Solid-State Behaviour of the Dichlorobenzenes: Actual, Semi-Virtual and Virtual Crystallography

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For *Edgar*, a teacher whose influence will never stop

The crystal structures of the low-melting 1,2- and 1,3-dichlorobenzene isomers have been determined by X-ray analysis and *in situ* crystallisation techniques. Attempts to predict these structures in advance by force-field calculations were not successful, although the known crystal structures of two of the three polymorphs of the 1,4-isomer were successfully '*a posteriori*' predicted. Calculated lattice energies were supplemented with estimated lattice-vibrational entropies obtained in the rigid-body approximation. Energy calculations for actual and virtual crystal structures indicate that the higher melting point of the 1,4-isomer can be largely attributed to more efficient crystal packing.

Introduction. – Many practising chemists are aware that there are striking differences in the melting points of the three isomeric dichlorobenzenes. Whereas 1,4-dichlorobenzene is a crystalline compound under normal conditions (m.p. 326 K), the 1,2- and 1,3-isomers are liquids at room temperature (m.p. 256 and 248 K, resp.). This pattern, 1,4-isomer melting higher than the other two, is quite general among disubstituted benzene derivatives, independent of the nature of the substituents, and of whether the two substituents are equal or not. The few exceptions involve H-bonding substituents, especially where a cyclic intramolecular H-bond can be formed for the 1,2-isomer, resulting in a more compact molecular structure that can achieve tighter packing [1]. Similarly, for the tetrachlorobenzenes, the more symmetrical 1,2,4,5-isomer has a much higher melting point (413 K) than the other two (321 and 327 K). In the trichlorobenzene series, the same pattern is found: 1,3,5-isomer (336 K), 1,2,3- (326 K), 1,2,4- (290 K).

In contrast to the melting point differences, the boiling point within each group of Cl_n-substituted isomers is practically constant, showing a steady rise from benzene to hexachlorobenzene (Cl_0, 353, Cl_1, 403, Cl_2, 448, Cl_3, 488, Cl_4, 523, Cl_5, 553, Cl_6, 593 K). The same regularity can be seen in the observed enthalpies of phase transitions in chlorinated benzenes. *Fig. 1* shows the good linear dependence of the cohesive energy in the isotropic liquids on the number of Cl-atoms. Enthalpies of melting and sublimation show similar trends (*Fig. 1,b* and *c*) but with additional scatter connected with differences in crystal structure and packing energy among the isomers. With their much larger atom polarisability compared with C- and H-atom, the Cl-atoms of chlorinated hydrocarbons contribute the major part of the cohesive energy, which is mainly of dispersive origin. Approximate values of atom polarisabilities, based on

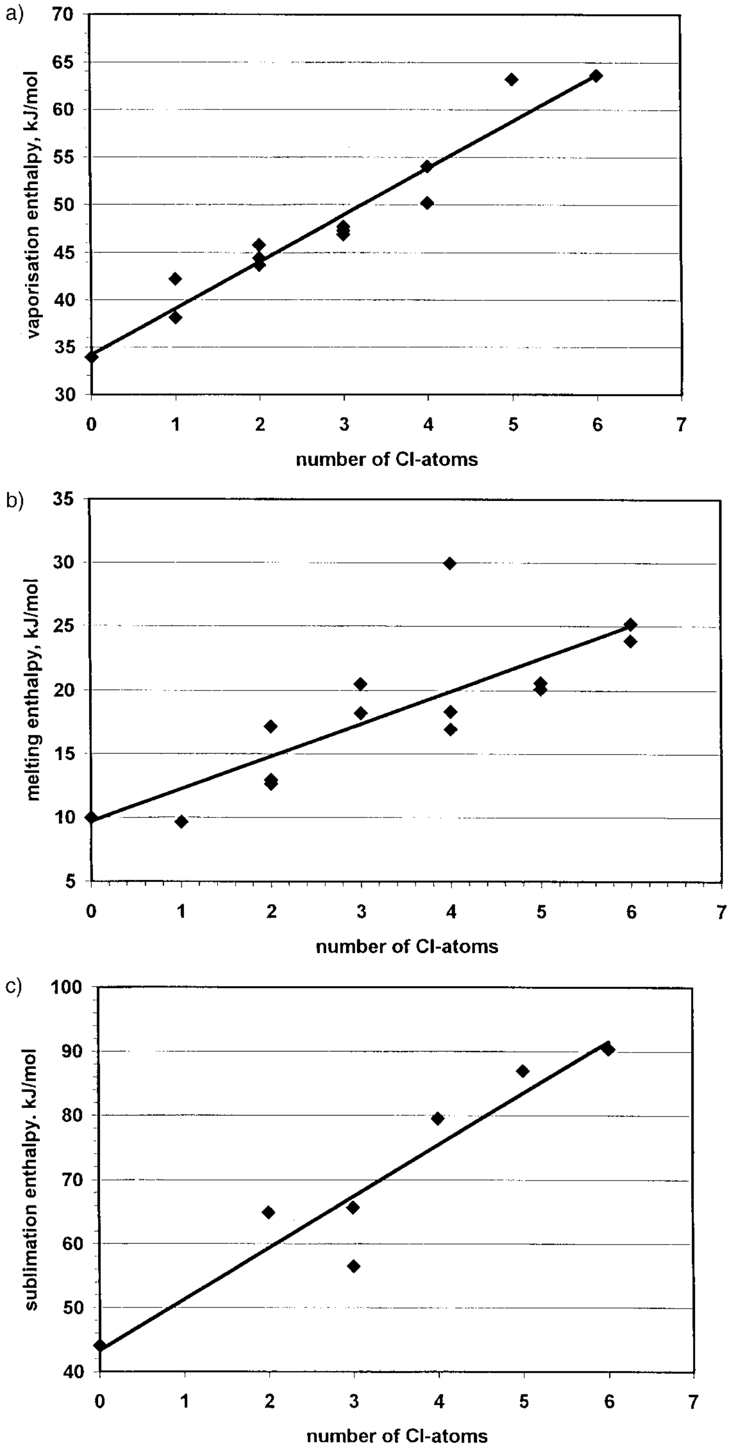

Fig. 1. *Plots of* a) *heat of vaporization*, b) *heat of melting, and* c) *heat of sublimation as a function of number of Cl-atoms in chlorinated benzenes.* Data from [2][3].

assumed additivity in observed electronic polarisabilities of simple molecules [4] may be taken as 2.3, 1.0, and 0.4 Å^3 for Cl, C, and H, respectively [5].

