J. Phys. Chem. A **1999,** *103,* 7709−7714 **7709**

Conformational Composition of Gaseous *trans*-1,4-Dichlorocyclohexane. Molecular Structures and Energy Differences of the aa and ee Components from Gas-Phase Electron Diffraction and ab Initio Calculations

Alan D. Richardson,[†] Kenneth Hedberg,*[,†] and Kenneth B. Wiberg*[,‡]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003, and Department of Chemistry, Yale University, New Haven, Connecticut 06520−81

Received: May 4, 1999; In Final Form: July 26, 1999

Electron-diffraction patterns from gaseous *trans*-1,4-dichlorocyclohexane at a temperature of 105 °C have been analyzed with the help of results from ab initio molecular orbital calculations to yield the structures of the ee and aa forms (equatorially and axially disposed chlorine atoms, respectively) of the molecule and the composition of the mixture. The model of this complicated system was defined in terms of the structure of the ee form, tying many of the parameters of the aa form to those of the ee by parameter differences calculated ab initio. Some of the results (r_g/Å, $\angle_e$/deg; 2σ uncertainties) for the ee (aa) forms from the preferred model are $\langle r(\mathrm{C{-}H})\rangle = 1.115(4)$ (1.113); $r(\mathrm{C_1{-}C_2}) = 1.525(6)$ (1.525); $r(\mathrm{C_2{-}C_3}) = 1.542(13)$ (1.535); $r(\mathrm{C{-}Cl}) = 1.799(3)$ (1.812); $r(\mathrm{Cl\cdots Cl}) = 6.309(11)$ (5.236); $\angle(\mathrm{C_2C_1C_6}) = 109.9(14)$ (110.1); $\angle(\mathrm{CCCl}) = 109.7(4)$ (109.8); flap (the angle between the planes $C_2C_1C_6$ and $C_2C_3C_5C_6$) = 51.7(19) (47.2(12)). The mole fraction of the ee form was determined to be 0.46(6). The structural predictions of ab initio calculations were tested by optimizations at several levels, among them HF/6-31G*, MP2/6-311G*, QCISD/6-311+G(2df,p), MPw1PW91/6-311G*, B3P86/6-311G*, and B3P86/6-311+G(2df,p). Parameter values from each of these calculations are in good agreement with experiment, but those from the HF/6-31G* are poorest. The experimental composition is most accurately predicted by the MP2/6-311G* and QCISD/6-311+G(2df,p) calculations from the conformational energy differences $\Delta E_{\mathrm{theor}}$ corrected for zero-point energy and entropy differences. The composition of the system is discussed in relation to that of monochlorocyclohexane.

Introduction

The aa and ee forms of *trans*-1,4-dichlorocyclohexane (T14D, Figure 1) readily interconvert by what may be viewed as internal rotations of the six-member ring. Inasmuch as the spatial arrangement of the chlorine atoms in the two forms is quite different, the relative stabilities of the two components becomes an interesting question. An apparent answer to this question was provided over 40 years ago by Atkinson and Hassel[1] (hereafter AH) who, by analyzing gaseous electron-diffraction (GED) patterns, found essentially a 1:1 mixture of the aa and ee forms and were able to provide values for the important structural parameters of the molecules. AH's result for the mixture composition is especially interesting for the following reason. In monochlorocyclohexane the equatorial conformer is favored over the axial ($\Delta G° = 0.6$ kcal/mol)[2], and if the energy difference were additive,[3] the ee form of *trans*-1,4-dichlorocyclohexane would be preferred by 1.2 kcal/mol. However, the gas-phase energy difference ($\Delta G°$) between the *trans*-1,4-dichlorocyclohexane conformers has been estimated from solution phase NMR measurements in a variety of solvents to be 0.8 kcal/mol with the aa form the more stable.[4] Thus, both the GED and NMR results lead to the conclusion that there must be some special interaction of the C−Cl bonds that reduces the energy difference of the conformers, although the magnitude of the interaction is quite different from the two studies.

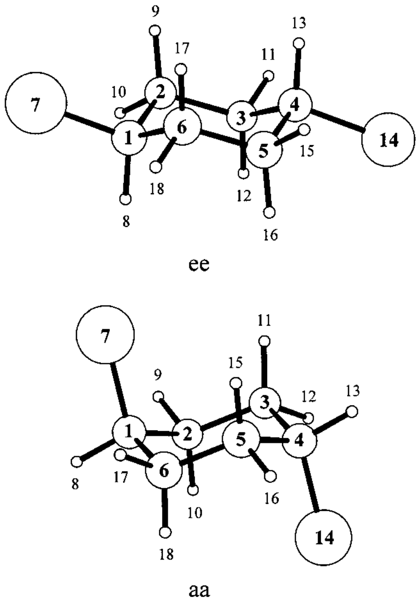

Figure 1. Diagrams of the two forms of *trans*-1,4-dichlorocyclohexane.

