the elements of the **Q** matrix become:

$$\begin{aligned} &Q_{11} = Q_{31} = Q_{41} = (1-p)\varepsilon_1;\\ &Q_{12} = Q_{32} = Q_{42} = p\varepsilon_2;\\ &Q_{23} = Q_{63} = (1-p')\varepsilon_2;\\ &Q_{54} = (1-p')\varepsilon_1;\\ &Q_{25} = Q_{65} = p'\varepsilon_1;\\ &Q_{56} = p'\varepsilon_2; \end{aligned} \qquad (6)$$

and the other elements are zero. The calculation of diffracted intensities with an electronic computer was programmed for the **Q** matrix given by (6). The **Q** matrix reduces to that of the first problem if $p' = 0$, and to that of the second problem if $p = p'$. The calculated intensity profiles are shown in Fig. 2.

The author wishes to express his sincere thanks to Mr T. Kakuta of Institute of Earth Sciences, Faculty of Science, and to Mr H. Ushijima of Electronic Computer Room of Kagoshima University for their kind help in programming this calculation.

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*Acta Cryst.* (1978). A**34**, 346–348

## α, β and γ forms of *p*-dichlorobenzene: calculation of crystal structure and potential energy.

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(*Received* 16 *August* 1977; *accepted* 21 *November* 1977)

A new potential function for non-bonded atom···atom interactions of chlorine atoms has been used to calculate equilibrium crystal structures and potential energies of the three polymorphs of solid *p*-dichlorobenzene.

There has been considerable interest in potential functions describing non-bonded atom···atom interactions of Cl atoms. Recently, we have introduced (Mirsky & Cohen, 1977) a new Cl···Cl potential function: this is of Buckingham form, $\varphi = -Ar^{-6} + B\exp(-\alpha r)$, with $A = 2980$ Kcal mol$^{-1}$, $B = 4580$ Kcal mol$^{-1}$, and $\alpha = 2{\cdot}262$ Å$^{-1}$. Compared with other available potentials this has a large value (4·2 Å) of $r_0$, the minimum-energy interatomic distance, and is soft (the steepness parameter $\lambda = \alpha r_0 = 9{\cdot}5$). This function was successfully used for calculating the crystal structure parameters and lattice energies of a number of chloroaromatics, without additional terms to allow for electrostatic interactions.

One of the substances for which these calculations were performed was the γ form of *p*-dichlorobenzene (DCB). There are by now considerable structural data available on the three polymorphs of this compound. There have been studies at various temperatures of the monoclinic α phase [space group $P2_1/a$, $Z = 2$ (Reynolds, Kjems & White, 1974; Wheeler & Colson, 1976; and references therein)], of the triclinic β phase [space group $P\bar{1}$, $Z = 1$ (Reynolds *et al.*, 1974; Wheeler & Colson, 1976; and references therein)], and

Table 1. *β, α and γ phases of DCB: comparison of the calculated equilibrium unit-cell parameters with those extrapolated to* 0 K

Polymorph

| | β | | | α | | | γ | | |
|---|---|---|---|---|---|---|---|---|---|
| Unit-cell parameter* | Calculated | 0 K | $\% \frac{\text{theory}}{\text{experiment}}$ | Calculated | 0 K | $\% \frac{\text{theory}}{\text{experiment}}$ | Calculated | 0 K | $\% \frac{\text{theory}}{\text{experiment}}$ |
| $a$ (Å) | 7·32 | 7·29 | 0·4 | 14·65 | 14·64 | 0 | 8·57 | 8·60 | −0·4 |
| $b$ (Å) | 5·75 | 5·85 | −1·7 | 5·63 | 5·72 | −1·6 | 5·98 | 6·00 | −0·3 |
| $c$ (Å) | 3·74 | 3·86 | −3·2 | 3·83 | 3·90 | −1·8 | 7·32 | 7·39 | −1·0 |
| α (°)† | 91·8 | 90·9 | 0·9 | 90·0 | 90·0 | | 90·0 | 90·0 | |
| β (°) | 109·7 | 112·4 | −2·4 | 109·8 | 111·6 | −1·6 | 127·3 | 127·5 | −0·2 |
| γ (°)† | 94·1 | 92·7 | 1·5 | 90·0 | 90·0 | | 90·0 | 90·0 | |
| $V_{\text{mol}}$ (Å$^3$) | 147·9 | 151·9 | −2·7 | 148·5 | 151·8 | −2·2 | 149·2 | 151·3 | −1·4 |

* The 0 K values for the β and α forms are found by extrapolation; those for the γ form are estimated with contractions of about 0·02 Å assumed in all cell dimensions between 100 and 0 K, as is found for β and α forms.