Brominated and iodinated benzenes show similar regularities to the chlorinated benzenes in their cohesion behaviour. In contrast, the melting points of the fluorinated benzenes vary over a relatively small temperature range, between 225 K (pentafluorobenzene) and 278 K (1,2,4,5-tetrafluorobenzene and hexafluorobenzene). They show a quite erratic behaviour, with benzene and hexafluorobenzene melting at practically the same temperature (278–279 K) and pentafluorobenzene having a lower melting point than fluorobenzene (231 K). Moreover, the behaviour of fluorine in the crystal packing is quite different from that of the heavier halogens since the crystal structures do not show any marked tendency of the F-atoms to segregate [6]. We may also note that although 1,2-difluorobenzene has a lower melting point than the 1,4-isomer (239 *vs.* 260 K), it has a higher crystal density (1.493 g cm^{-3} at 123 K against 1.420 g cm^{-3} at 215 K) [7], contrary to the general trend among isomers; the 5% density difference is probably more than can be compensated by contraction of the unit cell of the 1,4-isomer over the given temperature range. Without going into details, it would appear that the anomalous behaviour of fluorine in crystal packing can be attributed mainly to its low electronic polarisability (*ca.* 0.7 Å^3) compared with chlorine and the other halogens.

In the absence of a theory of melting at the molecular level, there are only empirical rules with limited scope and uncertain basis. Perhaps the best known is the one originally due to *Carnelly* [8], recently rediscovered and discussed by *Brown* and *Brown* [9]: '*That of two or more isomeric compounds, those whose atoms are the more symmetrically and the more compactly arranged melt higher than those in which the atomic arrangement is asymmetrical or in the form of long chains*'. Similar statements have since been made by other authors, notably *Hückel* [10], but without much theoretical justification. From a thermodynamic standpoint, we have the relationship, $T_f = \Delta H_f / \Delta S_f$, so the higher fusion temperature of a solid built from symmetric molecules could be due to a larger enthalpy of fusion or to a lower entropy of fusion (or, of course, to a combination of these). The first possibility would imply that symmetric isomers have a better packing energy than asymmetric ones, but, as far as we are aware, no sound structural basis for such a relationship has ever been proposed. The second possibility would imply that for a symmetric isomer, either the entropy of the solid is unusually high (as in plastic crystals showing rotational disorder of symmetric molecules such as neopentane), or the entropy of the liquid is unusually low. Indeed, the entropy of the liquid should be lowered by an amount $R \ln \sigma$, where R is the gas constant and σ is the molecular symmetry number or rather the ratio of the molecular symmetry numbers in the liquid and crystalline states (*e.g.*, for 1,4-xylene, the appropriate ratio of symmetry numbers would be $4 \times 3^2/3^2 = 4$, if we assume that free or nearly free rotation of the Me groups takes place in the solid close to the melting point).

Much of the relevant empirical evidence concerns substituted benzenes and naphthalenes, and molecular symmetries, melting temperatures, and melting enthalpies of these compounds have been reviewed recently [1]. *Yalkowsky* and co-workers [11] have emphasised the role of the molecular symmetry number σ in lowering the entropy of fusion ΔS_f and hence increasing the fusion temperature T_f for a given packing energy. Although there are many examples where this holds, *e.g.*, the high melting point of neopentane compared with pentane and isopentane, the most symmetric isomer does not always have the lowest ΔS_f. Indeed, it is often the case that the most symmetric isomer has a higher ΔS_f *and* a higher melting point – in other words, its packing energy is greater.

Within the dichlorobenzene series, with its striking melting point differences, the crystal structures of the 1,2- and 1,3-isomers have remained unknown until now (although a search of the *Cambridge Structural Database* (*CSD*) [12] revealed more than 40 crystal structures in which molecules of the 1,2-isomer are present as crystal solvate). On the other hand, the 1,4-isomer is a well-known example of a polymorphic compound. At least three polymorphs, designated α, β, and γ, have been identified and their structures established in several X-ray crystallographic studies over a wide temperature range.

In the present paper, we review earlier results for the 1,4-isomer, provide experimental crystal structures for the 1,2- and 1,3-isomers grown by the *in situ* method, and estimate packing energies of these crystal structures by force-field calculations. In addition, we summarise results of a crystal-structure prediction run, where large numbers of possible crystal structures for all three isomers were computer-generated and graded according to their packing energies. These were calculated using empirical atom-atom potentials, with allowance for an approximate vibrational entropy term. Since these calculations were carried out without knowledge of the experimental results for the 1,2- and 1,3-isomers, they serve as a test of how well current crystal structure prediction methods can be expected to perform, as well as a test of the Cl–Cl empirical potentials. Our guarded conclusion will be that the melting-point differences among the dichlorobenzenes are attributable to differences in packing energy that arise from the different molecular shapes, as well as to differences in molecular symmetry.

The Dichlorobenzenes: Experimental Crystal Structures and Cl···Cl Contacts. – Several crystal structure analyses of the three polymorphs, designated α, β, and γ, of the 1,4-isomer have been made over the years. The triclinic β-form ($P\bar{1}$, $Z = 1$), the high-temperature phase, crystallises from the melt at 328 K. It transforms to the common monoclinic α-form ($P2_1/a$, $Z = 2$) at 304 K. Below 273 K, the compound crystallises in another monoclinic form ($P2_1/c$, $Z = 2$), called the γ-form, which appears to be the thermodynamically stable form at low temperatures. The nomenclature is historical rather than logical. A thorough study of all three polymorphs at 100 K was made by *Wheeler* and *Colson* [13], and we can do no better than review their results briefly. Unit cell dimensions at 100 K are given in *Table 1*, and the three structures are illustrated in *Figure 2*.

As *Wheeler* and *Colson* point out, the number of short Cl···Cl interactions (< 3.9 Å) increases from three in the β-form, to four in the α-form, to five in the γ-form, thus paralleling the order of packing energy.

It is convenient, and perhaps not too much of an oversimplification, to distinguish between three main types of Cl···Cl contacts in the crystal structures of chlorobenzenes.

i) A nearly linear C–Cl···Cl–C arrangement with both C–Cl···Cl angles close to 180° (the type-I contact of *Desiraju* and *Parthasarathy* [14]), which often occurs between symmetry-related groupings across a crystallographic inversion centre. This arrangement would appear to involve an energetically unfavourable disposition of the

Table 1. *Cell Parameters and Lattice Energies of the Dichlorobenzenes.* X-Ray values are compared to potential-relaxed (OPT) structures

