

Effects of Molecular Electric Potential and Anisotropic Atomic Repulsion in the Dichlorine Dimer and Crystalline Chlorine

Donald E. Williams* and Daquan Gao

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

Received May 29, 1996[⊗]

Molecular packing analysis of crystalline dichlorine (Cl₂) shows that the crystal structure is compatible with an isotropic intermolecular force field that includes polar flattening of the exchange repulsion energy and a five-center distributed monopole representation of the molecular electric potential. Polar flattening largely accounts for the short intermolecular contacts in the crystal, and the molecular electric potential is critical in determining the molecular orientation and space group. Neither an atom-centered model for repulsion nor a molecular quadrupole model for the electric potential is adequate to describe the force field of this molecule.

Introduction

It has long been known that crystalline dichlorine is not a normal van der Waals solid.¹ In the crystal, the molecules form planar sheets with short intermolecular Cl···Cl distances of 3.27 Å, compared to the usually quoted² van der Waals diameter of 3.6 Å. Previous attempts to model this crystal with atom-atom intermolecular force fields and molecular quadrupoles have failed.^{3,4} Subsequent studies have probed for the reasons that Cl₂ deviates from the expected van der Waals behavior. The possibility that a weak intermolecular bond exists between dichlorine molecules was proposed.^{5–7} However, recent studies indicate that the repulsion between dichlorine molecules, on the basis of chlorine atom positions, is anisotropic.^{8–16} In this work we confirm the existence of atomic anisotropy in Cl₂ using ab initio wave functions and model this anisotropic repulsion with isotropic sites on the basis of a foreshortened Cl–Cl bond. The use of foreshortened isotropic repulsion sites is particularly convenient in making lattice energy summations, as contrasted to an atom-centered anisotropic repulsion model. The quantum mechanical molecular electric potential (QM-MEP) is represented by a distributed monopole model. We show that the MEP is a significant factor in determining the space group and molecular packing in the crystal and that anisotropic repulsion allows the very short intermolecular Cl···Cl contacts in the crystal. The resulting isotropic intermolecular force field model

is consistent with the observed *Cmca* crystal structure of Cl₂. This force field yields higher energy crystal structures in space groups *C2/c*, *R3m*, *Pa3*, and *P6m2* that are found or predicted for other homonuclear diatomic molecules.

Molecular Electric Potential

The MEP of Cl₂ in its van der Waals envelope has an important directional effect on the intermolecular energy. The ground state ab initio wave function of Hartree–Fock 6-31+G* quality for Cl₂ was found¹⁷ using the bond distance of 1.988 Å observed in the crystal.¹⁸ This Gaussian basis set is of the split valence type; the plus sign indicates the addition of diffuse functions, and the asterisk indicates the addition of polarization functions. A set of cubic grid points was generated in a van der Waals envelope around the molecule, and the MEP was evaluated at these points. The van der Waals envelope began at 3.0 Å from the nearest atom and was 1.2 Å thick with point spacing 0.5 Å. This protocol gave about 2000 points around the molecule. Alternatively, it was found that a set of a comparable number of geodesic grid points¹⁹ for the MEP gave essentially the same results.

The computer program pdm96²⁰ was used to develop models to represent the Cl₂ MEP. The classical way of representing the MEP of a homonuclear diatomic molecule is to place a quadrupole at the molecular center. For Cl₂, this molecular quadrupole optimally represents the MEP with 33.6% relative rms (rrms) error and is therefore a poor model. Note that experimental measurements of the Cl₂ quadrupole, which assume that higher electric moments vanish, are similarly subject to error.

To better represent the MEP, we turn to distributed multipole models, placing the multipolar centers at the nuclear positions. Since a distributed atomic monopole model (net atomic charges) is not applicable for a homonuclear diatomic molecule (100% rms error), atomic dipoles and quadrupoles were fitted to the

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

- (1) English, C. A.; Venables, J. A. *Proc. R. Soc. London* **1974**, *A340*, 57–80.
- (2) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.
- (3) Mirsky, K.; Cohen, M. D. *Chem. Phys.* **1978**, *28*, 193–204.
- (4) Williams, D. E. *Chem. Phys.* **1981**, *55*, 163–167.
- (5) Yamasaki, K. *J. Phys. Soc. Jpn.* **1962**, *17*, 1262–1267.
- (6) Hsu, L. Y.; Williams, D. E. *Inorg. Chem.* **1979**, *18*, 79–82; **1980**, *19*, 2200.
- (7) Williams, D. E.; Hsu, L. Y. *Acta Crystallogr.* **1985**, *A41*, 296–301.
- (8) Nyburg, S. C.; Wong-Ng, W. *Inorg. Chem.* **1979**, *18*, 2790–2791.
- (9) Nyburg, S. C.; Wong-Ng, W. *Proc. R. Soc. London* **1979**, *A367*, 29–45.
- (10) Nyburg, S. C. *Acta Crystallogr.* **1979**, *A35*, 641–645.
- (11) Nyburg, S. C. *Acta Crystallogr.* **1985**, *B41*, 274–279.
- (12) Wheatley, R. J.; Price, S. L. *Mol. Phys.* **1990**, *71*, 1381–1404.
- (13) Price, S. L.; Stone, A. J.; Lucas, J.; Rowland, R. S.; Thornley, A. E. *J. Am. Chem. Soc.* **1994**, *116*, 4910–4918.
- (14) Peebles, S. A.; Fowler, P. W.; Legon, A. C. *Chem. Phys. Lett.* **1995**, *240*, 130–134.
- (15) Rodger, P. M.; Stone, A. J.; Tildesley, D. J. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 1689–1702.
- (16) Rodger, P. M.; Stone, A. J.; Tildesley, D. J. *Mol. Phys.* **1988**, *63*, 173–188.

