

Structure Analysis Restrained by *ab Initio* Calculations: The Molecular Structure of 2,5-Dichloropyrimidine in Gaseous and Crystalline Phases

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A new method to obtain improved structural parameters by supplementing gas-phase electron diffraction (GED) data with restraints based on the results of *ab initio* calculations is proposed. The procedure involves the use of *ab initio* parameters with estimated uncertainties as additional observations; this allows previously fixed parameters to refine, with all geometrical parameters included in the final refinement. The refinement of the molecular structure of 2,5-dichloropyrimidine is used as an example to illustrate the principle of this technique. In this simple case, the effects are not very great, but this new approach allowed refinement of all structural parameters. The nine independent structural parameters (r_α structure) were found to be: $r[\text{C}(4) - \text{C}(5)] = 139.3(11)$ pm, $r[\text{N}(1) - \text{C}(6)] = 133.2(4)$ pm, $r[\text{N}(1) - \text{C}(2)] = 132.5(5)$ pm, $r[\text{C}(5) - \text{Cl}(9)] = 172.2(3)$ pm, $r[\text{C}(2) - \text{Cl}(7)] = 172.8(3)$ pm, $r[\text{C}(6) - \text{H}(10)] = 109.9(12)$ pm, $\angle[\text{N}(1)\text{C}(2)\text{N}(3)] = 127.9(4)^\circ$, $\angle[\text{C}(2)\text{N}(3)\text{C}(4)] = 116.3(7)^\circ$, and $\angle[\text{N}(3)\text{C}(4)\text{H}(8)] = 117.2(5)^\circ$. All structural parameters were found to be in good agreement with both *ab initio* and crystallographic values, which are presented for comparison.

Introduction

The problems associated with refining a molecular structure using gas-phase electron diffraction (GED) data alone are well-known.¹ In particular, similar interatomic distances may be strongly correlated, and the positions of light atoms (particularly hydrogen) are poorly determined due to their low electron scattering ability. These problems make it necessary to fix some parameters at assumed values. This is undesirable for two reasons, which are closely related. First, because this fixed parameter is tacitly assumed to be absolutely correct, its effect on other refining parameters cannot be gauged; second, fixing parameters can result in unrealistically low estimated standard deviations for correlated parameters.

It has been found that the inadequacies of GED data can, to some extent, be overcome by combining the data with those obtained by other structural techniques, particularly rotational spectroscopy and/or liquid crystal NMR (LCNMR) spectroscopy. Structures of many small compounds have been determined successfully using this combined approach. Examples include an array of chlorobenzenes,^{2–5} heteroaromatics,^{1,6–8} silyl compounds,^{9,10} perfluorocyclobutene,¹¹ and *N*-chloroazetidene.¹²

Bartell also demonstrated¹³ that estimates of geometrical parameters, with their uncertainties (so-called predicate observations), could be used in the same way as extra experimental observations to supplement GED data. Schäfer first supplemented GED data with *ab initio* data by fixing difference parameters which could not be refined at values calculated *ab initio*.¹⁴

A new approach utilizing data obtained from *ab initio* calculations is now proposed to allow the refinement of all geometric parameters, and it is the natural extension of these two methodologies. In essence this method, called the SARACEN (Structure Analysis Restrained by *Ab initio* Calculations for Electron diffraction) method, hinges on two points: the use of calculated parameters as flexible restraints, instead of rigid

constraints, and choosing to refine all geometrical parameters as a matter of principle.

For example, if two bond distances are correlated, the difference between the *ab initio* predictions for these distances can be added to the GED refinement as an extra observation. It is necessary to provide an estimate of the uncertainty associated with this new information. There is, of course, no standard deviation associated with a parameter calculated *ab initio*, so the estimated uncertainty must be subjective to some extent. It can be obtained by performing a series of *ab initio* calculations and observing the size of any changes as the quality of the calculations is improved, or it can be based on experience of the known accuracy of calculations at that level. In practice these restraints are introduced to the electron diffraction analysis by means of an extra subroutine defining appropriate parts of the structure, written at the end of the mathematical model which describes the structure. Extra observations concerning these parameters (whether from spectroscopic experiments, *ab initio* calculations, or, for example, chemical intuition based on studying a series of closely related structures) can then be entered in the refinement in the usual way.

If the refined value for a parameter and its standard deviation turn out to be exactly the same as those entered as supplementary data, it is clear that the experimental data contain no information regarding that parameter. In this case it is particularly important to take great care to ensure that the value of the additional datum and its uncertainty represent the most realistic estimates that can be made. If, however, the refined value is different, or its standard deviation is lower than the uncertainty of the extra observation, then information about this parameter is contained within the experimental data set. But even in the less favorable case, it is possible to refine all geometric parameters, and the resulting structure is the best obtainable in light of all relevant information, experimental and theoretical, and all parameters have realistic standard deviations. Moreover, estimated standard deviations of other refining parameters may change. They may decrease as a consequence of the addition of extra "observations", or they may increase, if they are correlated with parameters which are added to the refinement.