Isomer	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V_{cell}/Å^3	$-E$/kJ mol^{-1}
1,4-γ, 100 K $P2_1/c$, $Z=2$	8.624	6.021	7.414		127.51			–
γ-OPT	8.60	5.94	7.31		128		148	67.2
id., reduced	7.11	5.94	7.31		73	–	–	–
1,4-β, 100 K $P\bar{1}$, $Z=1$	7.302	5.873	3.882	91.13	112.55	92.43		–
β-OPT, reduced	3.80	5.79	6.85	95	81	90	149	66.9
1,4-α, 100 K $P2_1/a$, $Z=2$	14.664	5.740	3.925		111.77			–
α-OPT	14.69	5.68	3.85		111		150	66.1
1,3: $P2_1/c$, $Z=8$ (220 K)	3.923	12.590	26.085		92.87		–	–
OPT	3.76	12.60	25.76		93.5		152	64.0
1,2: $P2_1/n$, $Z=4$ (223 K)	3.950	10.626	15.270		97.00			
OPT	3.81	10.37	15.24		96.3		150	64.6

bond dipoles, but it is nevertheless sometimes found with Cl ··· Cl distances that are markedly shorter than the standard *van der Waals* distance (3.60 Å).

ii) An L-type C–Cl ··· Cl–C arrangement where one C–Cl ··· Cl angle is close to 90° and the other close to 180° (the type-II contact of *Desiraju* and *Parthasarathy* [14]).

iii) A parallel periodic C–Cl stacking associated with a short unit cell direction. Although this would again seem to correspond to an energetically unfavourable disposition of the bond dipoles, many chlorobenzene crystal structures have short unit cell lengths around 3.8 Å.

Wheeler and *Colson* draw attention to the remarkably short, almost linear C–Cl ··· Cl–C contact (3.38 Å, C–Cl ··· Cl angle 170°) in the β-form. They point out that, according to standard isotropic atom-atom potential functions, such a contact should be associated with a strongly repulsive interaction. Introduction of *Coulomb* terms (negative charge on Cl, positive on C) would not improve the matter. The α- and γ-forms show no Cl ··· Cl contacts shorter than 3.73 Å (in α-form, L-type with C–Cl ··· Cl angles of 166° and 92°). We may note that, in solid chlorine, the shortest Cl ··· Cl distance is 3.29 Å and in Cl–F it is even as short as 3.07 Å. These are both L-type arrangements (see [15] and refs. cit. therein).

Experimental. – *Crystal Structure Determinations* (see *Table 2*). The crystallisations were carried out on the diffractometer with a miniature zone melting procedure using focused IR-laser radiation [16]. As a result of their formation and growth in capillaries, the crystals had a cylindrical shape exceeding the primary beam from our MoK_α X-ray source at an *R3 Siemens-Nicolet* four-circle diffractometer. The measured intensities were therefore corrected for a volume effect and for absorption, the latter correction being based on a 360°, 10° step ψ-scan, using the *Siemens P3* diffractometer software V.4.24 and data reduction software XDISK V.4.20.2 1991 PC. The cell dimensions were determined from 50 centered reflections in the 2θ range 20–25°. Both structures were solved by direct methods and refined on F^2 by use of *Bruker AXS* SHELXTL Vers. 5.10 software. H-Atoms were located in difference *Fourier* maps and refined using the riding model with isotropic U values taken as 1.2 times those of the corresponding C-atoms.

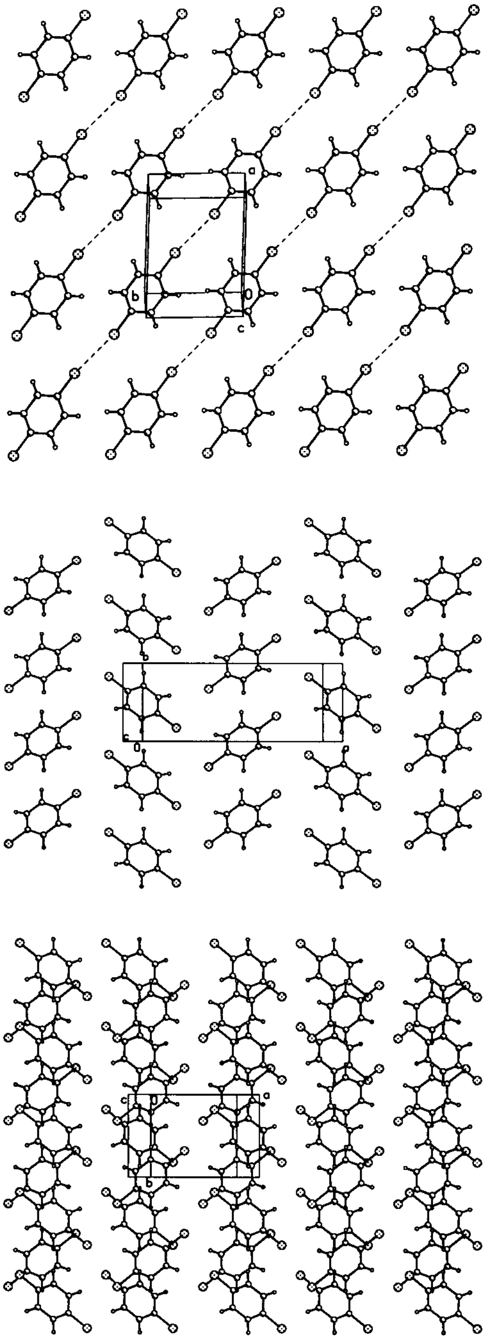

Fig. 2. *The crystal structures of polymorphs of 1,4-dichlorobenzene* (after [13]). Top to bottom: β (high temp.), α (room temp.), γ (low temp.).

Table 2. *Crystal Data and Structure Refinement Details for 1,2- and 1,3-Dichlorobenzene*

Empirical formula	1,2-$C_6H_4Cl_2$	1,3-$C_6H_4Cl_2$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	3.9495(14)	3.9234(6)
b/Å	10.626(5)	12.590(3)
c/Å	15.270(7)	26.085(5)
β/°	97.00(3)	92.868(14)
V/Å^3	636.1(5)	1286.9(4)
Z	4	8
D_{calc}/g cm^{-3}	1.535	1.517
$F(000)$	296	592
Crystal size/mm (diameter of the cylinder)	0.3	0.3
μ/mm^{-1}	0.898	0.887
Temp./K	223(2)	220(2)
Wavelength/Å	0.71073	0.71073
θ Range/°	2.69–30.16	1.56–25.06
hkl range	$-5 < h < 5$ $0 < k < 14$ $0 < l < 21$	$-4 < h < 4$ $0 < k < 15$ $0 < l < 30$
Reflections: collected, unique, observed ($F > 4\sigma(F)$)	1918, 1861, 1395	2316, 2267, 1808
Number of parameters	73	146
$R(F)$	0.0486	0.0318
$wR(F^2)$ all data	0.1479	0.0761
Goodness of fit	1.027	1.060
max/min resid. dens./e Å^{-3}	0.322, −0.459	0.228, −0.202

Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-165224 and CCDC-165223 for 1,2- and 1,3-dichlorobenzene, resp. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336033; e-mail deposit@ccdc.cam.ac.uk.).