- (17) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian-92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.
- (18) Stevens, E. D. *Mol. Phys.* **1979**, *37*, 27–45.
- (19) Spackman, M. A. *J. Comput. Chem.* **1996**, *17*, 1–8.
- (20) Williams, D. E. *Program pdm96, Potential Derived Multipoles*; Department of Chemistry, University of Louisville: Louisville, KY 40292, 1996. Email: dew01@xray5.chem.louisville.edu.

Table 1. Fit of Distributed Multipole Models to the MEP of Cl₂

	rms, %	$u_z, e $	$Q_{zz}, e \text{ \AA}^2$
atomic dipoles	27.7	+0.135	
atomic quadrupoles	15.4		0.575
both dipoles and quadrupoles	0.1	-0.172	1.280

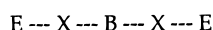
Table 2. Distributed Monopole Models for the MEP of Cl₂

model	rms, %	$q_X, e $	$q_B, e $	$q_E, e $	$r, \text{ \AA}$
XE	42.0	-0.240		0.240	0.215
XB	30.7	0.263	-0.526		
XBE	0.7	-2.534	2.321	1.373	0.215

MEP. Table 1 shows results for (1) atomic dipoles, (2) atomic quadrupoles, and (3) both dipoles and quadrupoles. The positive dipole direction is along the bond and is pointed away from the bond center.

It is seen that the atomic dipole model gives a fit only slightly better than a molecular quadrupole and that the dipoles are oriented consistent with the idea of charge accumulation in the bond, or decrementation in the lone pair region. However, the atomic quadrupole model gives a better fit to the MEP, casting doubt on the suitability of the using atomic dipoles alone. The last line of Table 1 shows that a nearly perfect fit is obtained with both atomic dipoles and quadrupoles, but now the dipoles are larger and oriented consistent with the idea of charge decrementation in the bond, or accumulation in the lone pair region.

In order to conveniently assess the effect of the MEP on the crystal structure, it is highly desirable to have a simplified monopole model for the lattice summation, such as distributed-site monopoles. Such a model can include, in addition to nuclear sites, additional sites located in the bonding and lone pair regions of the molecule.²¹ For a homonuclear diatomic molecule, the location of the bond monopole is obvious (at the bond center), but the placement of the lone pair monopole site(s) is to be determined. We found that there was no significant advantage in fitting the MEP by defining off-axis lone pair sites, so therefore only a single parameter needs to be determined, the axial atom-lone pair distance. This leads to a five-site monopole model



where the X's are Cl nuclear sites, B is the bond site, and the E's are extended sites at distance r from X. The extended sites can be thought of as representing the effects of a cylindrically symmetric lone pair electron distribution. A five-site monopole model has been used to represent multipole moments of N₂ and CO₂; in that application, the X site was not restricted to the nuclear position.²²

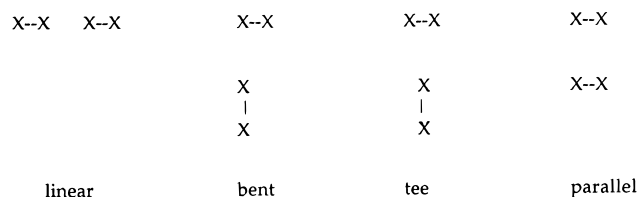
First, consider the extended charge model, which might be considered appropriate to model the cylindrically symmetric lone pair electron density. Table 2 shows that the fit to the MEP is poor, 42.0%, and that the value of the extended charge is positive, consistent with the directions of distributed atomic dipoles found above. As an alternative, consider the bond charge model, which might be considered appropriate to model electron density in the bond. The second line of Table 2 shows that the fit to the MEP is 30.7% and that the bond charge is $-0.526|e|$. The sign of the bond charge is also consistent with the atomic dipole model, where the dipoles showed negative accumulation in the bond, but the fit is still poor. The combination of both bond charge and extended (quasi) lone pair

sites gives a very good representation of the MEP, with a relative fitting error of only 0.7%. We adopted the XBE model to represent the MEP of Cl₂.

The fit of the XBE model is nearly as good as the more complicated distributed atomic (dipoles + quadrupoles) model. Further, it is seen that the bond charge becomes positive as expected from the distributed multipole results and that the E charge, while still positive, corresponds to a dipole with positive direction toward the bond center. The isotropic sites of the XBE model make it highly suitable for detailed lattice energy summations in crystalline dichlorine.

Anisotropic Repulsion Energy

The very convenient and practical idea that a molecule can be represented by an array of spherical atoms has a long history. Also, it is easy to recognize the possibility that atomic sphericities in a molecule might be modified in the bonding directions. However, we want to consider here deviations from atomic sphericity in nonbonded directions, because these deviations most affect the structure of the crystal. For the purpose of examining anisotropic repulsion between Cl₂ molecules, we calculated the wave function for two molecules in several orientations with the same basis set, using the Gaussian-92 program.¹⁷ The molecular structure was held constant with a bond distance of 1.988 Å. Table 3 shows calculated values of E_{ex} for several configurations of the Cl₂ dimer: linear, bent, tee, and parallel; d is the closest distance between X's of different molecules, or to the bond center in the case of the tee structure.



The intermolecular energy was defined as $E_{inter} = E(\text{Cl}_4) - 2E(\text{Cl}_2)$, where ghost atom sites were used in the Cl₂ calculation to implement a basis set superposition correction (BSSE). Column 2 of Table 3 shows BSSE-corrected values E_{inter} ; column 3 shows that the BSSE correction is not negligible. Column 4 shows the approximate electrostatic energy calculated from the distributed monopole model described above. Note that since the distributed monopole model represents the QM-MEP quite well, E_{el} obtained in this manner will be very close to a value calculated directly from interaction of two Cl₂ MEP's, assuming negligible polarization occurs at the van der Waals distance.