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TABLE 1: *Ab Initio* Molecular Geometries and Energies of 2,5-Dichloropyrimidine^a

parameter	basis set/level of theory					
	3-21G*/SCF	6-31G*/SCF	6-311G**/SCF	6-31G*/MP2	6-31+G*/MP2	6-311G**/MP2
bond lengths						
$r_{N(1)C(2)}$	132.0	131.0	130.8	133.6	133.8	133.4
$r_{N(1)C(6)}$	133.0	131.9	131.7	134.1	134.2	133.8
$r_{C(5)C(6)}$	138.0	138.1	137.9	139.4	139.5	139.5
$r_{C(2)Cl(7)}$	172.0	172.6	172.9	172.9	172.6	172.8
$r_{C(5)Cl(9)}$	172.8	172.8	173.0	172.4	172.4	172.1
$r_{C(6)H(10)}$	106.8	107.4	107.5	108.8	108.8	108.7
angles						
$\angle N(1)C(2)N(3)$	124.8	127.3	127.4	127.8	127.6	127.9
$\angle C(2)N(3)C(4)$	118.0	116.4	116.4	115.8	115.8	115.7
$\angle N(3)C(4)C(5)$	120.9	121.6	121.5	121.6	121.7	121.7
$\angle C(4)C(5)C(6)$	117.5	116.7	116.8	117.5	117.4	117.3
$\angle N(3)C(4)H(8)$	117.6	117.1	117.2	117.0	116.8	117.2
energy, hartree	-1 174.839 342 3	-1 180.486 148	-1 180.587 367 8	-1181.568 795	-1181.585 321	-1181.734 489 1

^a All distances are in pm, all angles in degrees.

TABLE 2: Derivation of Parameter Restraints^a

parameter	3-21G*/SCF	6-31G*/SCF	6-311G**/SCF	6-31G*/MP2	6-31+G*/MP2	6-311G**/MP2	value used
p_3 $r_{N(1)C(6)} - r_{N(1)C(2)}$	1.0	0.8	0.9	0.4	0.5	0.4	0.4(5)
p_5 $r_{C(5)Cl(9)} - r_{C(2)Cl(7)}$	0.1	0.2	0.1	-0.6	-0.2	-0.7	-0.7(5)
p_6 r_{CH}	106.8	107.4	107.5	108.8	108.8	108.7	108.7(15)
p_9 $\angle NCH$	117.6	117.1	117.2	117.0	116.8	117.2	117.2(5)

^a All distances are in pm, all angles in deg.

In this paper we present the molecular structure of 2,5-dichloropyrimidine, chosen as a straightforward example to illustrate this new procedure. The *ab initio* calculations performed are given in section I, and in addition a detailed discussion of the assignment of uncertainties to *ab initio* parameters is presented. The limited structural refinement obtained from just the GED data is presented in section II and the complete structural analysis based on a combination of GED data and *ab initio* restraints in section III. For comparison the crystal structure data are given in section IV. Finally the molecular structures obtained by the different techniques are compared in section V.

I. *Ab Initio* Calculations

Theoretical Methods. *Ab initio* molecular orbital calculations were performed to predict geometrical parameters and to obtain a theoretical harmonic force field using the ASYM40 program,¹⁵ from which estimates of vibrational amplitudes could be obtained. All calculations were carried out on a DEC Alpha APX 1000 workstation using the Gaussian suite of programs.^{16,17} Geometry optimizations were performed using standard gradient techniques at the SCF level of theory using the 3-21G,¹⁸⁻²⁰ 6-31G*,²¹⁻²³ and 6-311G**^{24,25} basis sets. Subsequently the two larger basis sets were used for optimizations at the MP2-(FC) level of theory. An additional calculation was undertaken at the 6-31+G*²¹⁻²³/MP2 level to gauge the effects of diffuse functions on molecular parameters.

Vibrational frequency calculations were performed at the 3-21G*/SCF and 6-31G*/SCF levels to verify that 2,5-dichloropyrimidine has C_{2v} symmetry. The force field used in the GED refinement was constructed from the 6-31G*/SCF calculation. Since no fully assigned vibrational spectra were available for this molecule, an attempt was made to scale the force field using typical scaling factors of the order 0.9 for bond stretches, angles, and torsions. Scaling the force field was found to have little effect on the vibrational amplitude values.

Results and Discussion. Geometry optimizations were performed at six levels in order to gauge the effects of improving theoretical treatment upon the molecular geometry. The results

are presented in Table 1. Calculated bond distances proved to be rather insensitive to the details of the basis set; improving the basis set from 3-21G* to 6-31G* at the SCF level of theory led to changes in bond distances which never exceeded 1 pm, while further improvements (to 6-311G**) led to smaller changes. As is characteristic of bonds which contain significant multiple-bond character, the inclusion of the effects of electron correlation at the MP2 level of theory led to a lengthening of ring bonds.²⁶ Bond angles were invariably found to be insensitive to the adopted theoretical treatment. If the results from the smallest of the basis sets (3-21G*) are excluded, calculated bond angles always fell within 1° of each other.

The apparent convergence of molecular parameters with respect to improvements in the theoretical treatment suggests that predicted parameters which are needed to refine the structure of 2,5-dichloropyrimidine should be reliable. The values of restraints were always chosen to be those calculated from the 6-311G**/MP2 level, and uncertainties were estimated by considering the variations in calculated parameters as the level of theory was improved, with heavier weighting being placed on the higher level calculations. At these high levels of theory it is unlikely that there are significant systematic errors for a molecule of this kind, but we have been conservative in estimating the uncertainties to avoid over-weighting the theoretical restraints. The values of the differences used in the GED refinement are presented in Table 2.

