3)–C(2)	121.0(3)	121.4
p_{30}	∠N(4)–C(5)–C(6)	122.2(3)	122.1
p_{31}	∠C(2)–N(1)–C(6)	115.0(4)	115.0
p_{32}	∠C(3)–N(4)–C(5)	116.2(3)	115.8
p_{33}	∠C(2)–C(3)–H(8)	122.2(7)	120.9
p_{34}	∠C(6)–C(5)–H(9)	120.2(10)	121.1
p_{35}	∠C(5)–C(6)–H(10)	122.1(9)	121.3

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] See text for parameter definitions. [c] Tables of final coordinates, selected distances and amplitudes of vibration, and the full least-squares correlation matrix are available in Tables 2, 3 and 4(a) of the electronic supplementary data.

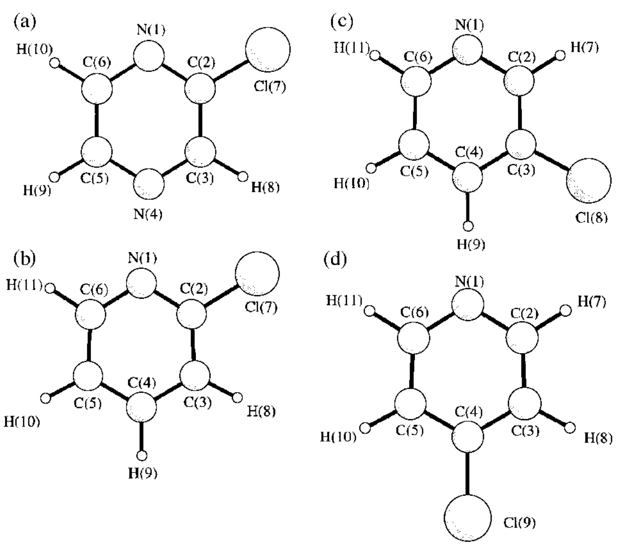

Fig. 1 The structures of (a) chloropyrazine, (b) 2-chloropyridine, (c) 3-chloropyridine and (d) 4-chloropyridine.

ing the SARACEN method in the present work it has been possible to refine the values of all structural parameters and all amplitudes of vibration with intensities of greater than 10% of the most intense peak in the radical distribution curve. The values of all additional observations used in the four sets of refinements can be found in Table 9 together with their respective weightings (uncertainties).

The effect of introducing rotation constants[2–5] (see Table 8) into the structural refinements was the same for each compound. No significant effect was observed in the overall geometries but a notable improvement in the precision of all heavy-atom distances was obtained in the least-squares refinements. In general standard deviations for bonded distances dropped by a factor of two and for long non-bonded distances by factors of three to five. This improvement in precision of non-bonded distances is a reflection of the greater precision now obtained in the internal ring angles.

Chloropyrazine [Fig. 1(*a*)]

The results obtained in the structural refinement for chloropyrazine are given in Table 4 and Tables 2–4(a) in the electronic supplementary data. Six parameters refined freely (p_1, rC–N$_{\text{av}}$; p_4, rC–Cl; p_5, rC–C; p_{10} ∠NCCl; p_{14}, ring angle average and p_{16}, ring angle difference). Parameters which could not refine without assistance [involving differences between similar distances ($p_{2,3,6,8,9}$) or angles ($p_{15,17}$), hydrogen ($p_{7,11-13}$) or strongly correlated to other refining parameters (p_{19})] were assigned restraints based on the results of the *ab intitio* calculations (Table 9). In addition, one further restraint was required on the dependent ring distances rC–C and rC–N (*i.e.* rC–C$_{\text{av}}$ − rC–N$_{\text{av}}$, see Table

Table 5 Refined and calculated geometric parameters for 2-chloropyridine (r_α°/pm, ∠/°) from the SARACEN study[a,b,c]