Since no dispersion energy is included in the Hartree-Fock energy, E_{inter} is assumed to be the sum of an exchange repulsion energy E_{ex} and the distributed monopole electrostatic energy E_{el} . Column 5 of Table 3 shows the values of E_{ex} thus obtained. In the classical van der Waals model E_{ex} can be represented by atom-atom terms $B \exp(-Cr)$, where r is a nonbonded interatomic (or intersite) distance. E_{ex} was fitted by least squares to two exponential models, E_{vdW} and E_{vdW}^* ; the former is an atom-centered model and the latter model is based on fore-shortened sites. The last two columns of Table 3 give the results of the least-squares fits.

For the atom-centered model, the C value of 2.3108 \AA^{-1} is lower than expected; for instance, a C value of 3.58 was derived from a study of crystalline argon.²³ The rms fit is poor at 0.58

(21) Williams, D. E. *Rev. Comput. Chem.* **1991**, 2, 219-271.

(22) Murthy, C. S.; O'Shea, S. F.; McDonald, I. R. *Mol. Phys.* **1983**, 50, 531-541.

(23) Williams, D. E. *Acta Crystallogr.* **1972**, A28, 84-88.

Table 3. Fitting of the Exchange Repulsion Energy of the Cl₂ Dimer

d , Å	E_{inter} , kJ mol ⁻¹	BSSE, kJ mol ⁻¹	E_{el} , kJ mol ⁻¹	E_{ex} , kJ mol ⁻¹	E_{vdW} , kJ mol ⁻¹	E_{vdW}^* , ^a kJ mol ⁻¹
Linear						
2.80	30.0247	-3.9960	11.4267	18.5980	19.0513	17.5730
3.00	17.0047	-3.1837	7.7998	9.2049	12.0007	8.7907
3.20	10.0056	-2.5394	5.4713	4.5343	7.5594	4.3974
3.40	6.1416	-2.0432	3.9303	2.2113	4.7618	2.1997
3.60	3.9380	-1.6882	2.8831	1.0549	2.9995	1.1004
Bent						
3.20	5.6974	-1.4178	-1.3882	7.0856	9.5132	7.8205
3.30	4.5946	-1.3128	-1.1232	5.7178	7.6055	5.5705
3.40	3.1243	-1.2603	-0.9184	4.0427	6.0794	3.9675
3.50	2.1364	-1.2077	-0.7589	2.8593	4.8587	2.8255
3.60	1.3915	-1.1552	-0.6339	2.0254	3.8825	2.0120
Tee						
3.00	20.1902	-1.5753	2.7470	17.4432	16.4278	17.5402
3.20	10.3183	-1.4178	1.5544	8.7639	10.5776	8.9889
3.40	5.2248	-1.2603	0.8595	4.3653	6.7944	4.5946
3.60	2.7043	-1.2077	0.4519	2.2524	4.3553	2.3432
Parallel						
3.25	30.0885	-1.1552	10.2601	19.8284	16.8214	20.5827
3.27	28.2244	-1.1552	9.4997	18.7247	16.0851	19.2336
3.29	26.4128	-1.1027	8.7968	17.6160	15.3810	17.9728
3.31	24.7587	-1.1027	8.1469	16.6118	14.7075	16.7946
3.33	23.1571	-1.0502	7.5458	15.6113	14.0635	15.6935
3.35	21.7131	-1.0502	6.9899	14.7232	13.4476	14.6646
3.45	15.7006	-0.9977	4.7743	10.9263	10.7486	10.4468
3.50	13.3377	-0.9452	3.9492	9.3885	9.6091	8.8169
3.55	11.3160	-0.8927	3.2688	8.0472	8.5900	7.4411
3.60	9.6619	-0.8927	2.7080	6.9539	7.6787	6.2797
3.65	8.2441	-0.8927	2.2465	5.9976	6.8638	5.2994
rms fit					0.58	0.05
B , kJ mol ⁻¹					12 060	653 600
C , Å ⁻¹					2.3108	3.4634

^a Bond length shortened by 0.24 Å.

kJ mol⁻¹. Comparison of energies for the linear and parallel configurations indicated that X...X repulsion is reduced at the ends of the molecule, as compared to the sides. This anisotropic effect (which may be called polar flattening²⁴) has previously been noted in crystalline dichlorine.⁸⁻¹⁶ Electron density studies show polar flattening in Cl₂ and an even larger polar flattening of Cl in the ClF molecule.²⁵

The last column of Table 3 shows results of fitting E_{ex} using repulsion sites shortened by 0.12 Å from the nuclei. This bond-foreshortening model retains the significant computational advantage of spherical atomic repulsion centers, as compared to treatments requiring an explicit angular dependence for E_{ex} . The foreshortening method for anisotropic repulsion was previously found successful for the H₂ dimer.^{26,27} The optimum foreshortening in Cl₂ was found to be 0.12 Å at each end of the molecule. The rms fit for the foreshortened model dramatically improved to 0.05 kJ mol⁻¹, and also the value $C = 3.4634$ was more reasonable, as compared to the case of argon.

Anisotropic Electron Density and Argon Repulsion Calculations

The electron density of Cl₂ was calculated in order to gain further confirmation of polar flattening. Because the Pauli exclusion principle prohibits overlap of filled electron shells,

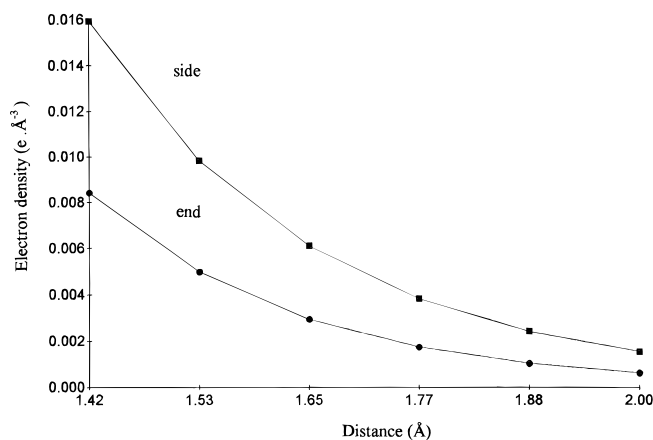


Figure 1. Electron density versus distance from the nearer Cl in Cl₂: squares, equatorial at 90° to bond axis (side); circles, polar along bond axis (end).