The molecular schemes are shown in *Fig. 3*. For 1,2-dichlorobenzene, C–Cl distances are 1.734(2) and 1.731(3) Å, and C–C distances are 1.375(4) to 1.389(3) Å, with bond angles between 118.9(2) and 120.9(2)°. For 1,3-dichlorobenzene, C–Cl distances are 1.740(2) to 1.746(3) Å, C–C distances are 1.375(3) to 1.385(4) Å, and bond angles lie between 117.8(2) and 122.0(2)°.

The structures are illustrated in *Figs. 4* and *5*. Both structures are built from buckled layers of molecules separated by nearly the same interlayer stacking distance, 3.95 and 3.92 Å, resp., practically the same as in the β- and α-forms of the 1,4-isomer (3.96 and 3.93 Å, resp.). In the crystal structure of the 1,2-isomer (*Fig. 4*), each Cl-atom is engaged in three Cl ··· Cl interactions, the two inter-layer ones and one L-type interaction within the layer (Cl ··· Cl, 3.57 Å, C–Cl ··· Cl angles close to 180° and 90°). The crystal structure of the 1,3-isomer (*Fig. 5*) contains two symmetry-independent molecules in the unit cell ($P2_1/c$, $Z = 8$). In many such structures, the two kinds of symmetry-independent molecules are related by an approximate symmetry operation, *e.g.*, a non-crystallographic translation, but here they have quite different crystal environments. One set of molecules forms centrosymmetric pairs through a nearly linear C–Cl(4) ··· Cl(4′)–C interaction with Cl(4) ··· Cl(4′) distance 3.46 Å, C–Cl ··· Cl angle 147°, another example of a short linear-type contact, as in the high-temperature

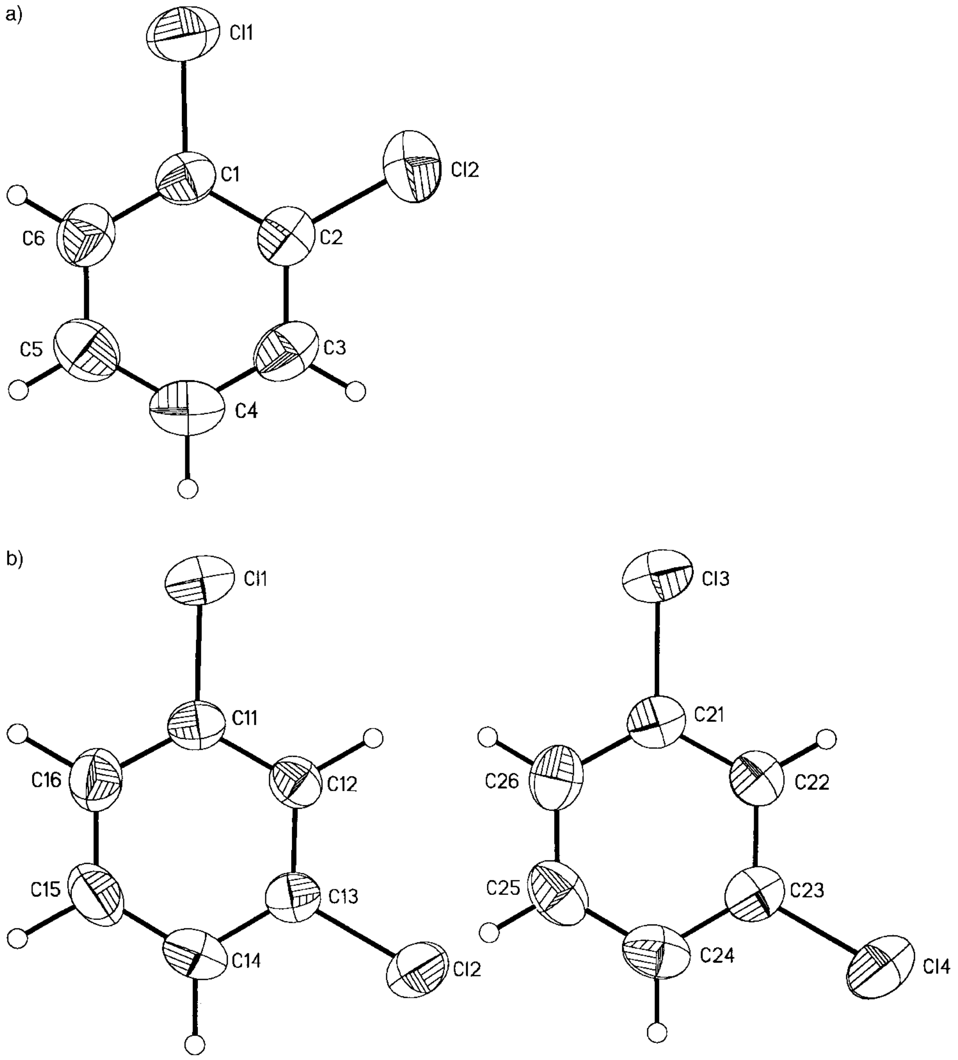

Fig. 3. *Thermal-ellipsoids plots* (50%) *and atom numbering for* a) *1,2- and* b) *1,3-dichlorobenzene molecules*

β-form of the 1,4-isomer. The second Cl-atom in this molecule forms an L-type contact to a Cl-atom in the other molecule: Cl(3) ··· Cl(2), 3.69 Å, C–Cl ··· Cl angles 163° and 81°. The remaining Cl-atom Cl(1) is not engaged in any intra-layer contact with other Cl-atoms, only with its two translation equivalent neighbours related by the 3.92-Å inter-layer separation. For an estimated molecular volume of 108 Å^3, both crystal structures have packing densities of *ca.* 0.67, close to the lower limit for organic solids [17].

Calculations with Empirical Potentials. – a) *Crystal-Structure Generation Methods.* Computer generation of crystal structures (virtual crystallography) reveals that, for a