In the course of other work, we had recent occasion to investigate the T14D system by ab initio methods. At lower levels of theory the results suggested that the composition could be quite different from that found in the GED experiments. Since the electron-diffraction method used by AH was primitive compared to that practiced today, the theoretical as well as the NMR results raised the possibility of error on the experimental side. We were thus motivated to repeat the diffraction experiments in order to resolve the question. Somewhat to our surprise, our diffraction results were in excellent agreement with the older

---

* Corresponding authors.

[†] Oregon State University.

[‡] Yale University.

10.1021/jp9914572 CCC: $18.00

TABLE 1: Equilibrium Parameter Values for *trans*-1,4-Dichlorocyclohexane Estimated from Experiment and from ab Initio Calculations

parameters	expt[a,b]	RHF 6-31G*	MP2 6-311G*	MPw1PW91 6-311G*	B3P86 6-311G*	B3P86 6-311+G(2df,p)
ee form						
C_1-H_8	1.096	1.081	1.095	1.092	1.093	1.092
C_2-H_9		1.086	1.097	1.095	1.096	1.095
C_2-H_{10}		1.084	1.094	1.092	1.093	1.092
C_1-C_2	1.516	1.524	1.521	1.518	1.518	1.516
C_2-C_3	1.522	1.535	1.533	1.531	1.531	1.529
C−Cl	1.789	1.807	1.796	1.809	1.812	1.804
∠(HCH)	104.6	107.1	107.1	106.8	106.8	106.9
$\angle(C_2C_1H_8)$	109.5	110.0	109.9	110.1	110.2	110.1
$\angle(C_1C_2H_9)$	108.6	109.1	108.7	108.9	108.9	108.8
$\angle C_1C_2H_{10}$	110.6	110.1	110.1	110.2	110.3	110.2
$\angle C_3C_2H_9$	111.1	110.1	110.3	110.2	110.2	110.2
$\angle C_3C_2H_{10}$	110.9	109.9	110.3	110.1	110.1	110.2
$\angle C_2C_1C_6$	109.9	111.7	111.5	111.8	111.8	111.8
∠CCCl	109.7	110.1	109.9	110.0	110.0	110.0
flap	51.7	51.5	51.7	51.3	51.3	51.3
aa form						
C_1-H_8	1.096	1.079	1.093	1.089	1.090	1.089
C_2-H_9		1.083	1.094	1.092	1.092	1.091
C_2-H_{10}		1.086	1.096	1.096	1.096	1.096
C_1-C_2	1.522	1.527	1.524	1.520	1.520	1.518
C_2-C_3	1.530	1.530	1.528	1.524	1.525	1.522
C−Cl	1.802	1.822	1.807	1.825	1.830	1.822
∠HCH	104.7	107.1	107.2	106.8	106.8	107.1
$\angle C_2C_1H_8$	109.7	110.2	110.2	110.5	110.6	110.5
$\angle C_1C_2H_9$	110.3	110.0	109.8	110.1	110.1	110.1
$\angle C_1C_2H_{10}$	106.9	107.0	107.5	107.2	107.1	107.1
$\angle C_3C_2H_9$	112.9	110.0	110.2	110.4	110.4	110.4
$\angle C_3C_2H_{10}$	110.6	109.6	109.7	109.5	109.5	109.4
$\angle C_2C_1C_6$	110.1	111.9	112.0	112.1	112.2	112.0
∠CCCl	109.8	110.3	109.7	109.9	109.9	109.9
flap	47.2	46.0	47.3	46.3	46.3	46.6

[a] Distances are rough estimates calculated from $r_e = r_g - (3/2)al^2$ with the Morse anharmonicity constant a equal to 2.0. [b] Angle values are $\angle_\alpha$.

ones and led us to a more thorough study of the system from the theoretical side. In broad terms, the higher-level theoretical calculations tended to predict compositions significantly different from lower level ones and in much better agreement with the experiment. An account of the experimental and theoretical work follows.

Theoretical Calculations

Ab initio molecular orbital predictions of the structures and energies of the two forms of T14D were carried out at Yale University with the program Gaussian94[5] at several levels of theory with different basis sets. The results of several of these are summarized in Table 1.

Cartesian force constants from the HF/6-31G* ab initio optimizations were symmetrized with use of the program ASYM40 in a version that incorporates this option.[6] Vibrational amplitudes were then calculated together with quantities that relate the various distance types (r_α, r_g, and r_a). Some of these results were intended for use as constraints in the GED analysis described below. Although the ab initio results from one of the higher level calculations could have been used instead of those from HF/6-31G* to help estimate these quantities, these results were not available until the GED analysis was well along. In any case, the type of the intended constraints—*differences* between parameter values and amplitude values—is not very sensitive to calculational level and basis set size, as may be seen from Table 1.