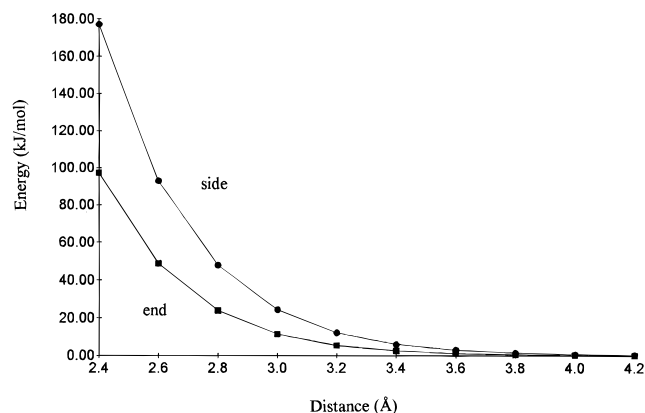


Figure 2. Ab initio exchange repulsion energy of Ar...Cl₂ versus distance of Ar to the nearer Cl in Cl₂: circles, equatorial at 90° to bond axis (side); squares, polar along bond axis (end).

intermolecular repulsion at a certain distance should increase monotonically with the electron density at that distance. The electron density was calculated using the same basis set as previously described. Figure 1 shows plots of electron density along a line from a chlorine atom extending the bond and along a second line perpendicular to the bond. The figure clearly shows that the electron density is flattened at the end of the molecule. Further, the amount of flattening is compatible with a bond foreshortening of 0.12 Å found in the previous section, and the exponential decline of the electron density in this range is $C = 3.66$.

Another way of confirming the existence of anisotropic repulsion in Cl₂ is to calculate the repulsion energy of an approaching argon atom.²⁵ Figure 2 shows the striking difference in the ab initio repulsion energy as Ar approaches Cl₂ from either the side or the end. This calculation has an advantage over the Cl₂ dimer calculation, in that no correction needs to be made for E_{el} . Table 4 lists the results of calculations for Ar...Cl₂ repulsion energy. In the table, d is the distance from Ar to the nearest Cl atom, except for the tee configuration where d is the distance from Ar to the bond center. The oblique configuration is such that the Ar...Cl line is 45° from the bond vector. Column 2 shows E_{ex} calculated from the wave function using the 6-31+G* basis set. Column 3 shows the BSSE correction, which again is not negligible. Column 4 shows values of E_{vdW}^* , which are based on foreshortened sites. The optimum foreshortening value obtained by this method (0.115 Å) is very close to that obtained from the Cl₂ dimer. Also, the C value is very close to the Cl₂ dimer value. This result further confirms the utility of the foreshortening approach and that polar

(24) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, B41, 274-279.

(25) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **1994**, 94, 1723-1765.

(26) Williams, D. E. *J. Chem. Phys.* **1965**, 43, 4424-4426.

(27) Starr, T. L.; Williams, D. E. *J. Chem. Phys.* **1977**, 66, 2054-2057.

Table 4. Fitting of the Argon...Cl₂ Repulsion Energy to a Foreshortened Model^a

<i>d</i> , Å	<i>E</i> _{ex} , kJ mol ⁻¹	BSSE, kJ mol ⁻¹	<i>E</i> _{vdw} [*] , kJ mol ⁻¹
Bent			
2.40	177.1439	-1.1857	163.2651
2.60	92.8647	-0.9756	81.5668
2.80	47.8632	-0.7919	40.7498
3.00	24.3123	-0.6343	20.3554
3.20	12.1824	-0.5030	10.1656
3.40	6.0650	-0.4243	5.0753
3.60	3.0456	-0.4243	2.5330
3.80	1.5228	-0.3980	1.2637
4.00	0.7877	-0.3980	0.6302
4.20	0.3676	-0.3455	0.3141
4.40	0.2100	-0.3455	0.1565
4.60	0.1050	-0.3193	0.0780
4.80	0.0525	-0.2668	0.0388
5.00	0.0263	-0.2405	0.0193
5.20	0.0000	-0.2142	0.0096
5.40	0.0000	-0.1880	0.0048
Tee			
2.40	155.0895	-1.2119	172.0590
2.60	82.1526	-0.9231	88.1722
2.80	42.6385	-0.7131	44.9442
3.00	21.7656	-0.5818	22.8100
3.20	11.0009	-0.5030	11.5349
3.40	5.5136	-0.4505	5.8157
3.60	2.8093	-0.4505	2.9247
3.80	1.4178	-0.4243	1.4677
4.00	0.7351	-0.4243	0.7351
4.20	0.3413	-0.3718	0.3676
4.40	0.1838	-0.3718	0.1836
4.60	0.1050	-0.3455	0.0916
4.80	0.0263	-0.2930	0.0456
5.00	0.0000	-0.2668	0.0227
5.20	0.0000	-0.2405	0.0113
5.40	0.0000	-0.2142	0.0056
Oblique			
2.8284	34.5781	-0.6606	24.5984
3.1113	13.1276	-0.4505	9.0342
3.3941	4.8835	-0.3193	3.3177
3.6770	1.8379	-0.2668	1.2183
3.9598	0.6826	-0.2405	0.4474
4.2426	0.2626	-0.2142	0.1643
4.5255	0.1050	-0.1880	0.0603
4.8083	0.0263	-0.1617	0.0221
5.0912	0.0000	-0.1355	0.0081
5.3740	0.0263	-0.1355	0.0030
5.6569	0.0000	-0.0830	0.0011
5.9397	0.0000	-0.0567	0.0004
6.2225	0.0263	-0.0567	0.0001
6.5054	-0.0263	-0.0042	0.0001
6.7882	0.0000	-0.0042	0.0000
7.0711	0.0000	-0.0042	0.0000
Linear			
2.40	97.1180	-1.7108	99.6442
2.60	48.7034	-1.3432	49.0521
2.80	23.8135	-1.0282	24.1470
3.00	11.3948	-0.8181	11.8869
3.20	5.3561	-0.6606	5.8516
3.40	2.4942	-0.5556	2.8806
3.60	1.1290	-0.5030	1.4180
3.80	0.5251	-0.4768	0.6981
4.00	0.2363	-0.4505	0.3436
4.20	0.1313	-0.4505	0.1692
4.40	0.0788	-0.4243	0.0833
4.60	0.0000	-0.3455	0.0410
4.80	0.0000	-0.3193	0.0202
5.00	0.0000	-0.2930	0.0099
5.20	0.0000	-0.2668	0.0049
5.40	0.0000	-0.2142	0.0024