No.	Parameter	GED (r_α°)	6-311G**/MP2 (r_e)
Independent parameters			
p_1	rC–C$_{av}$	139.5(2)	139.6
p_2	rC(5)–C(6) − rC(4)–C(5)	−0.4(4)	−0.3
p_3	rC(5)–C(6) − rC(3)–C(4)	0.3(4)	0.1
p_4	rC(3)–C(4) − rC(2)–C(3)	0.1(4)	−0.5
p_5	rC–Cl	173.8(2)	174.0
p_6	rC(6)–N(1)	134.5(4)	134.6
p_7	rC–H$_{av}$	108.8(4)	108.6
p_8	rC(6)–H(11) − rC(5)–H(10)	0.2(5)	0.2
p_9	rC(6)–H(11) − rC(4)–H(9)	0.0(5)	0.1
p_{10}	rC(4)–H(9) − rC(3)–H(8)	0.2(5)	0.2
p_{11}	∠C–C–C$_{av}$	118.1(1)	118.3
p_{12}	∠C(4)–C(5)–C(6) − ∠C(3)–C(4)–C(5)	−0.8(3)	−0.4
p_{13}	∠C(4)–C(5)–C(6) − ∠C(2)–C(3)–C(4)	0.9(3)	0.8
p_{14}	∠C–C–Cl	118.1(3)	118.3
p_{15}	∠N(1)–C(2)–C(3)	125.3(2)	125.0
p_{16}	[∠C(5)–C(6)–H(11) + ∠C(6)–C(5)–H(10) + ∠C(5)–C(4)–H(9) + ∠C(4)–C(3)–H(8)]/4	121.6(6)	121.0
p_{17}	∠C(5)–C(6)–H(11) − ∠C(6)–C(5)–H(10)	0.6(4)	0.6
p_{18}	∠C(5)–C(6)–H(11) − ∠C(5)–C(4)–H(9)	−0.2(5)	−0.1
p_{19}	∠C(5)–C(4)–H(9) − ∠C(4)–C(3)–H(8)	−1.2(5)	−1.0
Dependent parameters			
p_{20}	rC(5)–C(6)	139.5(3)	139.5
p_{21}	rC(4)–C(5)	140.0(4)	139.8
p_{22}	rC(3)–C(4)	139.3(3)	139.4
p_{23}	rC(2)–C(3)	139.2(4)	139.9
p_{24}	rN(1)–C(2)	131.9(3)	132.7
p_{25}	rC(6)–H(11)	108.9(5)	108.7
p_{26}	rC(5)–H(10)	108.7(6)	108.5
p_{27}	rC(4)–H(9)	108.9(5)	108.6
p_{28}	rC(3)–H(8)	108.7(6)	108.4
p_{29}	∠C(2)–N(1)–C(6)	117.0(4)	116.6
p_{30}	∠C(2)–C(3)–C(4)	117.3(3)	117.6
p_{31}	∠C(3)–C(4)–C(5)	119.0(3)	118.8
p_{32}	∠C(4)–C(5)–C(6)	118.2(1)	118.4
p_{33}	∠C(5)–C(6)–N(1)	123.3(3)	123.8
p_{34}	∠C(6)–C(5)–H(10)	120.7(8)	120.2
p_{35}	∠C(5)–C(4)–H(9)	121.5(7)	120.9
p_{36}	∠C(4)–C(3)–H(8)	122.7(9)	121.9

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] See text for parameter definitions. [c] Tables of final coordinates, selected distances and amplitudes of vibration, and the full least-squares correlation matrix are available in Tables 2, 3 and 4(b) of the electronic supplementary data.

9) to reduce the strong correlation observed between these similar distances. All restrained parameters refined to within one standard deviation of the imposed restraint with the exceptions of p_{15} and rC–C$_{av}$ − rC–N$_{av}$ which refined to values just outside one standard deviation. The final combined molecular scattering and radial distribution curves are given in Figs. 2(a) and 3(a), respectively, together with difference curves for the final refinement, for which R_G was 0.115.