The difference between the two C–N bonds, parameter 3, was given a value of 0.4 pm and an uncertainty of 0.5 pm; the uncertainty was chosen so that it encompassed all estimates using the two largest basis sets. Parameter 5, describing the difference between the two C–Cl bonds, was given the value of -0.7 pm and an uncertainty of 0.5 pm, which was derived from the MP2 level calculations only. Parameter 6 (the C–H distance) required a different type of restraint. Restraints for parameters 3 and 5 have involved differences between r_e bonds (r_e signifying the equilibrium bond length as calculated by *ab initio*). This value was used directly in the GED r_a refinement (which represents a vibrationally averaged structure). Since the differences between two bonds are largely independent of the

structure type (i.e., r_e or r_α) they may be equated with some confidence. However, if the absolute value of a bond distance computed *ab initio* is used in the GED refinement without vibrational correction, a larger uncertainty should be used to allow for any discrepancies due to the difference in structural type. Parameter 6 was therefore chosen to be 108.7 pm with an uncertainty of 1.5 pm. Parameter 9 (the NCH angle) was taken to have a value of 117.2° with an uncertainty of 0.5° . This uncertainty is somewhat larger than is needed to encompass the values obtained using the 6-31G* and 6-311G** basis sets, but it is chosen to allow for small differences in this parameter due to vibrational averaging in the GED refinement.

It can be seen that in the case of 2,5-dichloropyrimidine, the calculated ring bond differences change by only a small amount even though the absolute values of these bond lengths are altered by the inclusion of the effects of electron correlation. This result is not surprising since the electronic environments found in the C–C and C–N bonds are not dissimilar; both have a bond order of approximately 1.5. Consequently, it is expected that changes in bond lengths due to either an incomplete basis set or the neglect of electron correlation will be very similar for both bonds. Although there is a significant change in the absolute value of the bond lengths, the difference remains largely unchanged; for example, estimates of the difference between the two C–N ring bonds fall across a range of only 0.6 pm, while the absolute values of the two bond lengths vary by at least 2.5 pm. In general, when electronically similar bonds are correlated in the GED refinement, reliable estimates of the difference in bond lengths should be obtained, even at modest levels of theory.

Assigning values for the difference between two bond lengths and the associated uncertainty becomes much more problematic when electronically dissimilar bonds are considered. Under these circumstances, the limitations of the theoretical treatment may have different effects on the two bonds concerned, and hence the difference between the bond distances may change substantially with improvements in the theoretical method. In particular electron correlation is known to be important for describing multiple bonds or bonds between atoms which contain lone pairs. Thus, although a predicted C–N bond distance is expected to be essentially unaffected by electron correlation, a C=C double bond or an N–O or N–F bond is almost certain to become longer when the effects of electron correlation are included.²³

Unfortunately, there is a necessary degree of subjectivity in choosing both restraint parameter values and their uncertainties. For this reason we suggest a series of broad guidelines based upon different computational resources for estimating bond differences and uncertainties.

1. Restraints should preferably be applied to differences between electronically similar bond distances or angles, rather than to absolute values of structural parameters.

2. Ideally, a graded series of calculations in which both the size of the basis set and the level of theory are varied should be performed. A series of calculations of this type should allow the effects of improving both basis set and level of theory to be gauged with confidence and hence allow reliable estimates of structural parameters and their uncertainties to be obtained.

3. When ambitious calculations of the type described in 2 are beyond available resources, one must rely on experience of calculations at various levels to assess their reliability. Calculations using basis sets of double- ζ plus polarization quality (for example, 6-31G* or the double- ζ basis sets of Dunning²⁷) at the MP2 level of theory should allow satisfactory estimates of differences in most instances, even when comparing bonds

which are electronically dissimilar. However, we urge particular care if the molecule contains O–F, O–O or N–F bonds, since it is well established that bonds between electronegative elements are particularly sensitive to the level of correlation.²⁶

4. In cases where calculations are restricted to the SCF level of theory, differences will in general be reliable if bonds are electronically similar, although care is urged when distances between two electron-rich atoms or two highly electronegative atoms are involved. We urge extreme caution when the lengths of electronically dissimilar bonds are correlated in the GED refinement. In cases such as these it may be that more reliable estimates of bond length differences can be obtained by estimating the effects of electron correlation from reported bonds of the same type in other systems. Clearly the value of both the restraint and its uncertainty need to be chosen carefully in this case.

5. Uncertainties in restraints of this type should always be set too high rather than too low. This method is intended to allow the maximum information to be extracted from experimental data. Overtight restraints will always guarantee that the results agree with the theory, regardless of the experimental evidence: this pitfall must be avoided at all costs.

It is worth mentioning at this stage that the use of restraints need not be solely confined to the independent parameters used to define the structure. It could be equally well applied to a specific bond distance, for example, the C–C distance in our structure, which is not defined as an independent parameter in our model. In principle, restraints can also be applied to vibrational amplitudes; however, calculated force constants obtained *ab initio* are subject to systematic errors which must be reduced by application of empirical or refined scale factors.²⁸ For this reason we urge that care be taken. Two methods are available:

1. A restraint is applied directly to a specific vibrational amplitude. In such a case we recommend that an uncertainty of the order of 10% be adopted.

2. Preferably, a restraint is applied to the ratio of the amplitudes of vibration for two atom pairs which are electronically similar and whose interatomic distances lie very close together. Since *ab initio* force fields are more accurate at determining ratios of vibrational amplitudes, rather than their absolute values, we recommend the use of a lower uncertainty (of the order of 5%) for such cases. For example, in the case of 2,5-dichloropyrimidine, this method would be suitable for restraining vibrational amplitude ratios of C–C and C–N bonds but less suitable for pairing C–Cl and C–(C, N, or H) bonds together due to strongly differing electronic environments, which may be more or less affected by the use of a finite basis set and an incomplete description of electron correlation.

In 2,5-dichloropyrimidine several restraints were applied to vibrational amplitude ratios and values. With reference to Table 6, where a full bond listing is given, bond distances were grouped together in the following way:

1. Restraints were placed on the three amplitudes of vibration for the ring-bonded distances. All three amplitudes were allowed to refine freely but the ratios of u_2 [N(1)–C(2)] and u_3 [C(5)–C(6)] to u_1 [N(1)–C(6)] were restrained.