† For monoclinic space groups, only the monoclinic angle was varied.

Table 2. Cl···Cl *intermolecular contact distances, r* (Å) *shorter than* 4·2 Å *and corresponding interaction energies,* $\varphi$ (Kcal mol$^{-1}$)

| | Experimental (100 K) | | In the energy minimum with respect to molecular orientations | | In the general minimum with respect to molecular orientations and unit-cell parameters | | Number of contacts |
|---|---|---|---|---|---|---|---|
| Phase | $r$ | $\varphi$ | $r$ | $\varphi$ | $r$ | $\varphi$ | |
| $\beta$ | 3·383 | 0·190 | 3·381 | 0·191 | 3·453 | 0·099 | 1 |
| | 4·178 | –0·200 | 4·169 | –0·200 | 4·004 | –0·189 | 1 |
| | 3·882 | –0·167 | 3·882 | –0·167 | 3·741 | –0·119 | 4 |
| $\alpha$ | 3·729 | –0·114 | 3·730 | –0·114 | 3·691 | –0·095 | 2 |
| | 3·925 | –0·177 | 3·925 | –0·177 | 3·810 | –0·146 | 4 |
| $\gamma$ | 3·789 | –0·139 | 3·810 | –0·146 | 3·774 | –0·133 | 2 |
| | 3·801 | –0·143 | 3·814 | –0·148 | 3·775 | –0·133 | 4 |
| | 3·824 | –0·150 | 3·822 | –0·150 | 3·768 | –0·131 | 1 |

of the monoclinic $\gamma$ phase [space group $P2_1/c$, $Z = 2$ (Fourme, Clec'h, Figuiere, Ghelfenstein & Szwarc, 1974; Wheeler & Colson, 1976).

Sublimation energies of the $\alpha$ and $\beta$ phases have been measured [15·5 and 15·1 Kcal mol$^{-1}$, respectively (Walsh & Smith, 1961)], and the energies of the various solid–solid phase transitions have been obtained [0·2 to 0·4 Kcal mol$^{-1}$; (Figuiere & Szwarc, 1974)]. These structural and energy data provide a good basis for testing the validity of possible potentials for non-bonded Cl···Cl atom···atom interactions.

From such a test of several potential functions available in the literature it has been concluded (Wheeler & Colson, 1976; Wheeler, 1977) that no central potential for Cl atoms can adequately explain the structural features of DCB. In particular, all the Cl···Cl potential functions tested could not reproduce a very short contact distance of 3·38 Å found in the $\beta$ phase: they gave rise to a very strong repulsion for this contact, and minimization of the energy led to crystal structures in which this contact expanded to 3·6 Å or more. The aim of the present paper is to show that the structural features characteristic of all polymorphs of DCB and their lattice energies can be successfully reproduced if the Mirsky–Cohen Cl potential, described above, is used together with the potential functions for C and H atoms and combining rules for mixed Cl···C and Cl···H interactions taken from Mirsky (1976). In the calculations the structural data of Wheeler & Colson (1976), with the corrections in atomic coordinates sent to us by Wheeler (1977), were used. The original H atom positions were changed to give C—H hydrogen bond lengths of 1·08 Å throughout.