Experimental Section

T14D was obtained from TCI America (99+%) and used as received. The diffraction experiments were made with the Oregon State apparatus using a nozzle-tip temperature of 105 °C. Four diffraction photographs were taken at the long camera distance (LC) and two at the middle camera distance (MC), nominally 746 and 300 mm, respectively. All the photographs except one were recorded on Kodak electron image plates. The unique long camera picture was recorded on Kodak electron image film. Plates and film were developed for 10 min in Kodak D-19 developer diluted 1:1. Each of the photographs was traced at least three times using a modified Joyce-Lobel microdensitometer. The data ranges were $2.00 \leq s/Å \geq 16.25$ (LC) and $8.00 \leq s/Å \geq 39.00$ (MC), and the data interval was $\Delta s = 0.25$ Å. Other experimental conditions included an r^3 sector opening; a nominal accelerating voltage of 60 kV; beam currents, 0.45−0.76 μA; ambient apparatus pressure during sample run-in $(4.0-8.1) \times 10^{-6}$ Torr; exposure times, 0.75−4.5 min; electron wavelength, 0.04893 Å; wavelength calibration standard, CO_2 (r_a(C−O) = 1.1646 Å, r_a(O···O) = 2.3244 Å).

Curves of total scattered intensity (s^4I_t) are shown in Figure 2. Radial distribution curves shown in Figure 3 were calculated from variable coefficient molecular intensity curves ($sI_M(s)$) after multiplication by the factor $(Z_C/A_C)^2 \exp(-0.002s^2)$ and addition of a theoretical inner peak in the unobserved region $s < 2.00$ Å. Improved procedures[7] for obtaining these curves were used; the principles are similar to those previously described.[8,9] The electron-scattering factors and phases used in various calculations were obtained from tables.[10] The intensity data are available as Supporting Information.

Electron-Diffraction Analysis

Model Specification. The two forms of T14D have similar values for many of the parameters and cannot be independently

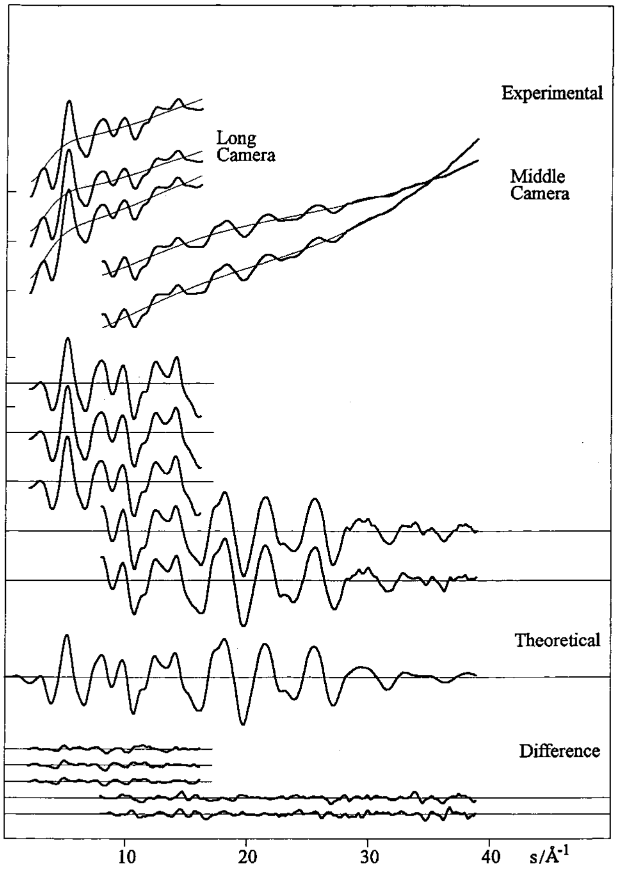

Figure 2. Intensity curves. The five topmost curves are the averages of repeated traces of each plate and are in the form $s^4I_t(s)$. The next set has the backgrounds removed. The theoretical curve is for model A and the differences are experimental minus theoretical.