2. The two C–Cl bond distance amplitudes were refined, with the ratio u_5 to u_4 restrained.

3. The two-bond ring distances were grouped, such that the ratios u_7/u_8 and u_{12}/u_8 were restrained. The remaining two-bond ring distance, C(2)···C(6), was treated separately, since it was shorter than the rest of the group by more than 10 pm. This amplitude, u_{11} , was therefore restrained directly. All four amplitudes were refined.

TABLE 3: ED Data Analysis Parameters

camera dist, mm	weighting functions, nm ⁻¹					correlation parameter	scale factor, k ^a	electron wavelength, bpm
	Δs	s_{\min}	s_1	s_2	s_{\max}			
95.44	4	80	100	304	356	0.1613	0.860(27)	5.707
255.56	2	20	40	140	164	0.4762	0.905(17)	5.710

^a Figures in parentheses are the estimated standard deviations.

^b Determined by reference to the scattering patterns of benzene vapor.

4. The two-bond N(C)···Cl distances refined freely, with the ratio u_{13}/u_9 restrained.

5. The two three-bond ring distances were refined, with the ratio u_{17}/u_{15} restrained. In this case it was found that u_{15} also had to be directly restrained to give a meaningful refinement.

6. The three-bond N(C)···Cl distances were refined, with u_{19}/u_{16} restrained.

7. Finally, the two four-bond C···Cl distances were refined, with u_{26}/u_{23} restrained.

It will be shown in section III that with the introduction of these 11 vibrational amplitude restraints the amplitude of each distance giving rise to a feature larger than 10% of the most intense component peak of the radial distribution curve could refine independently, giving values in good agreement with the *ab initio* force field.

II. Gas Electron Diffraction Results

Sample Preparation. 2,5-Dichloropyrimidine was synthesised from 2-hydroxypyrimidine hydrochloride by treatment with aqueous chlorine solution.²⁹ Reaction of the product with phosphoryl chloride in the presence of *N,N*-dimethylaniline³⁰ gave the desired product in 40% yield. The sample was then purified by sublimation.

Method. Electron diffraction data were captured on Kodak Electron Image photographic plates using the Edinburgh apparatus.³¹ The sample was maintained at a temperature of 404 K while the nozzle was held at 460 K. The four plates (two from the long camera distance and two from the short distance) were traced digitally using a computer-controlled Joyce-Loebl MDM6 microdensitometer at the EPSRC Daresbury laboratory.³² Standard programs were used for data reduction^{32,33} with the scattering factors of Fink et al.³⁴ The weighting points used in setting up the off-diagonal weight matrix, s range, scale factors, correlation parameters, and electron wavelengths are given in Table 3.

Results and Discussion. 2,5-Dichloropyrimidine was assumed to be planar with C_{2v} symmetry. Nine independent geometrical parameters were used to define the structure. With reference to the molecular frame shown in Figure 1, they are the average $r(\text{C}-\text{C})/r(\text{C}-\text{N})$ ring distance, the difference between $r(\text{C}-\text{C})$ and the average $r(\text{C}-\text{N})$ distance, the difference between the two $r(\text{C}-\text{N})$ ring distances, the sum of and difference between the two $r(\text{C}-\text{Cl})$ distances, $r(\text{C}-\text{H})$, angle $\text{N}(1)\text{C}(2)\text{N}(3)$, angle $\text{C}(2)\text{N}(3)\text{C}(4)$, and angle NCH .

The r_{α}^0 structural parameters determined from the GED data alone are given in the first column in Table 4. As expected the three distinct ring bond distances $r[\text{N}(1)-\text{C}(2)]$, $r[\text{N}(1)-\text{C}(6)]$, and $r[\text{C}(5)-\text{C}(6)]$ could not be refined together because they were strongly correlated, and so parameter 3 was fixed at the calculated 6-311G**/MP2 *ab initio* value. The difference between the two C-Cl bond lengths could also not be determined: parameter 5 was therefore fixed at the *ab initio* value from the same calculation. Finally, the data set contained little information regarding the positions of the two hydrogen atoms, leading to parameters 6 and 9 also being fixed at the 6-311G**/MP2 *ab initio* values.

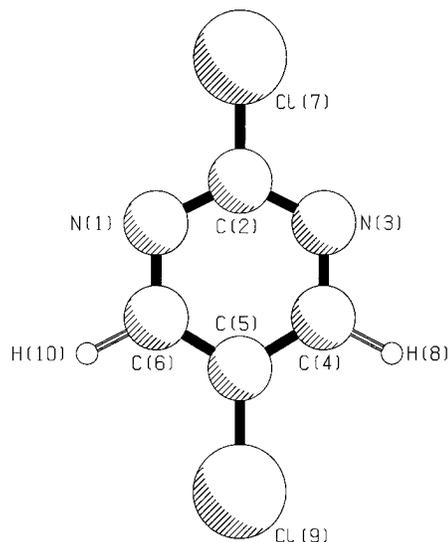


Figure 1. Molecular framework of 2,5-dichloropyrimidine.