2-Chloropyridine [Fig. 1(*b*)]

The results obtained from the final refinement of 2-chloropyridine are reported in Table 5 and Tables 2–4(b) of the electronic supplementary data. Five parameters refined without the aid of restraints, namely p_1, rC–C$_{av}$; p_5, rC–Cl; p_6, N(1)–C(6); p_{11}, ∠C–C–C$_{av}$ and p_{14} ∠C–C–Cl. The remaining parameters (involving differences between similar interatomic distances or angles, p_{2-4}, p_{8-10}, p_{12-13} and p_{17-19}, or hydrogen, p_7 and p_{15-16}) were assigned restraints in accordance with the SARACEN method (see Table 9). Two further parameters were required to reduce the effects of correlation between the six similar ring distances, namely rC–C$_{av}$ − rC–N$_{av}$ and rC(6)–N(1) − rC(2)–N(1). All restrained geometric parameters returned values in the least-squares refinement to within one standard deviation of the restrained value, except for p_{13} and the dependent parameter restraint rC(6)–N(1) − rC(2)–N(1), which refined to within two standard deviations. The R_G factor recorded for this refinement was 0.084, indicating that the data are of good quality. The final combined molecular scattering curve and radial distribution curve are given in Figs. 2(b) and 3(b), respectively.

3-Chloropyridine [Fig. 1(*c*)]

Final results obtained for this refinement are given in Table 6 and Tables 2–4(c) of the electronic supplementary data. As with 2-chloropyridine p_1, rC–C$_{av}$; p_5, rC–Cl; p_6, rN(1)–C(6); p_{11}, ∠C–C–C$_{av}$ and p_{14}, ∠C–C–Cl refined unaided, with all remaining geometric parameters assigned restraints in accordance with the SARACEN method (see Table 9). Similarly, a dependent parameter restraint [rN(1)–C(2) − rC(5)–C(6)] was also required in this refinement. All restrained parameters refined to values within one standard deviation of the restraint, except p_3 which refined to a value just outside one standard deviation. The final combined molecular scattering curve and radial distribution curve are given in Figs. 2(c) and 3(c), respectively. The final R_G factor obtained was 0.074.

4-Chloropyridine [Fig. 1(*d*)]

The results obtained from this structural refinement are presented in Table 7 and Tables 2–4(d) of the electronic supplementary data. Five parameters refined freely [p_1, rC–Cl; p_2, rN(1)–C(4); p_3, rC–C$_{av}$; p_7, ∠C(3)–C(4)···N(1) and p_8, ∠C(2)–

Table 6 Refined and calculated geometric parameters for 3-chloropyridine (r_α°/pm, ∠/°) from the SARACEN study[a,b,c]

