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Potential Energy Interactions in Solid Dichlorine

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Received March 29, 1979

Hsu and Williams have proposed a model to explain the observed centric space group and cell dimensions of crystalline dichlorine. Although this model satisfies the "force-free" criterion, it requires the dichlorine molecules to be dipolar. We believe that it is physically unrealistic to assign a permanent dipole to a homopolar diatomic molecule in a centric lattice. Moreover, the model invokes partial intermolecular bonding between nearest atomic neighbors. If there is no restriction on the number of such neighbors, it can be shown that there are several crystalline structures available to dichlorine which would be more stable than that observed. The observed crystal structure can be explained in terms of anisotropic dispersion–repulsion forces and quadrupole–quadrupole interactions.

Introduction

In a recent article,[1] Hsu and Williams (H & W) postulate atom–atom interaction parameters to account for the observed cell dimensions, atomic coordinates, and space group (orthorhombic *Cmca*) of crystalline dichlorine.[2] The interactions they propose meet two of the criteria normally accepted to be necessary, namely, (i) obtaining a good match with the experimental lattice energy and (ii) obtaining satisfactorily small changes in cell dimensions and/or atomic coordinates on relaxation (force-free model). Criterion i is not demanding since all empirical atom–atom parameters have adjustable multipliers. Criterion ii is much more demanding. A third criterion is that, with the assumed atom–atom interaction parameters, it should not be possible to pack the molecules in an alternative (hypothetical) way to yield a more stable structure (with a more negative lattice energy) than that found experimentally. As we indicate below, we have doubts whether the H & W parameters satisfy this criterion but, in any case, we believe their choice of parameters to be physically unrealistic.

The molecules in the crystal are said to be dipolar, the atoms carrying charges of opposite sign of magnitude $0.0914|e|$. Support for this is said to come from fundamental infrared absorption frequencies which have been observed in solid specimens of Br_2 and I_2[3] but not in solid Cl_2.[4] (The crystals are isostructural.) In the absence of a permanent molecular dipole there should be no absorption at these frequencies. H & W refer to the high absorption background which might have prevented the band being observed for Cl_2, and they use this interpretation to support their view that dihalogen molecules have permanent dipoles in the crystal. We believe, on purely symmetry grounds, that this cannot be so. To us, the most likely explanation of the infrared bands observed with solid Br_2 and I_2 is that the specimens were not homogeneously crystalline but had extensive polycrystalline and amorphous regions. This could cause a significant proportion of the molecules to have weak dipoles, induced by the quadrupoles of noncentrosymmetrically arranged neighboring molecules. To us, the fact that the band is not observed with Cl_2 indicates a more homogeneously crystalline specimen in this case.

In addition, but somewhat less importantly, H & W did not include molecular quadrupole–quadrupole, Θ–Θ, interactions because criterion ii above was then better satisfied. Dichlorine is accepted to have a positive quadrupole moment (estimated as[5] $+3.38 \times 10^{-26}$ esu cm^2) and thus Θ–Θ interactions must be included in any crystal potential-energy calculations. It should, in any case, be stressed that point-charge interactions considered by H & W are a poor approximation to Θ–Θ interactions for neighboring molecules. Such interactions should be calculated by suitable integration using the molecular difference charge density.[6] A third feature of the H & W model concerns the use of a Morse potential to represent intermolecular ("partial") valence bonding between nearest-neighbor atoms. The case against this is harder to argue, but we point out that the interatomic distances used to justify intermolecular bonding are not unusually short. Comparisons are being made with inappropriate van der Waals radii.[7] The question of partial bonding is taken up again below. H & W allocate charges to the atoms so that the molecular dipoles all have their z components in the same direction (Figure 1a). They state that the allocation of charges they propose assigns the crystal to the monoclinic space group *Cc*.[8] It seems to us, however, from their diagram, and our calculations confirm, that the space group of their structure is orthorhombic $Cmc2_1$.[10,11]

Results

We have used a locally modified version of WMIN[12] and parameters given by H & W to carry out calculations to a limiting radius of 13.5 Å on various crystal structures. The results are set out in Table I. The only results not calculated by us are those of H & W in the first line of Table I. It will be noted that, on the second line, where we have repeated the H & W calculation with our program, there are slight differences in final cell parameters and energy contributions. This could be due to the following possible causes: our use of steepest descent plus interpolation for refinement rather than least squares; possible different treatment (i.e., exclusion vs. inclusion) of molecules intersected by the limiting sphere; the use of integration rather than accelerated convergence for dispersion interactions outside the summation sphere (magnitude $0.015253A/V$ kJ mol^{-1}, where V is the unit cell volume in Å^3). Despite these programming differences, the total energies are identical for three significant figures. We noted, in passing, that the assumed polarity of the molecules can be reversed in successive yz layers (allocating the crystal to *Pmca*,