TABLE 4: Structure (r_{α}^0) of 2,5-Dichloropyrimidine

parameter	results ^a		
	GED data alone	GED + restraints	
independent			
p_1	$[r\text{N}(1)\text{C}(2) + r\text{N}(1)\text{C}(6) + r\text{C}(5)\text{C}(6)]/3$	134.8(2)	135.0(2)
p_2	$r\text{C}(5)\text{C}(6) - [r\text{N}(1)\text{C}(2) + r\text{N}(1)\text{C}(6)]/2$	5.4(15)	6.4(15)
p_3	$r\text{N}(1)\text{C}(6) - r\text{N}(1)\text{C}(2)$	0.4 (fixed)	0.6(4)
p_4	$[r\text{C}(5)\text{Cl}(9) + r\text{C}(2)\text{Cl}(7)]/2$	172.5(2)	172.5(2)
p_5	$r\text{C}(5)\text{Cl}(9) - r\text{C}(2)\text{Cl}(7)$	-0.7 (fixed)	-0.6(5)
p_6	$r\text{CH}$	108.7 (fixed)	109.9(12)
p_7	$\angle\text{N}(1)\text{C}(2)\text{N}(3)$	127.4(4)	127.9(4)
p_8	$\angle\text{C}(2)\text{N}(3)\text{C}(4)$	116.1(7)	116.3(7)
p_9	$\angle\text{N}(3)\text{C}(4)\text{H}(8)$	117.2 (fixed)	117.2(5)
dependent			
	$\angle\text{N}(3)\text{C}(4)\text{C}(5)$	121.3(9)	120.6(8)
	$\angle\text{C}(4)\text{C}(5)\text{C}(6)$	117.9(7)	118.3(6)
	$r\text{CC}$	138.5(12)	139.3(11)
	$r\text{N}(1)\text{C}(6)$	133.3(3)	133.2(4)
	$r\text{N}(1)\text{C}(2)$	132.8(3)	132.5(5)
	$r\text{C}(5)\text{Cl}(9)$	172.1(2)	172.2(3)
	$r\text{C}(2)\text{Cl}(7)$	172.8(2)	172.8(3)

^a All distances are in picometers, all angles in degrees. Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses.

The average ring bond distance (parameter 1) was found to be 134.8(2) pm, and as the small uncertainty suggests, this value is determined to a high degree of accuracy. However, it is the individual bond distances, rather than the average, which are of most interest. To obtain all three of the distances in the ring separately, it is necessary to include parameters 2 and 3 in the refinement. Parameter 2, describing the difference between the C-C and average C-N bond distances, refined to 5.4(15) pm; the difference between the two C-N bond lengths (defined by parameter 3) remained fixed at 0.4 pm at this stage. The three ring distances were thus found to be 138.5(12), 133.3(3), and 132.8(3) pm for the C-C and two C-N bonds, respectively. The average C-Cl bond distance (parameter 4) refined satisfactorily to 172.5(2) pm, but the difference between the two bonds (parameter 5) had to be fixed at -0.7 pm. With this parameter fixed the quoted uncertainty for each of the individual bond distances must be identical to that of the average distance. The individual values and uncertainties for the two bonds were therefore 172.1(2) pm and 172.8(2) pm. Clearly, uncertainties of 0.2 pm are too small since there is insufficient information to allow the refinement of the two parameters which define them.

It seems that there is no straightforward way to obtain reliable uncertainties using this method and so invariably those which are reported are too small. Electron diffraction alone cannot lead to a set of structural parameters which are both reliable and have realistic uncertainties. It will be shown in section III that the introduction of restraints enables more realistic errors to be obtained and hence more reliable structures to be derived.

III. Structure Analysis Restrained by *Ab Initio* Calculations—the SARACEN Method

The introduction of the four independent parameter restraints presented in Table 2 allowed all nine independent geometric parameters to refine. In addition, the 11 vibrational amplitude restraints described in section I permitted amplitudes to refine for all distances responsible for features greater than 10% of the most intense component peak in the radial distribution curve. The final structural parameters obtained are given in column 2 of Table 4, along with the results based on the GED data alone for direct comparison. In general, the introduction of restraints and refinement of additional parameters lead to only modest changes in the values of the independent parameters which had already been refined. For example, the average ring bond distance changed by just 0.2 pm to 135.0(2) pm, while parameter 2 changed by 1 pm to 6.4(15) pm. The two parameters defining ring angles (parameters 7 and 8) changed by no more than 0.5° to 127.9(4)° and 116.3(7)°, respectively. In all four cases standard deviations remained unchanged.

Several specific points are worth noting about the consequences of introducing restraints:

1. Parameter 3, describing the difference between the two C–N bond distances, refined to 0.6(4) pm, which is different from the *ab initio* restraint of 0.4(5) pm, but lies well within the uncertainty limit. This demonstrates that the restraint was indeed flexible. Some information about this parameter must have been present in the GED data, but it was not sufficient to allow this parameter to refine unassisted. The introduction of the restraint permitted this information to be retrieved. With all three parameters describing the ring distances now refining, standard deviations for individual distances were expected to increase. This was found to be the case for the two C–N bonds, with final values found to be 133.2(4) pm and 132.5(5) pm. However, the standard deviation for the C–C bond distance fell by 0.1 pm as this parameter refined to 139.3(11) pm.

2. Similarly, parameter 5 refined to –0.6(5) pm as compared to its restraint of –0.7(5) pm. With this parameter now refining it was found that the absolute values of the two C–Cl bond distances changed by no more than 0.1 pm and standard deviations rose from 0.2 to 0.3 pm.

3. Parameter 6, the C–H distance, refined to 109.9(12) pm. This differs from the value used as a restraint (108.7(15) pm) but lies within its uncertainty limit. As in the cases given above, this indicates that some information about this parameter was contained within the experimental data set. However, if this parameter is not constrained in the way we suggest the bond distance refines to 120(3) pm, which is obviously an unreliable value.