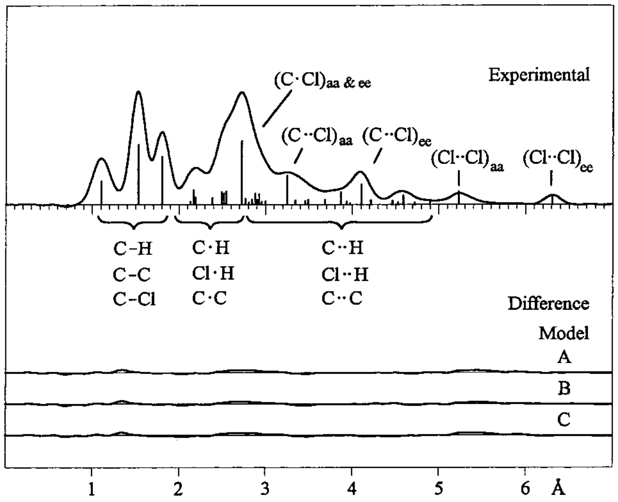

Figure 3. Radial distribution curves. The experimental curve was calculated from an average of the experimental intensities with data for the unobserved low-angle region calculated from model A; the multiplicative convergence factor was $\exp(-0.0020s^2)$. The interatomic distances are indicated by the vertical bars whose lengths are proportional to the weights of the terms. The difference curves are experimental minus theoretical.

measured by GED. For example, each of the forms has two nonequivalent carbon−carbon bond distances which are expected to differ by only 0.01−0.02 Å, and the averages of these values are expected to be only slightly different in the two forms. Similar small differences exist for other bonds, for bond angles, and for vibrational amplitudes. As mentioned in the Theoretical Calculations section, we have used results from the molecular orbital calculations as constraints on a number of these parameters in order to obtain experimental values for the others. For convenience we chose to define a model in r_α space for the entire system in terms of the structure of the ee form, tying the structure of the aa form to it through constraints drawn from theory. The model has the following parameters, all but the last two referring only to the ee form: (1) $\langle r(\mathrm{C-H})\rangle = [2r(\mathrm{C_1-H_8}) + 4r(\mathrm{C_2-H_9}) + 4r(\mathrm{C_2-H_{10}})]/10$; (2) $\langle r(\mathrm{C-C})\rangle = [4r(\mathrm{C_1-C_2}) + 2r(\mathrm{C_2-C_3})]/6$; (3) $\Delta r(\mathrm{C-C}) = r(\mathrm{C_1-C_2}) - r(\mathrm{C_2-C_3})$; (4) $r(\mathrm{C-Cl})$; (5) $\angle(\mathrm{C_2C_1C_6})$; 6) $\angle(\mathrm{CCCl})$; (7) $\angle(\mathrm{C_2C_1H_8})$; (8) $\angle(\mathrm{C_3C_2H_9})$; (9) $\angle(\mathrm{C_3C_2H_{10}})$; (10) $\theta(\mathrm{H_9})$ (the angle between the vector $r(\mathrm{C-H_9})\sin\angle(\mathrm{C_3C_2H_9})$ and the plane $\mathrm{C_2C_3C_5C_6}$); (11) $\theta(\mathrm{H_{10}})$ (similarly defined); (12) flap(ee) = $\angle_{\mathrm{dihed}}(\mathrm{C_2C_1C_6,C_2C_3C_5C_6})$; (13) flap(aa); and (14) χ_{ee} (the mole fraction of the ee form; mole fractions are simply scale factors that vary the relative contributions of the two forms). The values of these parameters were tied to those of the aa form by the differences, p(ee) − p(aa), as follows: (1) 0.0005, (2) 0.0004, (3) −0.0074, (4) −0.0148, (5) −0.195, (6) −0.175, (7) −0.187, (8) −1.85, (9) 0.346, (10) 117.8, (11) 116.7. There are also 62 root-mean-square amplitudes of vibration to be considered which of course cannot be refined independently. These were formed into the groups seen in Table 3, keeping frozen the differences between group members taken from the results of our normal coordinate calculations.

Structure Refinements. The refinements were carried out by the least-squares method[11] by fitting theoretical intensity curves in the form $sI_m(s)$ simultaneously to the five experimental curves seen in Figure 2. In preliminary refinements it was found that the parameters $\angle(\mathrm{C_3C_2H_9})$ and $\angle(\mathrm{C_3C_2H_{10}})$ did not obtain reliable values which required the introduction of additional geometrical constraints. We chose the method of "predicate values" suggested by Bartell[12] for these constraints. In this method the recalcitrant parameter is linked to a chosen value, the predicate, by a flexible tether which allows it to adjust during the refinement in accordance with a weight assigned to the predicate, in effect the force constant of the tether. The predicate values of $\angle(\mathrm{C_3C_2H_9})$ and $\angle(\mathrm{C_3C_2H_{10}})$ were chosen to be close to the theoretical values from the HF/6-31G* calculation. Refinements of the T14D structure under these constraints yielded parameter values which were in generally good agreement with higher-level theoretical predictions with the exception of $\angle(\mathrm{C_2C_1C_6})$: the refined value of this angle was invariably about 3° smaller than predicted. Since this is a larger difference than is usually found in the case of simple organic molecules, it seemed important to explore the significance of the difference. This was done by imposing a predicate value on $\angle(\mathrm{C_2C_1C_6})$ as well and testing the effect with different weights. Our final refinements were based on models incorporating both the geometrical constraints described in the Model Specification subsection and constraints in the form of predicate values on the three angles just described.