No.	Parameter	GED (r_α°)	6-311G**/MP2 (r_e)
Independent parameters			
p_1	rC–C$_{\text{av}}$	139.6(2)	139.7
p_2	rC(5)–C(6) − rC(4)–C(5)	0.1(4)	0.2
p_3	rC(5)–C(6) − rC(3)–C(4)	0.9(4)	0.4
p_4	rC(3)–C(4) − rC(2)–C(3)	−0.4(5)	−0.6
p_5	rC(3)–Cl(8)	173.4(2)	173.1
p_6	rN(1)–C(6)	133.9(6)	134.3
p_7	rC–H$_{\text{av}}$	110.2(5)	108.6
p_8	rC(6)–H(11) − rC(5)–H(10)	0.0(5)	0.1
p_9	rC(6)–H(11) − rC(4)–H(9)	0.2(5)	0.2
p_{10}	rC(4)–H(9) − rC(2)–H(7)	−0.2(5)	−0.2
p_{11}	∠C–C–C$_{\text{av}}$	118.7(1)	118.7
p_{12}	∠C(4)–C(5)–C(6) − ∠C(3)–C(4)–C(5)	2.0(4)	1.6
p_{13}	∠C(3)–C(5)–C(6) − ∠C(2)–C(3)–C(4)	−1.2(3)	−0.5
p_{14}	∠C(4)–C(3)–Cl(8)	120.9(4)	120.6
p_{15}	∠N(1)–C(6)–H(11)	116.1(9)	116.5
p_{16}	∠N(1)–C(6)–C(5)	122.9(3)	123.5
p_{17}	[∠C(6)–C(5)–H(10) + ∠C(5)–C(4)–H(9) + ∠C(3)–C(2)–H(7)]/3	121.0(8)	120.7
p_{18}	∠C(6)–C(5)–H(10) − ∠C(5)–C(4)–H(9)	−1.7(5)	−1.7
p_{19}	∠C(6)–C(5)–H(10) − ∠C(3)–C(2)–H(7)	0.3(5)	0.2
Dependent parameters			
p_{20}	rN(1)–C(2)	132.6(5)	134.0
p_{21}	rC(5)–C(6)	140.0(4)	139.8
p_{22}	rC(4)–C(5)	139.9(4)	139.6
p_{23}	rC(3)–C(4)	139.1(3)	139.4
p_{24}	rC(2)–C(3)	139.5(4)	140.0
p_{25}	rC(4)–H(9)	110.0(6)	173.1
p_{26}	rC(6)–H(11)	110.2(6)	108.7
p_{27}	rC(5)–H(10)	110.2(7)	108.6
p_{28}	rC(2)–H(7)	110.2(6)	108.5
p_{29}	∠N(1)–C(2)–C(3)	122.3(3)	122.9
p_{30}	∠C(2)–N(1)–C(6)	118.6(5)	117.4
p_{31}	∠C(4)–C(5)–C(6)	119.0(3)	119.1
p_{32}	∠C(3)–C(4)–C(5)	117.0(2)	117.5
p_{33}	∠C(2)–C(3)–C(4)	120.9(4)	119.6

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] See text for parameter definitions. [c] Tables of final coordinates, selected distances and amplitudes of vibration, and the full least-squares correlation matrix are available in Tables 2, 3 and 4(c) of the electronic supplementary data.

Table 7 Refined and calculated geometric parameters for 4-chloropyridine (r_α°/pm, ∠/°) from the SARACEN study[a,b,c]

No.	Parameter	GED (r_α°)	6-311G**/MP2 (r_e)
Independent parameters			
p_1	rC(4)–Cl(9)	174.2(3)	173.1
p_2	rC(1)···N(4)	278.2(4)	280.1
p_3	rC–C$_{\text{av}}$	139.2(2)	139.6
p_4	rC(3)–C(4) − rC(2)–C(3)	−0.8(4)	0.4
p_5	rC–H$_{\text{av}}$	109.8(6)	108.7
p_6	rC(3)–H(8) − rC(2)–H(7)	−0.3(5)	−0.3
p_7	∠N(1)···C(4)–C(3)	60.7(2)	59.6
p_8	∠C(2)–C(3)–C(4)	116.2(3)	117.9
p_9	[∠C(4)–C(3)–H(8) + ∠C(3)–C(2)–H(7)]/2	121.5(8)	120.4
p_{10}	∠C(4)–C(3)–H(8) − ∠C(3)–C(2)–H(7)	1.2(5)	1.3
Dependent parameters			
p_{11}	rN(1)–C(2)	133.6(3)	134.3
p_{12}	rC(3)–C(4)	138.9(2)	139.4
p_{13}	rC(2)–C(3)	139.6(3)	139.8
p_{14}	rC(3)–H(8)	109.7(6)	108.5
p_{15}	rC(2)–H(7)	109.9(6)	108.8
p_{16}	∠C(3)–C(4)–C(5)	121.3(3)	119.2
p_{17}	∠N(1)–C(2)–C(3)	125.1(3)	124.3
p_{18}	∠C(2)–N(1)–C(6)	116.1(4)	116.4
p_{19}	∠C(3)–C(4)–Cl(9)	119.4(2)	120.4
p_{20}	∠C(4)–C(3)–H(8)	122.1(4)	121.0
p_{21}	∠C(3)–C(2)–H(7)	120.9(12)	119.7

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] See text for parameter definitions. [c] Tables of final coordinates, selected distances and amplitudes of vibration, and the full least-squares correlation matrix are available in Tables 2, 3 and 4(d) of the electronic supplementary data.