Table 3. *Lattice energies of three crystalline forms of DCB as a function of temperature* (Kcal mol$^{-1}$)

| | Polymorph | | |
|---|---|---|---|
| $T$ (K) | $\beta$ | $\alpha$ | $\gamma$ |
| 300 | –14·93 | –14·83 | – |
| 100 | –15·28 | –15·14 | –15·12 |
| 0 | –15·52 | –15·34 | –15·19 |

The lattice energy for each polymorph was calculated and minimized in steps: first with respect to molecular orientations keeping the experimental unit-cell parameters fixed, then with respect to unit-cell parameters and, finally, again with respect to molecular orientations, all this with retention of monoclinic crystal symmetry for the $\alpha$ and $\gamma$ phases and of triclinic symmetry for the $\beta$ phase. The molecular geometry for each phase was taken from the experimental data and kept fixed. The results of the calculations are compared with the experimental data in Tables 1 to 3.

Table 1 shows that all the calculated unit-cell geometries agree with the experimental ones to an accuracy of 1–3%, which is within the accuracy of the atom–atom potential method. All the calculated unit-cell volumes per molecule ($V_{\text{mol}}$) are slightly smaller than the experimental ones, in agreement with the fact that zero-point vibrational effects are present in the experimental data and are not included in the calculation procedure.

In Table 2 experimental and calculated Cl···Cl intermolecular contact distances are given, together with the corresponding interaction energies. After the first step of minimization the Cl···Cl contact distances remain practically unchanged (in all the three phases molecular rotations do not exceed 1°). The short distance in the $\beta$-phase (3·383 Å) becomes even shorter (3·381 Å). The positive (repulsive) energy for this contact (0·191 Kcal mol$^{-1}$) is compensated by the strong attraction (–0·200 Kcal mol$^{-1}$) between one of the Cl atoms involved and its other neighbour, 4·17 Å away. Note that the latter distance is equal to the $r_0$ value for our Cl···Cl potential function.

After minimization with respect to all crystal variables, the contact distances become reasonably shorter than they are at 100 K, except for the shortest one in question which increases to 3·453 Å, but still remains very short compared with the average van der Waals distance (3·6 Å). In agreement with experiment, in the theoretical $\gamma$ phase all the closest contacts remain equal in length (3·77Å).

The calculated values of the lattice energies of the three phases (Table 3) are very similar. Their absolute values are in good agreement with the experimental heats of sublimation (see above) which means that our potential functions are quite adequate for the energy calculations. The differences of about 1% in the lattice energies and in the calculated values of $V_{\text{mol}}$ (see Table 1) are too small to be physically significant. They may simply arise from the details of the computational procedure. Our results show, however, that the potential energy surface for the DCB crystal has a number of minima of almost equal depths. This is probably the main reason why the phase transitions in this crystal are so sluggish [there is a marked tendency to supercooling and superheating in this series; the phase transformation is usually initiated at defective sites in the crystal and it cannot be induced, even by mechanical coercion, in highly perfect crystals (Kitaigorodsky, Mnyukh & Asadov, 1965; Ghelfenstein & Szwarc, 1971; Reynolds, Kjems & White, 1972; Wheeler & Colson, 1975; Reynolds, 1977)]. The real crystal structure of each polymorph corresponds to the minimum of its free energy. In the absence of significant differences in the potential energies the relative stabilities of the three phases become essentially functions of the lattice dynamics.

The probability of phase transformation depends on the height of the free-energy barrier between the relevant phases. The potential-energy contribution to this barrier can be calculated with the above force field provided a molecular model of the transformation process is built (see, for example, Reynolds, 1977). It would also be of interest to use the same potential functions for studying the possibility of orientational disordering in the $\alpha$ and $\beta$ phases suggested by X-ray data (Wheeler & Colson, 1975), which may be related to the mechanism of the phase transformation. A technique can be applied here similar to that developed for the case of orientational disorder in *trans*-stilbene (Bernstein & Mirsky, 1978).

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*Acta Cryst.* (1978). A**34**, 348

## About sequences of maximal subgroups, a few answers to a question from Bertaut: erratum.

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(*Received* 15 *December* 1977)

In Billiet [*Acta Cryst.* (1977), A**33**, 1007–1008] the printer has omitted line 17. The last sentence of the first paragraph should read: One knows, at the present time, no complete and definitive answer to this question, but may invoke some general elements which are likely to occur in the resolution of this problem.

All information is given in the abstract.

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