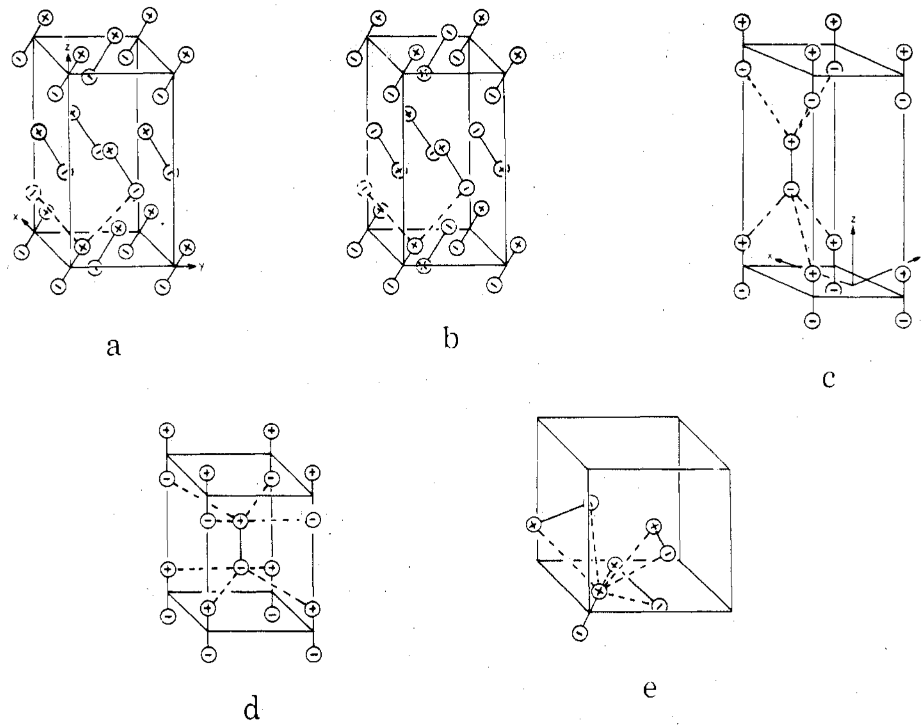

Figure 1. Possible crystal structures for dichlorine based on H & W parameters: (a) *Cmc*2$_1$, (b) *Pmca*, (c) *P*6$_3$, (d) *I*4/*mm*, (e) *P*2$_1$3. Broken lines indicate shortest contacts.

Table I. Crystal Models for Dichlorine Using H & W Energy Parameters[a]

	a	*b*	*c*	repulsion	dispersion[h]	Coulombic	Morse	*n*	d_M	total
*Cmc*2$_1$[b,c]	6.25	4.43	8.34	54.8	−80.4	−1.1	−5.2	2	3.32	−31.9
*Cmc*2$_1$[c]	6.26_6	4.50_3	8.27_5	52.7_6	-78.5_8	-1.1_3	-4.9_6	2	3.33_7	-31.9_1
Pmca[d]	6.28_7	4.43_1	8.36_0	53.0_4	-78.9_5	-1.1_1	-4.8_8	2	3.34_4	-31.9_0
*P*6$_3$[e]	6.56_3	(3.78_9)	9.18_0	55.6_9	-81.8_5	-0.8_1	-6.4_1	3	3.41_2	-33.3_8
*I*4/*mm*[f]	4.52_7	(4.52_7)	5.67_9	61.4_8	-83.1_4	-1.4_1	-10.3_1	4	3.31_7	-33.3_8
*P*2$_1$3[g]	6.02_0	(6.02_0)	(6.02_0)	64.4_4	-90.7_3	-0.9_4	-9.8_6	6	3.54_9	-36.0_9

[a] Force-free cell dimensions are in Å and energy contributions are in kJ mol^{-1}; the number of "Morse" closest contacts (*n*) have lengths d_M in Å. "Total" refers to calculated lattice energy in kJ mol^{-1}. [b] Calculated by H & W. [c] Space group No. 36. Eight atoms in two sets of special positions *a*. [d] Space group No. 57. Add $^1/_4$ to *y* coordinates of *Cmc*2$_1$. Eight atoms in two sets of special positions *d*. [e] Space group No. 173. Twelve atoms in two sets of equivalent positions with $x = 0, y = {}^2/_3$. [f] Space group No. 107. Four atoms in two sets of special positions *a*. [g] Space group No. 198. Eight atoms in two sets of special positions *a*. [h] Including integral for region outside limiting sphere, radius 13.5 Å.

Figure 1b) without significantly affecting the total energy. Since, as we have said, we do not subscribe to the use of the parameters used by H & W, we regard this result simply as an interesting curiosity.

H & W do not specify whether they have grounds for restricting the partial bonding of any one atom to *two* others equidistant from it. If this is not a requirement, there are, as is clear from Table I, several possible structures more stable than the experimental *Cmca* (Figure 1c–e). These could only be rejected on some cogent molecular orbital arguments. If they cannot be so rejected, we can only conclude that the H & W parameters not only fail in being, in our opinion, physically unrealistic but also fail under criterion iii in predicting the wrong crystal structure.

Discussion

We believe that the observed *Cmca* space group of solid dichlorine can be explained by a combination of anisotropic (i.e., nonspherical) dispersion–repulsion and quadrupole–quadrupole forces.[6] Anisotropic dispersion–repulsion forces have also been invoked to explain the lattice frequencies of solid N_2.[13] Our model is force free and is calculated to be far more stable than the *Pa*3 or *P*$\bar{6}$*c*2 structures (corresponding to *P*2$_1$3 and *P*6$_3$ above). Because of the extensive computation required, this model has not yet been checked for stability with respect to molecular rotation. We aim to undertake these calculations in due course.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. Cl_2, 7782-50-5.

References and Notes

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(8) H & W give "the corresponding noncentrosymmetric space group" as orthorhombic *C*2*ca*. This is not a technically incorrect designation because there are both *a* and *b* glide planes normal to the *z* axis in this space group. However, the designation given in ref 9 is *C*2*cb*.
(9) "International Tables for Crystallography"; Kynoch Press: Birmingham, England, 1976; Vol. I, Table 6.2.1.
(10) Reference 9. Space group No. 36.
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