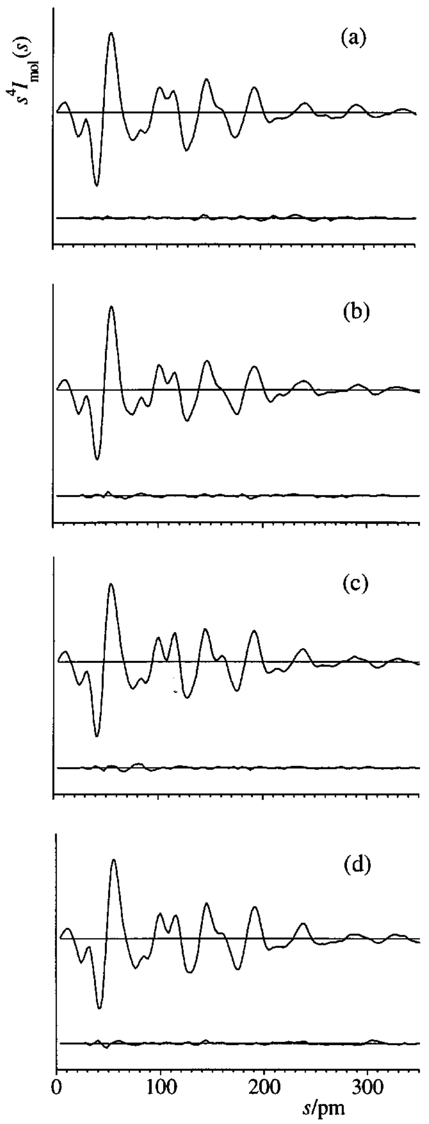

Fig. 2 Observed and final difference combined molecular scattering curves for (a) chloropyrazine, (b) 2-chloropyridine, (c) 3-chloropyridine and (d) 4-chloropyridine.

C(3)–C(4)], with the remaining five parameters assigned restraints (see Table 9). One dependent parameter restraint [rC–C$_{av}$ − rC–N$_{av}$] was also required. All restrained parameters returned values in the least-squares analysis in agreement with the restraints to within one (p_4, p_6 and p_{10}) or two (p_5 and p_9) standard deviations. The final molecular scattering curve and radial distribution curve are shown in Figs. 2(d) and 3(d), respectively. The final R_G factor recorded was 0.109.

Effects of monochlorination on ring geometry of pyridine and pyrazine

The gas-phase molecular structures of the monochloro derivatives of pyridine and pyrazine were compared to those of their respective parent molecules[20,21] to determine the effects of electron-withdrawing substituents on the overall ring geometry. The observed changes are presented in Table 10, where the main structural effects identified by experiment are also shown by the structures calculated by *ab initio* methods. In addition the observations are consistent with those from previous studies of dichloro derivatives of pyrimidine, pyrazine and pyridazine[1] (also shown in Table 10). The main structural changes upon chlorination can be summarised as widening of the *ipso* ring angle, narrowing of the adjacent ring angles and shortening of the adjacent C–N bond, with the adjacent C–C bond largely unaffected by the presence of the chlorine atom. These effects are similar to those observed on replacement of hydrogen atoms on benzene by chlorine (and other electronegative atoms), except that shortening of the adjacent C–C bonds also occurs.[22] The structural changes observed can be readily explained in terms of bonding hybridisation effects: since chlorine withdraws electron density from the ring an increase in p character of the *ipso* carbon sp^2 hybrid orbital will be required along the direction of the C–Cl bond. This will lead to a decrease in p character of the remaining sp^2 orbitals, thus giving rise to a widening of the *ipso* angle and shortening of the adjacent bonds. The electronegativity of the chlorine atom also helps explain the greater sensitivity of C–N bonds to change compared to C–C bonds. As the chlorine atom withdraws electron density the carbon atom will acquire a net positive charge. The lone pair on the neighbouring nitrogen atom will then be attracted towards the carbon atom, thereby increasing the bond order (and thus reducing the length) of the C–N bond.