4. Parameter 9, the NCH angle, refined to 117.2(5)°, in exact agreement with its *ab initio* restraint. Clearly the GED data contained no information about this parameter. Special care is needed in choosing such a restraint, since the GED refinement will always echo the *ab initio* result, but nevertheless this situation is still an improvement on the earlier method (*i.e.*, using fixed constraints) since the uncertainty suggested by the restraint generates the same realistic uncertainty (*i.e.* standard deviation) in the GED refinement, rather than an artificial uncertainty of

TABLE 5: Least-Squares Correlation Matrix for 2,5-Dichloropyrimidine^a

parameter	amplitude													
	p_2	p_8	u_1	u_2	u_3	u_5	u_8	u_9	u_{12}	u_{13}	u_{17}	u_{19}	u_{26}	k_2
p_1	74	65	–60	–63	–53			–68		–64				
p_2		81	–87	–85	–84			–81		–77				
p_8			–73	–72	–70			–53						
u_1				93	94			75		73				
u_2					89			74		72				
u_3								72		70				
u_4							78							56
u_5														56
u_7							83		69					
u_8									84					
u_9											92			
u_{15}												86		
u_{16}													78	
u_{23}														82

^a All elements are scaled by a factor of 100, and only off-diagonal elements with absolute values >50% are included.

zero. Moreover, the effects of uncertainty in this parameter are now included in standard deviations for other parameters, which are therefore more reliable.

5. The 11 vibrational amplitude restraints enabled the amplitudes of the 18 most significant interatomic distances to refine. Refined amplitudes gave values well within the uncertainties of the applied restraints in all but one case, with u_{13}/u_9 just falling outside the 5% uncertainty range.

The final least-squares correlation matrix, presented in Table 5, highlights another important feature relating to the use of restraints. In addition to obtaining realistic uncertainties, the introduction of restraints results in greatly reduced correlations between parameters in the GED refinement. With the restraints in place 36 incidences of correlation between refining parameters higher than 50% were found. In contrast, when a refinement was performed with the same parameters and amplitudes refining, but with the restraints removed, the number of incidences rose to fifty-one. This is, of course, expected, since each restraint will enable a previously unrefinable parameter (or amplitude) to refine or, in other words, to become less dependent on other parameters. Since high correlation between parameters is often the cause of a parameter failing to refine properly, use of restraints can be a useful technique to relieve high correlation effects found in some GED mathematical models.

The complete list of interatomic distances (r_a structure) and amplitudes of vibration determined in this final refinement is given in Table 6. In addition, the combined molecular scattering intensities and final differences are shown in Figure 2, and the final radial distribution and difference curves can be found in Figure 3.

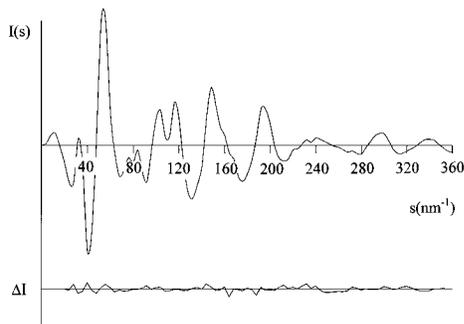
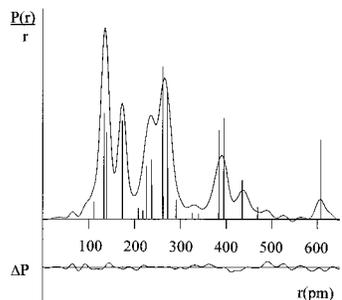
IV. Crystal Structure

Crystal Data. $C_4H_2Cl_2N_2$, $M = 148.98$ monoclinic, space group $P2_1/m$ with $a = 6.077(3)$, $b = 19.771(8)$, $c = 7.399(3)$ Å, $\beta = 101.23(6)^\circ$, $U = 872$ Å³ [from 2θ values of 29 reflections measured at $\pm\omega$, $25 \leq 2\theta \leq 38^\circ$, $\lambda = 0.71073$ Å, $T = 150.0$ K], $D_{\text{calc}} = 1.702$ g cm^{–3}, $Z = 6$, $\mu = 0.993$ mm^{–1}. The crystal selected was a colorless lath, $0.66 \times 0.23 \times 0.08$ mm. Diffraction data were collected on a Stoe Stadi-4 four-circle diffractometer employing graphite-monochromated Mo $K\alpha$ X-radiation and $\omega/2\theta$ scans, with the crystal cooled using an Oxford Cryosystems low-temperature device³⁵ operating at 150.0(2) K. Of 1591 unique reflections collected to $2\theta_{\text{max}} = 50^\circ$, 1134 had $F \geq 4\sigma(F)$ and 1586 were used in all calculations.

TABLE 6: Interatomic Distances (r_d) and Amplitudes of Vibration for 2,5-Dichloropyrimidine^a

i	atoms	distance	amplitude u_i
1	N(1)—C(6)	133.4(4)	4.2(6)
2	N(1)—C(2)	132.6(4)	4.4(6)
3	C(5)—C(6)	139.4(11)	4.3(6)
4	C(2)—Cl(7)	173.3(3)	4.5(3)
5	C(5)—Cl(9)	172.7(3)	4.4(3)
6	C(6)—H(10)	110.9(12)	7.7 fixed ^b
7	N(1)···N(3)	238.1(9)	6.1(5)
8	N(1)···C(5)	236.8(6)	6.4(5)
9	N(1)···Cl(7)	260.1(5)	8.0(8)
10	N(1)···H(10)	208.4(11)	9.3 fixed ^b
11	C(2)···C(6)	225.8(6)	4.9(5)
12	C(4)···C(6)	239.1(22)	6.4(6)
13	C(4)···Cl(9)	271.5(10)	9.1(10)
14	C(5)···H(10)	219.1(22)	9.4 fixed ^b
15	N(1)···C(4)	273.2(7)	6.2(5)
16	N(1)···Cl(9)	395.2(6)	10.1(6)
17	C(2)···C(5)	262.8(6)	5.9(6)
18	C(2)···H(8)	325.2(12)	9.0 fixed ^b
19	C(4)···Cl(7)	383.3(6)	10.1(7)
20	C(4)···H(10)	341(3)	9.0 fixed ^b
21	Cl(9)···H(10)	292(2)	13.2 fixed ^b
22	N(1)···H(8)	383.3(15)	8.9 fixed ^b
23	C(2)···Cl(9)	434.9(6)	10.2(8)
24	Cl(7)···H(8)	468.0(12)	10.3 fixed ^b
25	H(8)···H(10)	435(4)	12.1 fixed ^b
26	C(5)···Cl(7)	435.5(6)	10.2(8)
27	Cl(7)···Cl(9)	607.5(5)	11.6(7)