Results and Discussion

Results for three of the many models characterized by different predicate assignments and weights are shown in Table 2. These models were chosen because, although they differ in the value of the important parameter $\angle(\mathrm{C_2C_1C_6})$, they give essentially equally good fits to the GED data as judged by the quality-of-fit factor R (see footnote e, Table 2). The choice of a "best model" for T14D thus depends on how much credence is given to the accuracy of the predicate values drawn from theory. In model B $\angle(\mathrm{C_2C_1C_6})$ is allowed to refine without

TABLE 2: Refined Distance (r_g/Å) and Bond-Angle ($\angle_\alpha$/deg) Values for *trans*-1,4-Dichlorocylohexane[a]

		preferred model A		model B		model C	
		ee	aa[b]	ee	aa[b]	ee	aa[b]
		Structure-Defining Parameters					
1.	$\langle r(C-H)\rangle$	1.115(4)	1.113	1.115(4)	1.113	1.115(4)	1.113
2.	$\langle r(C-C)\rangle$	1.531(2)	1.530	1.531(2)	1.530	1.530(2)	1.529
3.	$\Delta\langle r(C-C)\rangle$	−0.017(19)	−0.008	−0.013(21)	−0.005	−0.021(18)	−0.013
4.	$r(C-Cl)$	1.799(3)	1.812	1.799(3)	1.811	1.799(3)	1.812
5.	$\angle C_2C_1C_6$	109.9(14)	110.1	108.8(9)	109.0	110.9(11)	111.1
6.	$\angle CCCl$	109.7(4)	109.8	109.5(4)	109.7	109.8(3)	110.0
7.	$\angle C_2C_1H_8$	109.5(32)	109.7	111.0(31)	111.2	109.2(29)	109.4
8.	$\angle C_3C_2H_9$	111.1(33)	112.9	110.8(32)	112.7	110.4(14)	112.2
9.	$\angle C_3C_2H_{10}$	110.9(33)	110.6	110.6(32)	110.2	110.1(14)	109.7
10.	$\angle\theta(H_9)$	92.0(73)	151.6	91.9(66)	150.3	90.8(71)	152.6
11.	$\angle\theta(H_{10})$	207.9(59)	267.4	209.2(49)	267.5	206.9(60)	268.6
12.	flap(ee)	−51.7(19)		−51.9(20)		−51.7(20)	
13.	flap(aa)		47.2(12)		46.9(11)		47.6(11)
14.	χ^c	0.46(6)	0.54	0.47(6)	0.53	0.48(6)	0.52
		Calculated Parameters					
15.	$\angle C_1C_2C_3$	110.9(10)	112.9	111.0(11)	113.4	110.6(9)	112.4

	predicates[d]	value	rel wt	value	rel wt	value	rel wt
5.	$\angle C_2C_1C_6$	111.5	1			111.5	6
7.	$\angle C_3C_2H_9$	110.1	1	110.1	1	110.1	6
9.	$\angle C_3C_2H_{10}$	109.9	1	109.9	1	109.9	6
	R^e	0.102		0.102		0.103	

[a] Uncertainties are 2σ and contain estimates of correlation and systematic error. [b] Except for flap(aa), values are tied to those of the ee form via differences calculated ab initio (HF/6-31G*). Unlisted uncertainties as for ee form. [c] Mole fraction. [d] Predicated constraints; see text for description. [e] Goodness of fit factor: $R = [\sum_i w_i\Delta_i^2/\sum_i w_i(s_iI_{m,i}(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_iI_{m,i}(\text{obsd}) - s_iI_{m,i}(\text{calc})$.

TABLE 3: Values of Distances (r/Å) and Root-Mean-Square Amplitudes of Vibration (l/Å) for Model A of *trans*-1,4-Dichlorocyclohexane