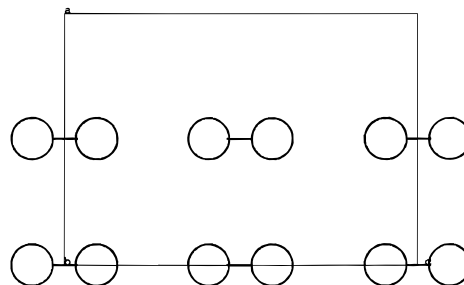
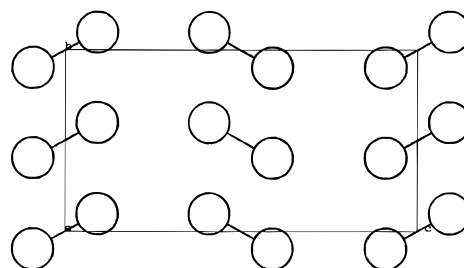
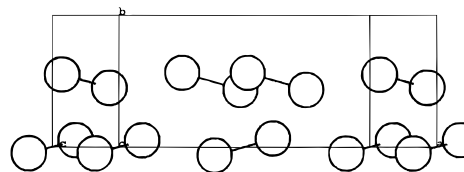
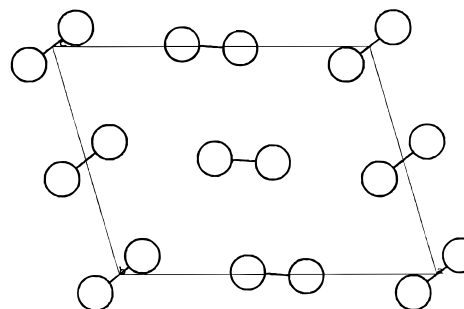
^a rms fit = 0.327; *B* = 783 100, kJ mol⁻¹; *C* = 3.5436 Å⁻¹. Repulsion site is foreshortened by 0.115 Å.

Table 5. Comparison of Anisotropic¹² and Isotropic Intermolecular Force Field Models for Crystalline Cl₂

param	force field model		obsd at 22 K ³¹
	anisotropic	isotropic	
<i>a</i> , Å	6.020	6.038	6.145
<i>b</i> , Å	4.526	4.365	4.395
<i>c</i> , Å	8.021	8.467	8.154
<i>θ</i> , deg	56	61	57

Table 6. Van der Waals and Electrostatic Energies (kJ mol⁻¹) in Alternative Space Groups

space group	van der Waals	electrostatic
<i>Cmca</i>	-25.24	-5.13
<i>Pa3</i>	-22.00	-1.04
<i>R3m</i>	-22.94	-1.94
<i>C2/c</i>	-23.87	-3.98
<i>P6m2</i>	-22.91	-1.92

**Figure 3.** Two views of the relaxed observed crystal structure obtained with the present force field.**Figure 4.** Two views of an unobserved monoclinic crystal structure predicted with the present force field.

flattening exists in Cl₂. Peebles, Fowler, and Legon¹⁴ recently performed SCF calculations for the He...Cl₂ system. They concluded that the chlorine atom in Cl₂ is flattened by about 0.32 Å for a head-on approach. This larger estimate for polar flattening does not agree well with our results for the Ar...Cl₂ and Cl₂...Cl₂ systems.

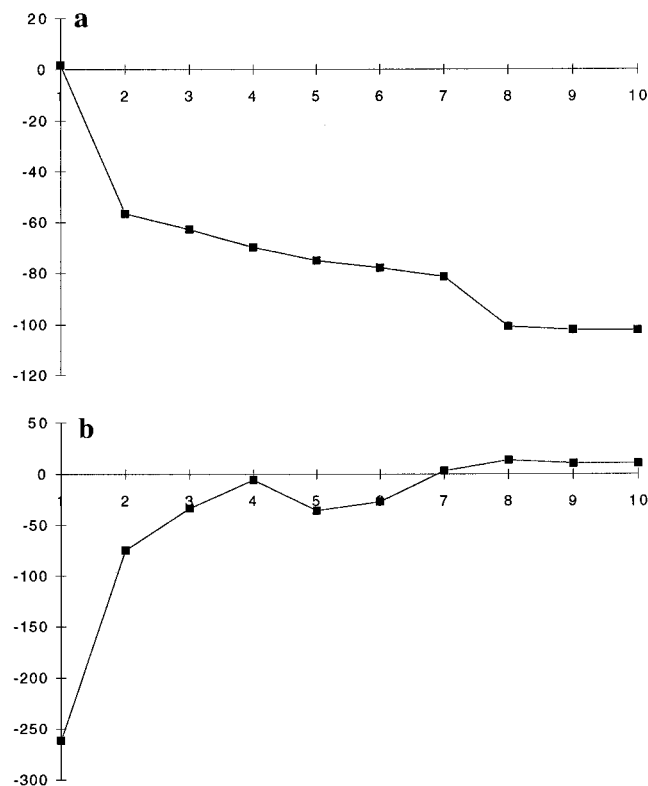


Figure 5. Ab initio crystal structure prediction of the monoclinic structure: (a) lattice energy versus nonbonded contact table number; (b) most negative eigenvalue of the Hessian; (c) cell edges; (d) cell angles.