^a All distances and amplitudes are in picometers. Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses. ^b Amplitudes fixed at values derived from a scaled 6-31G*/SCF force field.

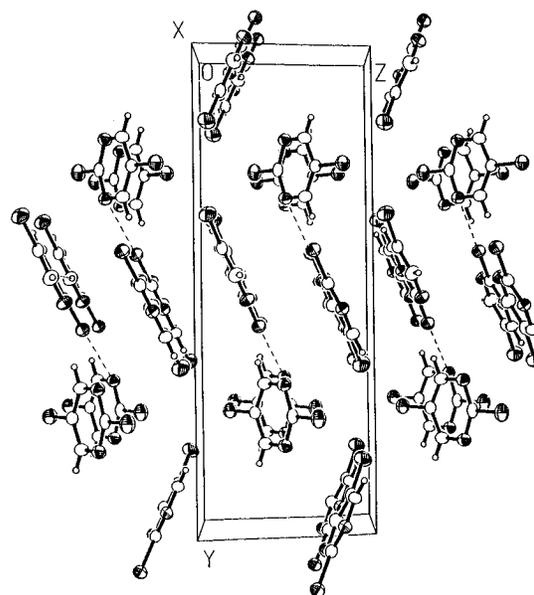
**Figure 2.** Observed and final difference combined molecular scattering curves for 2,5-dichloropyrimidine.**Figure 3.** Observed and final difference radial distribution curves for 2,5-dichloropyrimidine. Before Fourier inversion the data were multiplied by $s \exp(-0.00002s^2)/(Z_{Cl}f_{Cl})(Z_Nf_N)$.

Structure Solution and Refinement. Automatic direct methods³⁶ identified the positions of all non-H atoms and iterative cycles of least-squares refinement and difference Fourier syntheses located the hydrogen atoms.³⁷ At isotropic convergence corrections for absorption (min 0.822, max 1.161) were applied empirically using *DIFABS*.³⁸ All non-H atoms were refined anisotropically and H atoms isotropically. A

TABLE 7: Crystal Structure Parameters for 2,5-Dichloropyrimidine^a

	C_1 symmetry		C_s symmetry
bond lengths			
$rN(1)-C(2)/rN(3)-C(2)$	131.4(5)	132.6(5)	131.0(4)
$rN(1)-C(6)/rN(3)-C(4)$	134.0(5)	133.7(5)	133.4(5)
$rC(5)-C(6)/rC(4)-C(5)$	137.4(6)	136.2(6)	137.3(5)
$rC(2)-Cl(7)$		173.5(4)	174.6(6)
$rC(5)-Cl(9)$		172.5(4)	173.6(6)
angles			
$N(1)-C(2)-N(3)$		129.2(4)	130.8(4)
$C(2)-N(3)-C(4)/$ $C(2)-N(1)-C(6)$	114.5(3)	114.5(4)	114.4(4)
$N(3)-C(4)-C(5)/$ $N(1)-C(6)-C(5)$	122.2(4)	121.9(4)	120.6(4)
$C(4)-C(5)-C(6)$		117.8(4)	119.4(6)

^a All distances are in picometers; all angles are in degrees.

**Figure 4.** Crystal packing structure of 2,5-dichloropyrimidine.

correction for secondary extinction³⁷ refined to 0.003(3). The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.082P)^2]$, where $P = 1/3[\text{MAX}(F_o^2, 0) + 2F_o^2]$, led to a convergence with $R_1 [F \geq 4\sigma(F)] = 0.0460$, $wR_2 [\text{all data}] = 0.1305$, respectively, and $S[F^2] = 1.014$ for 128 refined parameters. In the final cycle $(\Delta/\sigma)_{\text{max}}$ was 0.20 and the final ΔF synthesis showed no feature outside $+0.46$ to $-0.55 e \text{ \AA}^{-3}$.

Results. One and a half molecules were found in the unit cell, giving two symmetrically different structures (of C_1 and C_s symmetry), for 2,5-dichloropyrimidine in the solid phase. The individual parameters derived for the two structures are given in Table 7 and a diagram of the crystal packing arrangement is shown in Figure 4.

The values of the N—C(2) bond distances ranged from 131.0(4) to 132.6(5) pm, the range of 1.6 pm suggesting that bonds in the two different unit cells are in substantially different electronic environments. Similarly the C(5)—C(4/6) distances lay within a range of 1.2 pm, 136.2(6) to 137.4(6) pm. In contrast, the N(1)—C(6)/N(3)—C(4) distance was more consistent, ranging from 133.4(5) to 134.0(5) pm, a difference of only 0.6 pm. Differences in internal ring angles were also found, with the values of angles NCN, NCC, and CCC falling within a range of 1.6°, in contrast to angle CNC whose value only changes by 0.1°.