conformer term	ee					aa[a]			
	r_α	r_g	r_a	l		r_α	r_g	r_a	l^b
$\langle C-H\rangle$	1.097	1.115(4)	1.109	0.079	(5)	1.096	1.113(4)	1.107	0.079
C_1-C_2	1.520	1.525(6)	1.523	0.056	(3)	1.522	1.527(6)	1.525	0.056
C_2-C_3	1.535	1.542(13)	1.540	0.056		1.529	1.535(13)	1.533	0.056
$C-Cl$	1.787	1.799(3)	1.797	0.057	(3)	1.802	1.812(3)	1.810	0.059
$C_1\cdot H_9$	2.139	2.153(74)	2.147	0.116	(12)	2.163	2.176(62)	2.170	0.115
$C_2\cdot H_8$	2.151	2.164(41)	2.158	0.115		2.155	2.167(40)	2.161	0.115
$C_1\cdot H_{10}$	2.164	2.178(66)	2.172	0.115		2.119	2.133(72)	2.126	0.118
$C_3\cdot H_{10}$	2.182	2.198(40)	2.192	0.117		2.172	2.187(40)	2.180	0.116
$C_3\cdot H_9$	2.184	2.200(43)	2.194	0.117		2.178	2.192(43)	2.186	0.116
$Cl_7\cdot H_8$	2.375	2.392(85)	2.386	0.118		2.375	2.389(88)	2.383	0.118
$C_1\cdot C_3$	2.516	2.520(11)	2.518	0.072	(7)	2.543	2.547(11)	2.546	0.067
$C_3\cdot C_5$	2.489	2.492(20)	2.490	0.070		2.496	2.499(20)	2.497	0.070
$C_2\cdot Cl_7$	2.708	2.719(6)	2.717	0.080	(4)	2.725	2.734(6)	2.732	0.079
$C_6\cdot H_9$	2.752	2.762(118)	2.754	0.143	(37)	3.453	3.462(46)	3.460	0.083
$C_4\cdot H_9$	2.803	2.814(90)	2.807	0.145		3.494	3.503(26)	3.501	0.083
$C_3\cdot H_8$	2.778	2.787(90)	2.780	0.142		3.482	3.490(34)	3.488	0.083
$Cl_7\cdot H_9$	2.834	2.850(70)	2.843	0.149		2.887	2.900(99)	2.893	0.149
$Cl_7\cdot H_{10}$	2.896	2.913(68)	2.907	0.136		3.673	3.686(38)	3.684	0.086
$C_1\cdot C_4$	2.954	2.957(36)	2.955	0.079	(14)	3.001	3.004(35)	3.002	0.076
$C_2\cdot C_5$	2.924	2.927(18)	2.925	0.080		2.927	2.930(18)	2.927	0.078
$C_4\cdot H_8$	3.351	3.358(109)	3.350	0.159	(58)	3.974	3.980(61)	3.977	0.108
$C_5\cdot H_9$	3.338	3.346(103)	3.338	0.163		3.932	3.940(44)	3.937	0.110
$C_4\cdot H_{10}$	3.474	3.484(30)	3.481	0.103		2.848	2.857(92)	2.849	0.155
$C_6\cdot H_{10}$	3.450	3.459(49)	3.456	0.102		2.768	2.777(120)	2.768	0.160
$C_5\cdot H_{10}$	3.932	3.940(41)	3.937	0.111		3.344	3.350(108)	3.343	0.160
$Cl_{14}\cdot H_9$	4.464	4.475(82)	4.468	0.167		4.211	4.223(35)	4.216	0.162
$Cl_{14}\cdot H_8$	4.725	4.731(114)	4.721	0.210		4.531	4.538(90)	4.529	0.208
$Cl_{14}\cdot H_{10}$	4.888	4.899(38)	4.896	0.124		2.879	2.893(100)	2.874	0.233
$C_3\cdot Cl_7$	4.103	4.110(7)	4.109	0.076	(9)	3.247	3.255(20)	3.250	0.129(17)
$C_4\cdot Cl_7$	4.589	4.594(17)	4.592	0.100	(20)	3.865	3.871(23)	3.866	0.132(48)
$Cl_7\cdot Cl_{14}$	6.307	6.309(11)	6.308	0.086	(14)	5.232	5.236(24)	5.233	0.122(19)

[a] Structure of the aa form tied to ee via ab initio differences (HF/6-31G*). [b] Excluding the last three amplitudes the uncertainties are the same as equivalent amplitudes from the ee form.

restriction, in model A a predicate equal to the theoretical value for this angle (in this case taken from the MP2/6-311G* calculation) is introduced with a small weight, and in model C this and the other predicates are given weights large enough to result in refined values very close to the predicated values. We choose model A as our preferred model. The choice is clearly