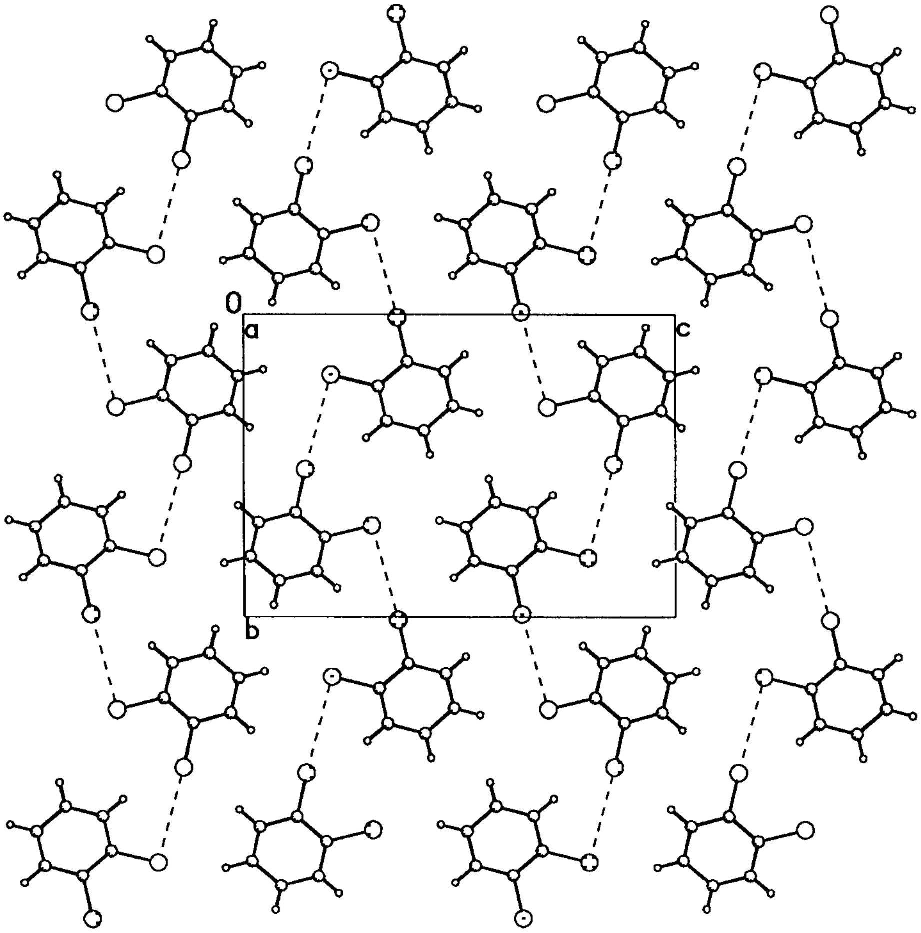

Fig. 4. *The crystal structure of 1,2-dichlorobenzene*

given molecule, there are many (sometimes a great many) crystal arrangements with nearly the same packing efficiency [18]. That is one reason why purely *ab initio* crystal structure prediction is so difficult.

Our computational work here uses a widely distributed computer package, Zip-Promet [19], for the generation of crystal structures from molecular structure. Briefly, the procedure consists in building dimers, ribbons, and layers of molecules according to partial space-group symmetry, selecting the most cohesive among such substructures, and applying further translation as required to obtain complete, but still approximately packed, three-dimensional crystal structures. Only the most popular space groups for organic crystals are considered, that is, $P\bar{1}$, $P2_1$, $P2_1/c$, $P2_12_12_1$, $Pbca$, $C2/c$, and only structures with one molecule or less in the asymmetric crystal unit. Optimisation of each of these raw structures with respect to rigid-body molecular degrees of freedom and cell parameters is performed with a recently developed algorithm [20]. In some cases, energy-

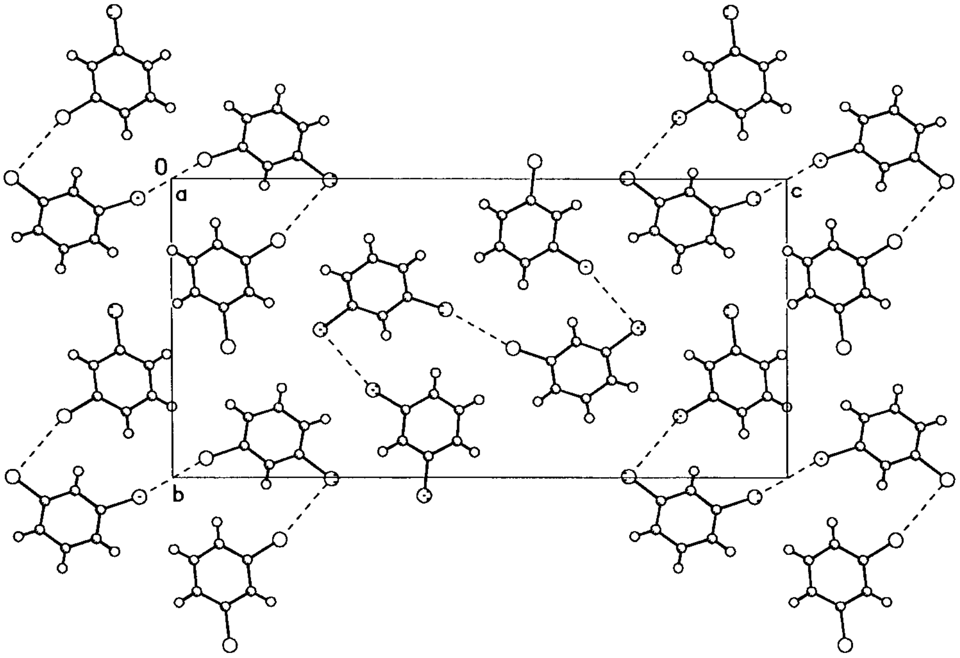

Fig. 5. *The crystal structure of 1,3-dichlorobenzene*

optimised calculated structures may have a higher symmetry than that corresponding to the initially chosen space group. This happens, for example, for a structure built from planar molecules where the molecular plane is perpendicular to a screw axis.

These calculated structures are built from stationary atoms; they are 'temperatureless' in the sense that no temperature is ever specified in the whole computational procedure and consequently no molecular motion is considered. For comparison with experimental crystal structures, these must be 'optimised' by exactly the same procedure. A unit-cell shrinkage of a few percent invariably results, as the experimental structure is formally brought to zero temperature; such optimised structures are labelled 'OPT'.

Molecular dimensions were taken as reasonable averages; C–C 1.39, C–Cl 1.72 Å, all angles 120°. H-Atoms were placed on the bisector of the CCC angle at C–H = 1.08 Å. The molecules were taken as planar, with twofold symmetry for 1,2- and 1,3-, and inversion centre symmetry for the 1,4-isomer. For the 1,4-isomer, only centrosymmetric space groups, where the molecular centre of symmetry could be carried over to the crystal, were considered.

b) *Empirical Potentials.* The UNI force field [21] has been used. It has been parameterised to reproduce heats of sublimation and experimental cell parameters for Cl-containing crystals, among others. For the observed crystal structures of the 1,2- and 1,3-isomers, the relaxation induced by the potentials is very small, *i.e.*, the 'OPT' structures are very close to experimental ones (see *Table 1*), thus meeting one of the primary requirements for reasonable crystal potentials.