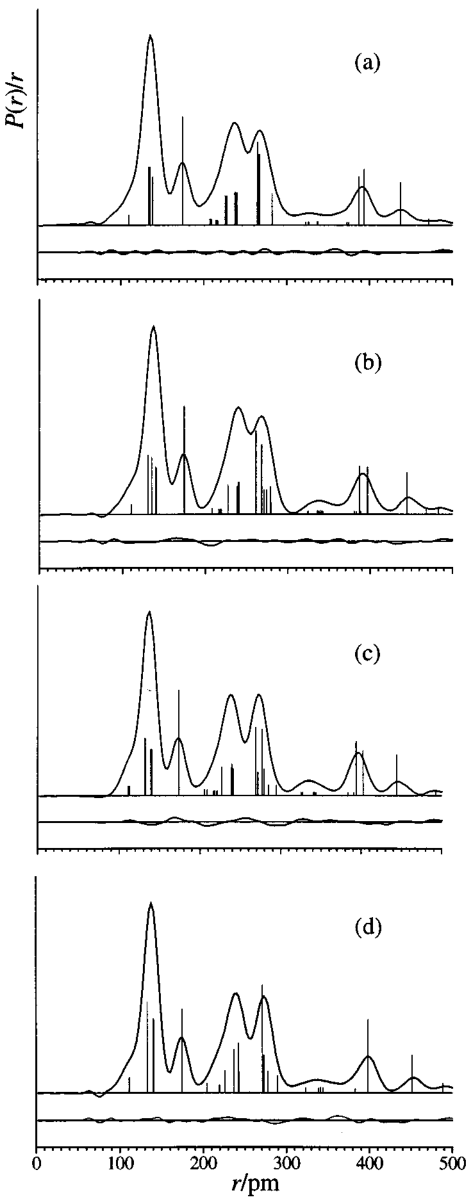

Fig. 3 Observed and final difference radial-distribution curves for (a) chloropyrazine, (b) 2-chloropyridine, (c) 3-chloropyridine and (d) 4-chloropyridine. Before Fourier inversion the data were multiplied by $s[\exp(-0.00002s^2)(Z_{Cl} - f_{Cl})(Z_{Cl} - f_{Cl})]$.

Whilst the same structural trends are clearly borne out by both experiment and theory, comparing actual parameter values obtained by the two methods (see Table 10) yields a

Table 8 Rotation constants (B/MHz) as used in the gas-phase structural studies

Compound	Rotation constant		Observed[a]		Calculated[c]	Difference	Uncertainty[d]
	Species	Axis	B_o	B_z[b]	B_z	B_z(obs. − calc.)	
Chloropyrazine	^{35}Cl	A	6042.281(115)	6042.046(115)	6041.847	0.200	0.12
		B	1664.099(3)	1663.656(3)	1663.548	0.108	0.05
		C	1304.622(3)	1304.436(3)	1304.398	0.038	0.03
	^{37}Cl	A	6041.942(103)	6041.750(103)	6041.763	−0.013	0.11
		B	1616.591(3)	1616.159(3)	1615.979	0.180	0.05
		C	1275.234(3)	1275.052(3)	1274.966	0.085	0.03
2-Chloropyridine	^{35}Cl	A	5872.0279(6)	5872.2787(1)	5872.4418	−0.1631	0.02
		B	1637.8348(1)	1639.4260(1)	1637.4226	0.0034	0.04
		C	1280.5136(1)	1280.3523(1)	1280.4051	−0.0528	0.02
	^{37}Cl	A	5871.996(1)	5872.285(1)	5872.427	−0.143	0.03
		B	1591.788(1)	1591.388(1)	1591.377	0.011	0.04
		C	1252.189(1)	1252.030(1)	1252.075	−0.045	0.02
3-Chloropyridine	^{35}Cl	A	5839.652(15)	5839.605(15)	5839.861	−0.256	0.03
		B	1604.392(7)	1603.961(7)	1603.938	0.023	0.04
		C	1258.531(7)	1258.379(7)	1258.333	0.046	0.02
	^{37}Cl	A	5839.575(24)	5839.565(24)	5839.839	−0.274	0.02
		B	1558.825(5)	1558.405(5)	1558.451	−0.046	0.04
		C	1230.299(5)	1230.149(5)	1230.163	−0.014	0.02
4-Chloropyridine	^{35}Cl	A	6018.9(6)	6019.6(6)	6019.8	−0.2	0.60
		B	1572.621(8)	1572.168(8)	1572.165	0.003	0.16
		C	1246.73(1)	1246.57(1)	1246.59	−0.02	0.13
	^{37}Cl	A	6022.3(17)	6023.0(17)	6019.8	3.2	1.70
		B	1528.24(2)	1527.80(2)	1527.71	0.09	0.43
		C	1218.61(2)	1218.46(2)	1218.48	−0.02	0.34