TABLE 4: Correlation Matrix (×100) for Selected Parameters of Model A of *trans*-1,4-Dichlorocyclohexane

	parameter[a]	$100\sigma_{LS}$[b]	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	$\angle_9$	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	χ_{18}
r_1	$\langle r(C-H)\rangle$	0.15	100																	
r_2	$\langle r(C-C)\rangle$	0.04	−10	100																
r_3	$\Delta\langle r(C-C)\rangle$	0.69	7	−25	100															
r_4	$r(C-Cl)$	0.07	−2	8	<1	100														
$\angle_5$	$\angle C_2C_1C_6$	51	−3	−3	−39	7	100													
$\angle_6$	$\angle CCCl$	12	4	2	−47	−37	64	100												
$\angle_7$	$\angle C_1C_2C_3$	36	7	−37	81	−6	−50	−50	100											
$\angle_8$	flap(ee)	67	7	−44	75	−4	−14	−29	93	100										
$\angle_9$	flap(aa)	41	4	6	−30	−24	39	61	−21	−7	100									
l_{10}	$l(C_1-C_2)$	0.06	15	−13	50	−16	−19	−5	33	30	1	100								
l_{11}	$l(C_1-Cl_7)$	0.06	14	−3	−4	−9	5	12	−6	−4	9	34	100							
l_{12}	$l(C_1 \cdot C_3)$	0.22	7	−12	18	−3	66	52	<1	28	39	22	9	100						
l_{13}	$l(C_1 \cdot C_4)$	0.48	−9	−2	−40	18	58	11	−35	−16	−7	−36	−2	16	100					
l_{14}	$l(C_2 \cdot C_7)$	0.10	8	2	−18	−13	10	30	−26	−26	44	20	19	15	−4	100				
l_{15}	$l(C_3 \cdot C_7)$	0.29	−6	−5	6	28	17	−11	−5	2	−21	−2	2	7	−7	27	100			
l_{16}	$l(C_4 \cdot C_7)$	0.70	−7	−8	6	23	13	−16	6	13	−19	−5	<1	6	−14	24	25	100		
l_{17}	$l(C_7 \cdot C_{14})$	0.49	−3	−2	2	18	12	−4	−3	2	−6	−4	2	6	−2	18	32	20	100	
χ_{18}	χ[c]	46	−13	−7	3	46	28	−17	−3	9	−17	−24	−10	9	−14	43	65	46	44	100

[a] All parameters except $\angle_7$ were independently refined. [b] Standard deviations from least squares. Distances (r) and amplitudes (l) in angstroms, angles (∠) in degrees. [c] Mole fraction.

TABLE 5: Theoretical and Experimental Energy Differences and Compositions for *trans*-1,4-Dichlorocyclohexane

level of theory	(energy + 1152)/E_h ee form	(energy + 1152)/E_h aa form	$\Delta E_{ee\rightarrow aa}$/ kcal·mol^{-1}	$\Delta G°$ [a]	χ_{ee}
HF/6-31G*	−0.019 32	−0.018 02	−0.82	−1.30	0.15
MP2/6-311G*	−1.218 71	−1.219 16	0.28	−0.20	0.43
QCISD/6-311+G(2df,p)	−1.592 06	−1.592 51	0.28	−0.20	0.43
MPw1PW91/6-311G*	−3.172 58	−3.172 49	−0.06	−0.54	0.33
B3P86/6-311G*	−4.673 42	−4.673 59	0.11	−0.37	0.38
B3P86/6-311+G(2df,p)	−4.703 74	−4.703 90	0.10	−0.38	0.38
experimental (this work)				−0.09(18)[b]	0.46(6)

[a] Includes the 0.12 kcal/mol calculated difference in zero-point energy (aa > ee) and the 0.98 cal/deg difference in entropy (ee > aa) to give a net difference between between ΔE and $\Delta G°$ (380 K) of 0.48 kcal/mol. [b] $\Delta G°$ at 380 K with estimated 2σ uncertainty.

somewhat arbitrary, but it represents a good compromise between the independent indications of the GED data and theoretical prediction. It is worth noting that except for the $C_2C_1C_6$ bond angle all parameters including the mole fractions are insignificantly different in the three models. A complete listing of distances and vibrational amplitudes for model A is given in Table 3. Table 4 is an abbreviated correlation matrix for the parameters of this model.

The early GED results of AH[1] were obtained by matching theoretical radial distribution curves, constructed by summing Gaussian peaks representing the interatomic distances, to the experimental curve. This was a difficult, largely trial and error procedure that by today's standards did not give very accurate results, particularly for systems comprising mixtures of conformers. It is thus pleasing and at the same time remarkable that these early results agree as closely with ours as they do. For example, AH measured the (r_a) bond distances $\langle r(C-H)\rangle$, $\langle r(C-C)\rangle$, and $\langle r(C-Cl)\rangle$ to be 1.10, 1.53, and 1.81 Å, compared to our 1.109(4), 1.531(2), and 1.804(2) Å. AH report the CCC bond angle to be 111.5° having apparently assumed all ring angles to be equal and recognizing the necessity for a flattening of the cyclohexane skeleton to obtain a fit. Our structure has different values for the ring angles $\angle(C_2C_1C_6)$ and $\angle(C_1C_2C_3)$ which are respectively 109.9° and 110.9° in the ee and 110.1° and 112.9° in the aa form, and which average to 111.3°. AH also report the angle between the assumed 3-fold axis of the flattened ring and the C−Cl bonds in the aa form to be 6.3°where the C−Cl bond vector points away from the axis. The C_{2v} skeleton of our molecule similarly oriented leads to a value of 7.4° for this angle. Finally, AH estimate the conformational composition of the system to be 49/51 ee/aa in essentially perfect agreement with our 46/54 with its estimated uncertainty of 6%.