Table 7. Atomic Coordinates (in Fractions of the Cell Edge) for the Monoclinic Structure

atom	<i>x</i>	<i>y</i>	<i>z</i>
Cl1	0.090 51	0.049 94	0.081 60
Cl2	0.590 58	0.435 38	-0.008 46

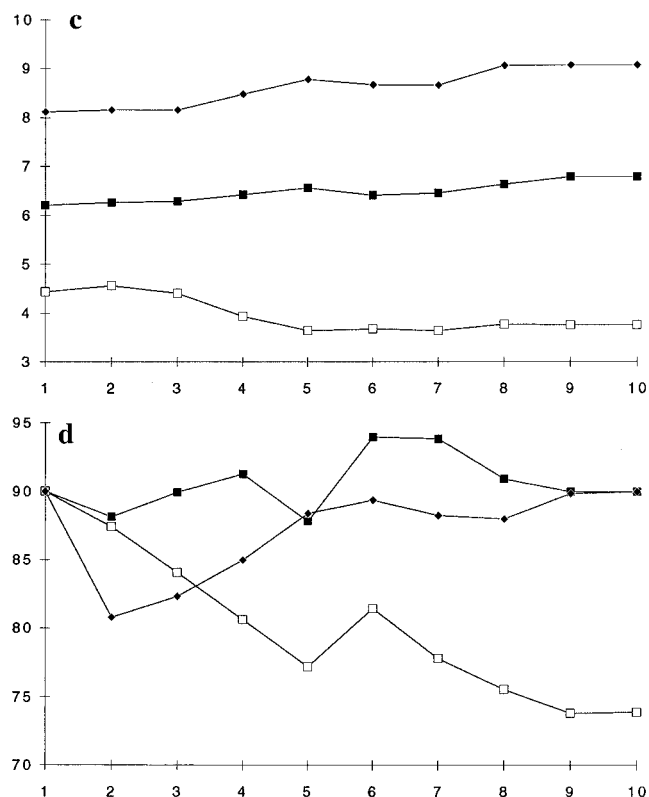
Crystal Structure of Chlorine

The ab initio QM calculations have provided an atom–atom repulsion function for chlorine, based on sites with a foreshortening of 0.12 Å. In addition, the five-site distributed monopole model gave a good representation of the MEP of Cl₂. The combination of the MEP model with foreshortened repulsion sites yields a seven-site model. To extend this model to the crystal, the coefficient of the r^{-6} dispersion attraction is necessary. This dispersion parameter, with the sites chosen to be the same as the repulsion centers, was obtained by obtaining a best fit to the observed crystal structure using lattice energy summation. The crystal lattice energy and the energy-minimized predicted crystal structure were calculated with the molecular packing analysis program mpa.²⁸

The final nonbonded potential function is of the (exp-6-1) type, and the lattice energy is its pairwise sum between atoms (or sites) in different molecules:

$$E = \sum_j^{\text{one molecule}} \sum_k^{\text{lattice}} -Ar_{jk}^{-6} + B \exp(-Cr_{jk}) + q_j q_k r_{jk}^{-1}$$

where the van der Waals sites are foreshortened by 0.12 Å and the monopole sites are located as described above. Accelerated convergence²⁹ was used to ensure the accuracy of the dispersion



and Coulombic energy sums. The parameters of q_i , B , and C were transferred from ab initio calculations as given above. The dispersion parameter, A , was obtained by fitting to the observed lattice constants while the molecular tilt angle was held fixed. The best fitted value for A was found to be 6800 kJ Å⁶ mol⁻¹.

The resulting potential model was tested by minimization of the intermolecular energy with respect to symmetry-allowed parameters of the observed space group. This space group is *Cmca* with four molecules per cell; the molecules lie on mirror planes in the x direction (site symmetry (f) in ref 30) with the molecular tilt angle measured from the y axis.

Table 5 compares crystal structure parameters predicted from the anisotropic intermolecular force field of ref 12 and the present isotropic force field; the anisotropic force field of ref 16 is claimed to reproduce the static crystal structure exactly. Both force fields predict a structure very close to the observed structure, which is shown in Figure 3. For the isotropic force field, the short contact in the crystal is 3.32 Å compared to the observed distance of 3.27 Å. The anisotropic model yields a slightly better tilt angle, but the isotropic model yields a slightly better fit to the unit cell. The lattice energy of the isotropic model is -25.24 kJ/mol, and the electrostatic part of the total energy is -5.13 kJ/mol.

To study the effect of the MEP on the molecular tilt angle, we set all of the monopole charges to zero and minimized the crystal energy in *Cmca*. The tilt angle increased to 90° and poor agreement was obtained for the lattice constants. The predicted lattice constants for the zero MEP structure are $a = 6.357$ Å, $b = 3.808$ Å, and $c = 9.704$ Å. Thus we can conclude that it is essential to include electrostatic effects in modeling the Cl₂ crystal structure. It is expected that a molecular-centered

(28) Williams, D. E. *Program mpa, Molecular Packing Analysis*; Department of Chemistry, University of Louisville: Louisville, KY 40292, 1996. Email: dew01@xray5.chem.louisville.edu.

(29) Williams, D. E. *Acta Crystallogr.* **1971**, A27, 452–455.

(30) Hahn, T., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. A.

(31) Powell, B. M.; Heal, K. M.; Torrie, B. H. *Mol. Phys.* **1984**, 53, 929–939.

quadrupole will not give good results for the tilt angle, since a molecular quadrupole does not give an accurate representation of the QM-MEP.