The two distinct C—Cl distances were both found to be longer by 1.1 pm in the C_s structure than in the C_1 structure. In each

TABLE 8: Comparison of the Molecular Structure of 2,5-Dichloropyrimidine from GED, *ab Initio* Calculations, and Crystallography^a

	GED + restraints ^b	6-311G**/ MP2	crystal structure (av values) ^c
bond lengths			
rN(1)C(2)	132.5(5)	133.4	131.5(5)
rN(1)C(6)	133.2(4)	133.8	133.6(5)
rC(5)C(6)	139.3(11)	139.5	137.1(6)
rC(2)Cl(7)	172.8(3)	172.8	174.0(5)
rC(5)Cl(9)	172.2(3)	172.1	173.0(5)
rC(6)H(10)	109.9(12)	108.7	
angles			
∠N(1)C(2)N(3)	127.9(4)	127.9	130.0(4)
∠C(2)N(3)C(4)	116.3(7)	115.7	114.4(4)
∠N(3)C(4)C(5)	120.6(8)	121.7	121.3(4)
∠C(4)C(5)C(6)	118.3(6)	117.3	118.6(4)
∠N(3)C(4)H(8)	117.2(5)	117.2	

^a All distances are in picometers, all angles in degrees. ^b GED results refer to r_{α}^0 structure; see Table 6 for r_a structure. ^c Figures in parentheses represent uncertainties on average structure, quoted to one σ .

case the internal ring angle associated with the C–Cl bond (i.e., NCN or CCC) was larger by 1.6° in the C_s structure than in the C_1 structure. Finally, in each structure the C(2)–Cl(7) distance (C_1 , 173.5(4) pm; C_s , 174.6(6) pm) was found to be 1 pm longer than the C(5)–Cl(9) distance (C_1 , 172.5(4) pm; C_s , 173.6(6) pm).

V. Comparison of Molecular Structures Obtained by Different Techniques

The final results for the molecular structure of 2,5-dichloropyrimidine found by gas-phase electron diffraction with flexible constraints, *ab initio* calculations, and X-ray crystallography are summarized in Table 8. Note that the C_1 and C_s molecular structures found in the crystal are of lower symmetry than the C_{2v} *ab initio* and gas ED structures and therefore require more independent intramolecular geometrical parameters. To allow for a direct comparison to be made between the two phases an average solid-phase structure with C_{2v} symmetry was calculated from the C_1 and C_s structures. It is these averaged values that are given in Table 8.

Ab initio calculations give a discrete molecular structure, which should therefore complement the results obtained from the GED experiment. Some differences would be expected, however, since *ab initio* calculations give the equilibrium structure and are not subject to the vibrational averaging effects which influence the GED dynamic structure. However, these differences are small and *ab initio* and GED parameters were found to be in excellent agreement, with all fitting within one or two standard deviations. The only substantial difference concerned the C–H bond length, found to be 109.9(12) pm by GED compared to 108.7 pm by *ab initio*. This parameter is poorly described in the GED experiment but can be refined satisfactorily when subject to a flexible constraint.

Although the absolute values of parameters from the gas-phase ED structure and the solid-phase crystal structure were found to differ substantially, in general the same structural trends were observed. The average ring distance measured by GED was 135.0(2) pm, in contrast to 134.1(5) pm from the crystal structure. This apparent contraction of the aromatic ring was expected, since X-ray diffraction locates the centers of electron density, which in the case of an aromatic ring lie just inside the ring. However, the same order of increasing ring bond distance found in the gas was also present in the solid: the shortest ring bond found was N(1)–C(2) at 132.5(5) pm in the gas (131.5(5) pm in the solid), followed by N(1)–C(6) measured at 133.2-

(4) pm in the gas (133.6(5) pm in the solid), with the longest distance, C(5)–C(6), found at 139.3(11) pm (or 137.1(6) pm) in the gas (or solid) phase. The crystal structure ring angles were also found to differ from the GED angles. Deviations ranged from 0.3° for the CCC angle to 2.1° for the NCN angle. Differences in angles are not surprising, since in the crystals the molecules are subjected to intermolecular forces, and it is energetically less demanding for a structure to distort by changing its bond angles than by changing bond lengths.³⁸ However, although there are small differences between ring angles in the two phases, the same sequence of angle magnitudes was found. The CNC angle was found to be the smallest, just 116.3(7)° in the gas or 114.4(4)° in the solid, followed by the CCC angle at 118.3(6)° (118.6(4)° in the solid). The next biggest angle was NCC at 120.6(8)° in the gas and 121.3(4)° in the solid, and finally the largest angle, NCN, was measured as 127.9(4)° (130.0(4)°) in the gas (or solid) state.

Conclusion

In this paper we have demonstrated a new method (SA-RACEN) to obtain improved geometric parameters by combining GED data with restraints based on a graded series of *ab initio* calculations. We have shown that in doing so, more reasonable estimates of uncertainties can be derived (and hence more realistic structures obtained) because previously fixed parameters can be allowed to refine, the restraints having relieved the effects of parameter correlation in the GED mathematical model of the structure. Parameters which correspond directly to restraints have been shown to behave in two ways; they may refine to give a sensible value different from the restraint but within the error limit, indicating that some information is present in the GED data, or they may refine to give the same value and error as the restraint, indicating that little or no information was provided by the experimental data. Even in this case we have demonstrated that the technique is valuable since parameters affected now have realistic standard deviations and the refined structures obtained in this way represent the sum of our knowledge, experimental and theoretical, and are thus as reliable as possible at present.

Supporting Information Available: Tables 1–5 listing crystal data and structure refinement, atomic coordinates and displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (4 pages); Table 6 listing observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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