Our simple force field can be criticised for not including charge parameters and coulomb-type interactions. This absence leads to significant deviations in the reproduction of the crystal structure of benzene, for example, where the interplanar intermolecular angles are calculated too small (for an extended discussion, see *Mirsky* and *Cohen* [22]). In our opinion, short range Cl $\cdots$ Cl interactions are likely to be more related to the polarisability of the atoms than to any kind of point charge allocated to the atoms or to their surroundings [23]. Even though the dipole moment of chlorobenzene in the gas phase is 1.69 D, the mutual orientations of C–Cl bond dipoles in crystals seldom correspond to energetically favourable types of dipole-dipole interaction. Indeed, type *i* and type *iii* Cl $\cdots$ Cl contacts are associated with strikingly unfavourable dipole orientations. Also, the so-caleld 'chloro effect' (see [14] for a discussion), leading to short Cl $\cdots$ Cl contacts and hence to segregation of Cl-atoms in crystals of chlorinated compounds, is counterintuitive in terms of coulombic interactions, which are repulsive between atoms of the same charge. For example, the total electrostatic energy in hexachlorobenzene has been estimated to be net destabilising by as much as 25 kJ mol^{-1} [24].

As seen in *Fig. 6*, the Cl $\cdots$ Cl UNI potential crosses zero energy at $r = 3.40$ Å and hence becomes destabilising for Cl $\cdots$ Cl distances shorter than this; the minimum of the rather broad potential is at $r = 3.83$ Å with $E_{\min} = -1.00$ kJ mol^{-1}. For the dichlorobenzene structures, tests were made by adding coulombic terms over moderate C–Cl bond dipoles (0.1 electrons), plus the usual 0.15 electron C–H bond dipole [24]. The ranking of lattice energies changes from that obtained using chargeless potentials but in a quite erratic manner, while results of relaxation of observed crystal structures were essentially unaffected. There was no indication that inclusion of coulombic terms led to better crystal-structure predictions; therefore, the unmodified UNI model was retained, as being about as reliable as many others and having the advantage of comparative simplicity. For all the structures considered here, both computer-generated and experimental, the lattice-vibrational (intermolecular) contribution to the crystal entropy, S_{ext}, was estimated in the rigid-molecule approximation [25].

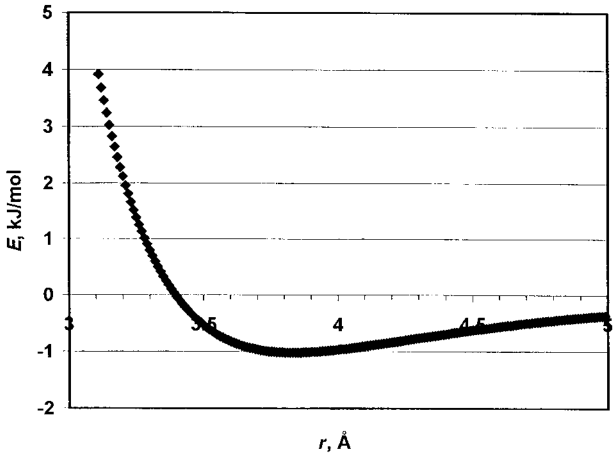

Fig. 6. *The UNI Cl $\cdots$ Cl atom-pair potential.* Note that the energy minimum of -1.00 kJ mol^{-1} occurs at a Cl $\cdots$ Cl distance of 3.83 Å and that the interaction energy becomes destabilizing at a Cl $\cdots$ Cl distance of 3.40 Å

c) *Results.* As usual in this kind of study (see *Fig. 7* and the discussion in [26]), a great many crystal structures were generated for each isomer, with lattice energies within a few kJ mol^{-1} range from the most stable one upwards. For example, for the 1,4-isomer the search routine generated 2430, 1841, 526, and 1921 raw structures in $P\bar{1}$, $P2_1/c$, *Pbca*, and *C2/c*, respectively; after merging and sorting, these numbers were reduced to 25, 32, 15, and 3, respectively. With a modern $ 5,000 workstation, the entire computation work on the three isomers took only a few days; for a single molecule in one space group, the time required is typically a couple of CPU hours.

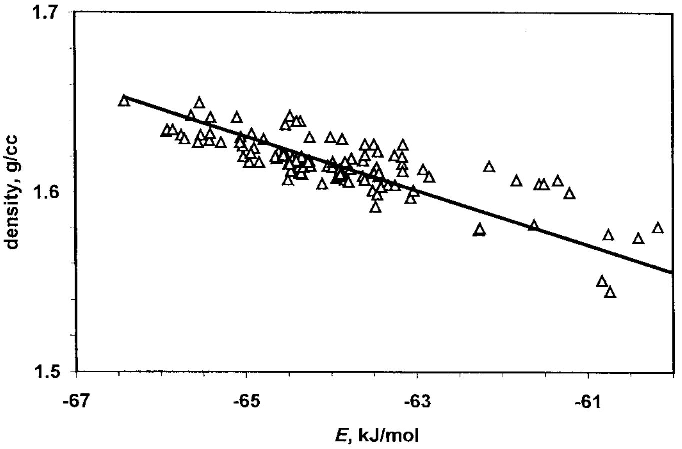

Fig. 7. *A lattice energy-crystal density plot for calculated crystal structures of 1,2-dichlorobenzene.* Quite similar plots result for the other two isomers.

For the 1,2-isomer, the virtual crystal structures listed in *Table 3* could be considered as the most likely ones on the basis of their calculated lattice energies alone, but the observed crystal structure is not among them. Neither is its 'OPT' structure among those with the lowest calculated lattice energy. In the calculated structure with the lowest lattice

Table 3. *Results for the Crystal-Structure Generation of 1,2-Dichlorobenzene.* Structure types are: HB: herringbone pattern, PL: parallel layers.

	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V_{cell}/Å^3	$-E$/kJ mol^{-1}	Type
$P\bar{1}$, $Z=2$	6.78	7.17	7.62	98	112	113	149	65.9	PL
$P2_1$, $Z=2$	7.31	3.76	11.73		111		151	63.5	HB
	6.48	4.13	11.23		90		150	63.5	HB
$P2_12_12_1$, $Z=4$	11.14	3.77	14.26				150	64.3	HB
	16.60	3.57	9.98				148	66.4	PL
$P2_1/c$, $Z=4$	5.90	6.19	16.62		77		149	65.5	HB
	5.95	9.98	10.99		66		148	65.6	HB
Pbca, $Z=8$	10.20	9.12	13.01				151	63.2	HB
	10.75	12.93	8.56				149	64.4	HB
$P2_1/c$, $Z=4$	3.74[a])	10.42	16.06		107		150	64.5	HB

[a]) Obtained by Zip-Promet with input experimental cell parameters and space group. Corresponds to the X-ray structure.

energy ($P2_12_12_1$, $E = -66.4$ kJ mol^{-1}), the planar molecules are oriented exactly perpendicular to the short *b* axis (3.57 Å). The molecular planes are thus all parallel, and the actual space group is elevated to *Pcma* (an alternative orientation of *Pbam*, D^9_{2h}). In the observed structure ($P2_1/n$), the planar molecules are oriented at an angle of 26° to the short *a* axis (3.95 Å), thus creating a herringbone pattern. Nevertheless, the view of the calculated structure in projection down its short axis (*Fig. 8*) shows remarkable similarity to the corresponding projection of the observed structure (*Fig. 4*). Indeed, this similarity between the best calculated structure and the observed one is perhaps the only minor consolation in an otherwise unsuccessful prediction exercise for this isomer. Of course, the other calculated crystal structures in *Table 3* can be regarded as possibilities for as yet unknown polymorphs of crystalline 1,2-dichlorobenzene. When the exercise was biased by using the correct space group and cell parameters, Zip-Promet produced the correct crystal structure in a few minutes.