Comparison with Crystal Structures of Other Homonuclear Diatomic Molecules

Homonuclear diatomic molecules have been observed to crystallize in space groups¹ $Cmca$, $Pa3$, $R\bar{3}m$, and $C2/c$. A hypothetical hexagonal space group, $P\bar{6}m2$, has also been found to give lower lattice energy when the force field omits intermolecular electrostatic energy. A minimum requirement for successful prediction of the chlorine crystal structure is that structures in these alternative space groups have higher energies. We evaluated the lattice energy of Cl_2 in each of these space groups, after relaxing all symmetry-allowed degrees of freedom. The results are shown in Table 6.

The $Cmca$ structure has the lowest lattice energy; note that $Cmca$ is especially favored by the electrostatic interaction. These calculations suggest that Cl_2 crystallizes in $Cmca$ instead of one of the other space groups commonly observed in diatomics because of the difference in the MEP's of the molecules. The MEP of Cl_2 allows a larger electrostatic interaction in $Cmca$ than in the other space groups. In addition, the MEP has a major effect in determining the tilt angle of the molecule in the crystal. Note again that a molecular quadrupole does not accurately represent the MEP of Cl_2 . We found that the anisotropic shape of the Cl atom in Cl_2 has only a minor effect in determining the tilt angle. The polar flattening of the atoms in Cl_2 , however, is the main reason that the very short $Cl\cdots Cl$ nonbonded contacts occur in the crystal.

Ab Initio Crystal Structure Prediction

This section describes calculations to predict crystal structures of Cl_2 given the molecular structure and an intermolecular force field. Certainly the molecular structure of Cl_2 is well established, but the force field is still under development. One way to test the validity of the force field is to relax all symmetry requirements for the crystal lattice energy minimization.³² In this calculation, four molecules are placed in a cell of triclinic symmetry. All six lattice constants are allowed to vary, and the molecules are allowed to freely rotate and translate in the cell. One molecule is translationally fixed to set the origin. Since it is possible that the starting $Cmca$ structure corresponds to a saddle point on the energy hypersurface, we applied random changes to all of the structural parameters. This agitation process simulates the effect of thermal motion in the crystal and causes the structure to move off any saddle points of the energy hypersurface. Then the energy of the desymmetrized and randomized structure is minimized with four independent molecules in a cell with no assumed symmetry.

The anticipated result of this process is the location of numerous local energy minima, one of which is the global minimum corresponding to the observed structure.^{33–35} Indeed, we found numerous local minima, but none corresponded to the observed structure. Nearly all of these minima were higher in energy than the observed structure; however, the lowest energy minimum found was a structure of monoclinic symmetry with slightly lower energy (-25.51 kJ/mol) than that of the observed structure (-25.24 kJ/mol). The predicted lattice constants are $a = 9.072$ Å, $b = 3.761$ Å, $c = 6.790$ Å, and $\beta = 106.12^\circ$. The

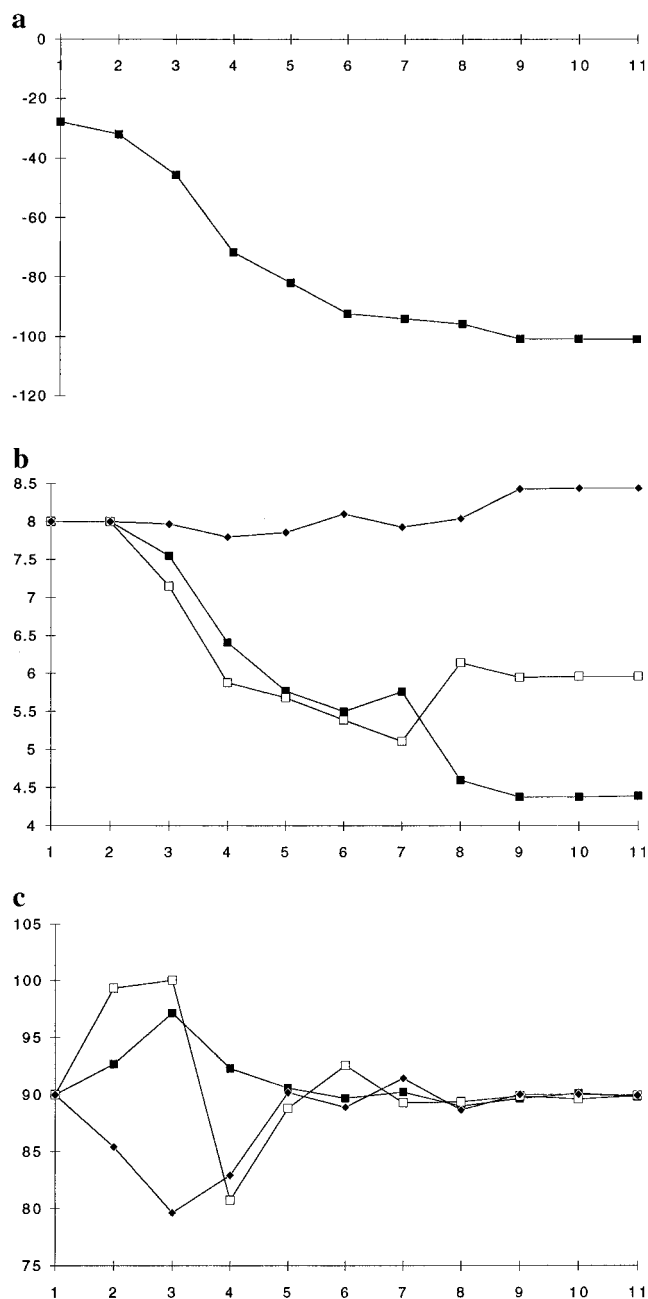


Figure 6. Prediction of the observed structure starting from a trial model with molecular axes parallel: (a) lattice energy; (b) cell edges; (c) cell angles.

electrostatic energy is -4.95 kJ/mol, not very different from that of the orthorhombic structure. Examination of the symmetry of this structure shows that the space group is $P2_1/c$ with two Cl_2 molecules placed on different inversion centers. Figure 4 shows that the tilt angle of the molecules is not very different from that of the observed structure. However, the edge view shows that the molecules do not lie in a plane, which is quite different from the observed structure. Since there are two crystallographically distinct molecules in the cell, there are two close contact distances: 3.51 and 3.57 Å, both considerably longer than the short distance in the relaxed orthorhombic structure, 3.32 Å. The unit cell volume of the monoclinic structure (222.53 Å³) is smaller than that of the orthorhombic structure (223.15 Å³). We are not aware of any observed crystal of a diatomic molecule with this type of monoclinic structure; Table 7 gives the atomic coordinates.