[a] Refs. 2–5, respectively. [b] Vibrational corrections obtained from scaled 6-31G*/MP2 *ab initio* force field. [c] Calculated from the final combined analysis/SARACEN refinement. [d] Uncertainties, used to weight the data, are derived from the largest percentage experimental error for each set of rotation constants plus a conservative estimate of 10% error in the vibrational corrections to allow for anharmonic effects.

Table 9 Restraints adopted for SARACEN GED refinements. Units are in pm or degrees, as appropriate for the restrained parameter

No.	Parameter	Restraint	Refined value
Chloropyrazine			
1	p_2	−1.0(5)	−1.1(4)
2	p_3	−1.7(5)	−1.8(5)
3	p_6	0.7(5)	0.3(5)
4	p_7	108.7(10)	108.0(7)
5	p_8	0.0(5)	0.0(5)
6	p_9	−0.1(5)	0.0(5)
7	p_{11}	119.7(10)	120.6(8)
8	p_{12}	4.1(5)	4.6(5)
9	p_{13}	−0.4(5)	0.1(5)
10	p_{15}	2.0(5)	2.8(4)
11	p_{17}	1.3(5)	1.7(4)
12	p_{19}	134.5(5)	135.1(3)
13	$r\text{C–C}_{\text{av}} - r\text{C–N}_{\text{av}}$	6.0(5)	5.4(4)
14	u_7	7.5(10)	7.7(8)
15	u_{19}	6.0(10)	6.3(8)
16	u_{20}	5.6(10)	6.0(9)
2-Chloropyridine			
1	p_2	−0.3(5)	−0.4(4)
2	p_3	0.1(5)	0.3(4)
3	p_4	−0.5(5)	0.1(4)
4	p_7	108.6(10)	108.8(4)
5	p_8	0.2(5)	0.2(5)
6	p_9	0.1(5)	0.0(5)
7	p_{10}	0.2(5)	0.2(5)
8	p_{12}	−0.4(5)	−0.8(3)
9	p_{13}	0.8(5)	0.9(3)
10	p_{15}	125.0(10)	125.3(2)
11	p_{16}	121.0(10)	121.6(6)
12	p_{17}	0.6(5)	0.6(4)
13	p_{18}	−0.1(5)	−0.2(5)
14	p_{19}	−1.0(5)	−1.2(5)
15	$r\text{C–C}_{\text{av}} - r\text{C–N}_{\text{av}}$	6.0(5)	6.3(4)
16	$r\text{C(6)–N(1)} - r\text{C(2)–N(1)}$	1.9(5)	2.6(4)
17	u_7	7.6(8)	7.7(7)
3-Chloropyridine			
1	p_2	0.2(5)	0.1(4)
2	p_3	0.4(5)	0.9(3)
3	p_4	−0.6(5)	−0.4(5)
4	p_8	0.1(5)	0.0(5)
5	p_9	0.2(5)	0.2(5)
6	p_{10}	−0.2(5)	−0.2(5)
7	p_{12}	1.6(5)	2.0(4)
8	p_{13}	−0.5(5)	−1.2(3)
9	p_{15}	116.5(10)	116.1(9)
10	p_{17}	120.7(10)	121.0(2)
11	p_{18}	−1.7(5)	−1.7(5)
12	p_{19}	0.2(5)	0.3(5)
13	$r\text{N(1)–C(2)} - r\text{C(5)–C(6)}$	0.3(5)	0.6(5)
14	u_7	7.6(8)	6.9(5)
15	u_{25}	13.1(13)	14.0(12)
4-Chloropyridine			
1	p_4	−0.4(5)	−0.8(4)
2	p_5	1.087(10)	109.8(6)
3	p_6	−0.3(5)	−0.3(5)
4	p_9	120.4(10)	121.5(8)
5	p_{10}	1.2(5)	1.2(5)
6	$r\text{C–C}_{\text{av}} - r\text{C–N}_{\text{av}}$	5.3(5)	5.6(4)
7	u_5	7.6(8)	7.9(6)
8	u_{11}	6.2(6)	5.6(4)