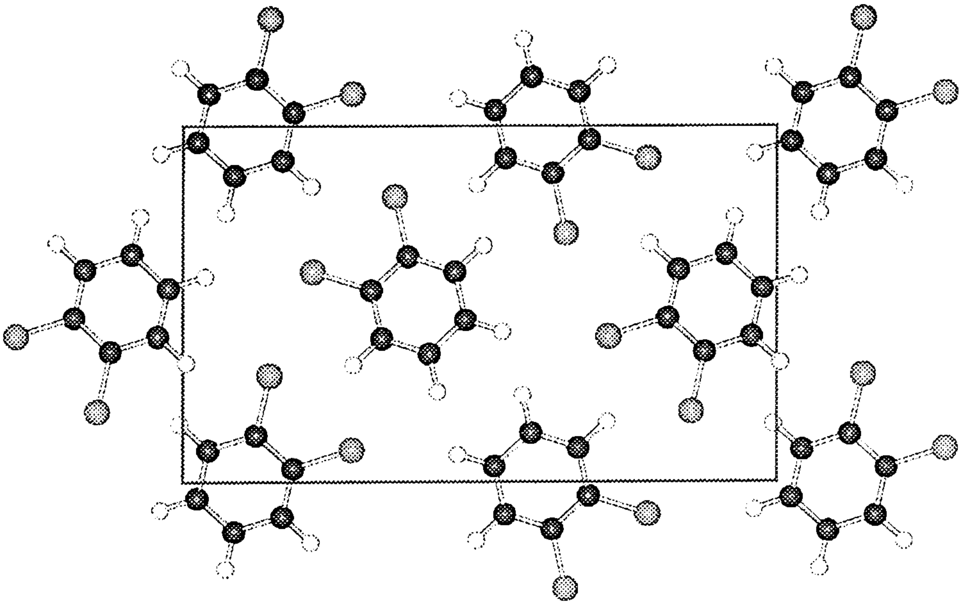

Fig. 8. *Projection of the calculated crystal structure of 1,2-dichlorobenzene with the highest packing energy.* Compare with *Fig. 4*. Drawing by SCHAKAL [28]

Lattice energies were corrected for the effects of lattice-vibrational entropy to give a pseudo-free energy at 295 K, $G = E - 295\ S_{\mathrm{vib}}$ (*Fig. 9*). The structure with the lowest lattice energy is not the best in free energy because its vibrational entropy is very low. Introduction of the $-TS$ term reshuffles the energy ranking but only within a 1–2 kJ mol^{-1} range. Quite similar results were obtained for the 1,3- and 1,4-isomers.

There is not much to say about our crystal structure predictions for the 1,3-isomer, because this crystallises with two molecules in the asymmetric unit ($Z = 2$), a possibility that is not implemented in our search routines. Some calculated structures for this

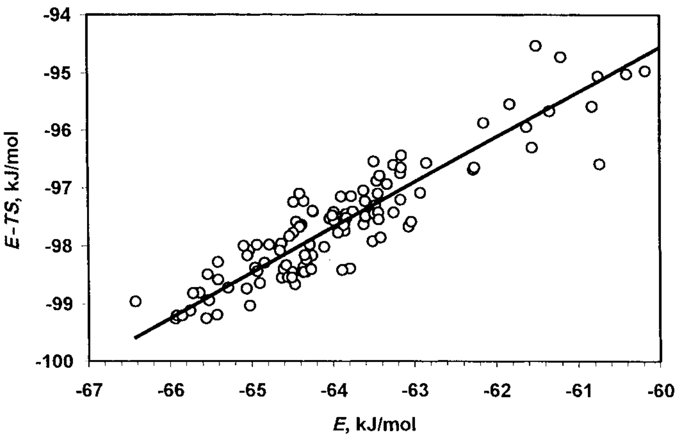

Fig. 9. *Pseudo-free energy against lattice energy for calculated crystal structures of 1,2-dichlorobenzene.* Results for the other two isomers are quite similar.

Table 4. *Results for the Crystal-Structure Generation of 1,3-Dichlorobenzene*

	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V_{cell}/Å^3	$-E$/kJ mol^{-1}
$P\bar{1}$, $Z=2$	3.70	7.64	12.75	57	88	92	151	64.6
	7.22	6.91	8.18	74	116	71	152	64.4
$P2_1$, $Z=2$	7.94[a])	3.55	12.14		120		148	66.1
$P2_1/c$, $Z=4$	7.94[a])	3.56	21.43		100		149	66.1
	13.76	3.72	14.25		55		150	66.1
	14.01	5.98	7.15		95		150	65.3
	6.88	11.19	8.31		71		152	64.5
$Pbca$, $Z=8$	28.19	5.96	7.18				151	64.1
$P2_12_12_1$, $Z=4$	5.19	7.46	15.30				149	64.6

[a]) Parallel layer structures.

isomer are collected in *Table 4*. As also for the 1,2-isomer, the 'OPT' structure corresponding to the experimental crystal structure does not have the best packing energy.

The 1,4-isomer, with its higher melting point, packs better than the other two isomers, as judged by the systematically lower lattice energy for predicted structures in all space groups (see *Table 5*). Two of the three known polymorphs were found by the automatic search program and identified as low-energy structures. In particular, the calculated lattice energy of the γ phase is among the most favourable, ranking second in absolute ordering and first among the monoclinic structures. This structure was found twice by our search and optimisation routines, in different cell settings; the energy optimisation in the non-reduced cell was less effective, leading to a lattice energy 3.5 kJ mol^{-1} higher than that obtained for the reduced cell. This could be a result of many cumulative effects, collectively called 'computational noise', which have to be resolved before consistent energy-based crystal structure prediction can be achieved, over and above the fundamental methodological problems due to inaccuracy of the crystal potential field.