Figure 5 gives details about the calculation leading to the monoclinic structure. Because of the initial random rotation

(32) Gibson, K. D.; Scheraga, H. A. *J. Phys. Chem.* **1995**, *99*, 3752–3764, 3765–3773.

(33) Gdanitz, R. *J. Chem. Phys. Lett.* **1992**, *190*, 391–396.

(34) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309–314.

(35) Williams, D. E. *Acta Crystallogr.* **1996**, *A52*, 326–328.

of the molecules, the initial lattice energy is large, +1.58 kJ/mol. The lattice energy quickly drops (Figure 5a) using off-ridge eigenvector minimization³⁶ (OREM). OREM is used by the mpa program whenever the Hessian (second derivative matrix of the energy hypersurface) is not positive definite. Figure 5b shows that the Hessian was not positive definite for the first six contact tables. A contact table is a list of site-site intermolecular distances up to a maximum summation limit. After positive definiteness was achieved with contact table 7, the lattice energy smoothly converged to the minimum using the Newton-Raphson method. Parts c and d of Figure 5 show the changes in the cell edges and angles during the energy minimization. Notice that in the intermediate stages the cell angles are triclinic but at table 9 two of the angles "snap" to nearly 90°, reminiscent of a phase transition involving the long-range symmetry of the crystal. We have previously noticed similar sudden transitions to higher symmetry in ab initio crystal structure predictions of benzene and urea.³⁵

One possibility is that the monoclinic structure is a new polymorph of crystalline chlorine so far not observed. More likely, we suspect that the prediction of the monoclinic structure results from a flaw in the intermolecular force field. Chalasinski and Szczesniak²⁵ point out that accurate QM calculations indicate the existence of small indentations at the ends of the Cl₂ molecule; the Cl-F molecule has an even larger indentation at the chlorine end. While bond foreshortening can model polar flattening, it cannot model polar indentation. Further work is needed to verify the possible existence of polar indentation of Cl₂ molecules in the crystal and to incorporate the findings into an improved intermolecular force field. In addition, no explicit thermal information is included in the present intermolecular force field. The necessity for making incremental improvements to obtain more accurate force fields is well-known in molecular mechanics, where a popular force field, MM3, is now in its fourth major revision, MM4.³⁷

Can the observed *Cmca* structure be predicted by molecular packing analysis with this force field starting from an unreasonable trial structure? As described above, we attempted to obtain the observed structure starting from an $8 \times 8 \times 8 \text{ \AA}^3$ cubic cell containing four Cl₂ molecules in random Lattman angle^{38,39} orientations at the face centers. All cell constants were allowed to vary, and each molecule was allowed to rotate and translate,

except that one molecule was translationally fixed to set the origin. This approach successfully predicted the observed crystal structures⁴⁰ of N₂ and CO₂, as well as benzene and urea.³⁵ (In the case of urea there are two molecules in the cell and a body-centered trial model was used.)

However, more than 30 such trials did not predict the observed crystal structure of Cl₂, although the lower energy monoclinic structure was predicted. Since the observed structure is indeed a local energy minimum with this force field, eventually it would be located by starting with randomized trial structures. We found, by trial and error, that by starting with all four molecules parallel in this large cubic cell (obviously not a randomized structure), we could predict the observed structure. Figure 6 shows the course of this calculation. The energy dropped rapidly, and the cell edges quickly changed from their initial values. Figure 6c shows that while the cell angles initially became triclinic, by table 9 they nearly converged to 90°; the cell edges had also nearly converged to the observed values of the orthorhombic structure.

Conclusion

Electrostatic intermolecular interaction is very important in determining the space group and molecular tilt angle in crystalline chlorine. The MEP of Cl₂ is not well represented by a molecular quadrupole but is well represented by a five-site monopole model. Ab initio QM calculations confirm that the Cl₂ molecule shows polar flattening, which can be approximated by a foreshortened site model. Polar flattening is mainly responsible for the existence of very short Cl...Cl nonbonded distances in the crystal. Crystal structure energy minimization studies show that the observed *Cmca* space group is favored mainly because of the Cl₂ electric potential, compared to other space groups observed for homonuclear diatomic molecules. A lower energy monoclinic crystal structure is predicted, which may indicate that further refinements are needed in the intermolecular force field.

Note Added in Proof. Some of the entries in Tables 3 and 4 show loss of accuracy because of truncation of Gaussian-92 results before obtaining the difference energies. The use of additional significant digits solved this problem. The reoptimized force field parameters are $A = 7000$, $B = 1\ 053\ 533$, and $C = 3.60$ with a foreshortening 0.15. The results obtained using this parametrization as a model for the crystal structure of dichlorine are very similar to those quoted above, and none of the conclusions are affected.

IC960592F

(36) Williams, D. E. *Chem. Phys. Lett.* **1992**, *192*, 538–543.

(37) Allinger, N. L.; Chen, K.; Lii, J. H. *J. Comput. Chem.* **1996**, *17*, 642–668.

(38) Lattman, E. A. *Acta Crystallogr.* **1972**, *B28*, 1065–1068.

(39) Williams, D. E. *Acta Crystallogr.* **1973**, *A29*, 408–414.

(40) Williams, D. E. Unpublished research, 1996.