Table 10 Effects of chlorination on the ring geometry of azines.[a] Units are in pm or degrees, as appropriate

	Parameter										
	Ring angle at Cl-substituted carbon			Ring angle at adjacent atoms			*r*C–N; carbon Cl-substituted		*r*C–C; one carbon Cl-substituted		
Molecule		Experiment	*ab initio*		Experiment	*ab initio*	Experiment	*ab initio*		Experiment	*ab initio*
2-Chloropyridine[b]		+0.7(2)	+1.1	CNC	+0.9(4)	−0.1	−2.3(3)	−1.7		−0.5(4)	+0.1
				CCC	−0.5(3)	−1.1					
3-Chloropyridine[b]		+3.1(4)	+0.9	NCC	−2.3(3)	−1.0	—	—	C(2)–C(3)	−0.2(4)	+0.2
				CCC	−2.1(2)	−0.7			C(3)–C(4)	−0.5(3)	−0.2
4-Chloropyridine[b]		+2.2(3)	+1.0		−1.6(3)	−0.8	—	—		−0.7(2)	−0.2
Chloropyrazine[b]		+1.6(3)	+0.9	CNC	−0.6(4)	0.0	−1.6(3)	−1.5		−0.5(4)	+0.5
				CCN	−1.2(4)	−1.1					
2,5-Dichloropyrimidine[c]	NCC	+0.1(5)	+0.3	CNC	+0.6(8)	+0.2	−0.3(9)	−0.7		0.0(11)	+0.1
	CCC	+0.5(6)	+0.5	NCC	−0.6(8)	−0.5					
4,6-Dichloropyrimidine[c]		+2.6(3)	+1.3	CNC	−1.1(5)	−0.4	−1.8(8)	−1.2		−1.0(7)	0.0
				CCC	−2.4(7)	−1.5					
2,6-Dichloropyrazine[c]		+1.6(5)	+0.6	CNC	−1.2(4)	+0.2	−0.4(2)	−1.2		−0.6(5)	+0.3
				CCN	−1.8(3)	−1.5					
3,6-Dichloropyridazine[c]		+0.9(4)	+0.4	NNC	−1.0(2)	−0.2	−0.8(3)	−0.9		0.0(3)	+0.3
				CCC	0.0(3)	−0.3					

[a] Results shown refer to chlorinated geometries minus parent azine geometries. [b] This work. [c] From ref. 1.

disappointing level of agreement. This is probably inevitable, as the structural changes involved are small, and the errors involved in the measurements may mask the subtle geometric effects. A more rigorous and extensive investigation can be undertaken using geometries obtained from just *ab initio* calculations. All parameters obtained in this way would be of the same structural type (r_e), and the enormous expenditure of time in sample preparation, data collection and structural analysis would be avoided. This investigation is currently under way.

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