Table 5. *Results for the Crystal-Structure Generation of 1,4-Dichlorobenzene*

Space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V_{cell}/Å^3	$-E$/kJ mol^{-1}
$P2_1/c$ (=γ)	7.14	5.89	7.24		74		147	67.3
$P2_1/c$	8.72	5.76	7.35		125		151	63.8
$P2_1/c$	6.00	4.55	10.98		99		148	66.9
$P\bar{1}$	4.79	5.60	5.65	77	85	85	146	68.2
$P\bar{1}$ (=β)	3.76	5.80	6.94	84	80	89	149	67.1
$C2/c$	9.07	8.69	7.57		87		149	66.2
$Pbca$	9.61	6.99	8.63				145	68.3

The triclinic β phase was also found by the polymorph predictor; its formal rank is third, but, as already discussed, the energy differences are well within the range of computational noise. On the other hand, the monoclinic α phase, with its short interlayer spacing and long glide translation, was not even hinted at by the polymorph predictor. The presence of other low-energy virtual crystal structures can be regarded as a weak indication that other polymorphs may still be possible for 1,4-dichlorobenzene.

Discussion. – a) *The UNI Force Field.* Although planar aromatic molecules tend to pack in herring-bone (HB) patterns rather than in flat parallel layers (PL), crystal structures calculated with the UNI force field are often of the latter type. In this work too, the polymorph-generator algorithm produced stable crystal structures in both HB and PL patterns, although none of the observed structures is of the latter type. In the triclinic β-form of the 1,4-isomer, the molecular planes are parallel by symmetry, but the plane normals are inclined at an angle of 28° to the short stacking axis, so that the layers are not flat but corrugated. The other four observed structures are of the HB pattern, and they share two common features: a short stacking periodicity of *ca.* 3.8 to 3.9 Å (doubled in the γ-form of the 1.4-isomer) and approximately the same angle (22 to 29°) between this axis and the molecular plane normals. (The extreme values of the angle are for the two independent molecules in the structure of the 1.3-isomer.)

This combination of stacking distance and angle makes it possible for successive aromatic rings in a stack to retain an optimal interplanar distance of *ca.* 3.6 Å, although the intermolecular Cl $\cdots$ Cl distance is by 0.2 to 0.3 Å longer than this. We earlier referred to this as a type *iii* Cl $\cdots$ Cl contact and pointed out that it corresponds to an energetically unfavourable disposition of the C–Cl bond dipoles.

In the calculated structures of the PL type, the interplanar stacking distance, along the short crystal axis, is *ca.* 3.55 Å (see *Tables 3* and *4*). In such structures, with the molecular planes perpendicular to the stacking axis, the intra-stack Cl $\cdots$ Cl contact distance would be the same as the interplanar distance, and the absence of such structures in the real world might suggest that type *iii* distances as short as 3.55 Å are energetically less favourable than those around 3.8 to 3.9 Å. The UNI force-field used in our calculations may leave something to be desired in this respect.

Nevertheless, short contact distances in Cl-containing crystals are often around 3.55 Å [23], corresponding to mildly repulsive but stabilising interactions. We may also recall here that the β-phase of the 1,4-isomer contains an intermolecular Cl $\cdots$ Cl distance as short as 3.38 Å. According to atom-atom partitioned energies, for what they are worth, this must be regarded as a repulsive and destabilising contact. The β-phase is the high-temperature form, stable just below the melting point, so its lattice energy must be the least stabilizing and its entropy the largest of the three polymorphs. The presence of this destabilising short contact does not prevent the β-phase from having a calculated lattice energy quite similar to that of other polymorphs.

b) *Lattice-Energy Calculations in Crystal-Structure Prediction.* In line with previous experience, the results of the crystal structure prediction test for the three dichlorobenzenes are mixed. The test was reasonably successful for the 1,4-isomer but failed for the other two isomers. We have no explanation why the 1,3-isomer chooses to pack with two molecules in the asymmetric unit, but, in any case, this complication makes a successful prediction impossible with the present structure-search procedure.

c) *Other Possible Polymorphs. In situ* crystallisation from the melt, involving zone-melting procedures, may not always produce the polymorph with the best packing energy but rather the one that happens to be thermodynamically stable close to the melting point. This could imply that other polymorphs, thermodynamically stable at lower temperatures, can exist. Further work would be necessary to test this possibility.

d) *Packing Energies and Melting Point.* Even if our calculations fail to provide reliable predictions of the actual crystal structures, the virtual structures obtained in our exercise show clearly that the 1,2- and 1,3-isomers do not pack as well as the 1,4-isomer. Calculated lattice energies for the best 1,2- and 1,3-structures tend to be 2–3 kJ mol^{-1} higher than those for the 1,4-structures. For the 'OPT' versions of the experimental 1,2-, 1,3-, and 1,4(β)-structures, the lattice energies are: -64.6, -64.0, and -66.9 kJ mol^{-1}, respectively. The 3% difference may not seem to amount to much, but it is quite sufficient to account at least qualitatively for the melting-point differences. Heat and entropy of fusion are available for the 1,4-isomer: $\Delta H_\mathrm{f} = 18.05$ kJ mol^{-1}, $\Delta S_\mathrm{f} = 55.3$ J $\mathrm{mol}^{-1}\mathrm{K}^{-1}$ [27]. Corresponding values for the other two isomers are unfortunately not available; to estimate these quantities from the above data, we would require a knowledge of the heat capacities of the solid and liquid phases for all three isomers, which we do not have. However, if we take the enthalpies of the liquid phases of the three isomers to be equal, we may estimate for the other two isomers roughly $\Delta H_\mathrm{f} = 15.5$ kJ mol^{-1}, $\Delta S_\mathrm{f} = 61$ J mol^{-1} K^{-1}, allowing for the $R\ln 2$ contribution from the difference in symmetry number. The estimated melting point of the 1,2- and 1,3-isomers is then *ca.* 15500/61 = 255 K, reasonably close to the actual melting points. The relatively small decrease in lattice energy on going from the 1,4-isomer to the 1,2- and 1,3-isomers can lead to a dramatic decrease in melting point.

The reason for the better packing of the 1,4-isomer may reside in a purely molecular shape factor. In the 1,4-isomer, each Cl-atom is open to close intermolecular Cl ··· Cl contacts with favourable dispersive energy contributions in five of the six possible directions, that is to say, up and down, north, east and west. Indeed, as noted by *Wheeler* and *Colson* [13], each Cl-atom in the γ-form makes full use of this and engages in five short Cl ··· Cl interactions. In the 1,2- or 1,3-isomers, the two Cl-atoms partially shield one another from intermolecular contact, and, as we have noted, the Cl-atoms in the observed crystal structures are engaged in at most three Cl ··· Cl interactions. This argument does not depend on the molecular symmetry and should apply for disubstituted benzenes in general, whether the two substituents are equal or not.

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