It is notable that the structure of gaseous monochlorocyclohexane is closely similar to that of *trans*-1,4-dichlorocyclohexane: Some values for parameters in the two forms of the former obtained by electron diffraction[13] are $r_g(C-H) = 1.112$ (5) Å, $\langle r_g(C-C)\rangle = 1.530$ (2) Å, $r_g(C-Cl) = 1.809$ (5) Å, $\langle \angle(CCC)\rangle = 111.3$ (4)°, $\langle \angle(CCCl)\rangle = 109.3$ (4)°. The mixture composition was measured to comprise 75 (5)% equatorial at room temperature, corresponding to $\Delta G° = 0.65$ kcal/mol in good agreement with the NMR estimate.[2]

One of the main concerns of our reinvestigation of T14D was the reliability of ab initio calculations for the prediction of the system composition and structures of the conformers. As mentioned in the Introduction, the first of our calculations, e.g., one at the HF/6-31G* level, suggested a significantly different composition from that found by AH while our experimental value agreed with AH's. This led to subsequent theoretical work at higher levels.

There are two interesting points of comparison between the calculations and the experimental results: the structures of the conformers and the system composition. In order to compare the theoretical and experimental structures more reliably, it was necessary to estimate the corrections from the measured thermal-average parameter values to the equilibrium ones. The "experimental" r_e bond lengths are given in Table 1, but the large uncertainties associated with similar estimates of the equilibrium bond angles did not make the effort for these parameters worthwhile; instead, the $\angle_\alpha$ values, which are thought to be similar, are given. Each of the sets of parameter values from all higher level calculations is seen from Table 1 to be in very good agreement with experiment, and even the ones from HF/6-31G* are quite satisfactory. We give a very slight edge to the MP2/6-311G* calculation as giving the best all around agreement with the experimental structure: the important C−Cl bond length in each form is reproduced best by it.

Table 5 summarizes the calculated energies at several theoretical levels. These energies were derived from geometry optimizations in all cases except QCISD where the MP2/6-311G* geometries were used. In order to compare the theoretical predictions at 0 K with those derived from our experiment done at 380 K, it is necessary to correct first for the difference in zero-point energy, and then for the change in free energy from indicated temperature difference. The vibrational frequencies used for this purpose were calculated at the B3P86/6-311G* level and were not scaled. The resulting $\Delta G°$(380 K) values are given in the table along with the corresponding compositions in terms of the mole fraction of the aa form.

The MP2/6-311G* and QCISD/6-311+G(2df,p) calculations give the best agreement with the experimental value of $\Delta G°$. In related work[14] we have found the QCISD calculations to give the best agreement with experimental conformational energies, and this is the case here also.

In the case of the monochlorocyclohexanes, the QCISD free energy change for the reaction axial → equatorial is 0.65 kcal/mol[15] in good agreement with the solution-phase NMR work.[2] Were this difference to be additive for the dichloro compound, the predicted mixture at 105 °C would have only about 15% of the axial form. The experimental result of more than twice this amount suggests some energy-lowering interaction between the halogens of this form. The most likely source of this stabilization is an electrostatic interaction involving the two chlorine substituents.[4] This cannot be modeled simply as an interaction between two C−Cl bond dipoles because the placement of a chlorine atom on the cyclohexane ring leads to significant charge redistribution involving the adjacent carbons and hydrogens. The "atomic charges" were estimated using the CHELPG procedure[16] that fits the electrostatic potential about a molecule and leads to charges that are useful in calculating intermolecular interactions.[17] A summation of the electrostatic energies ($\sum q_i q_j / r_{ij}$, $i > j$) based on the CHELPG charges gave −6.3 kcal/mol for the aa form and −4.2 kcal/mol for the ee form. The lower energy of the aa form is sufficient to overcome the predicted 1.3 kcal/mol lower energy of the ee form based on the energies of the monochlorocyclohexanes. This is, of course, a crude approximation since it ignores the question of whether a dielectric constant of one is appropriate for interactions between atoms on opposite sides of the cyclohexane ring[18] and assumes that the CHELPG charges are appropriate. However, this simple model does provide an explanation for the observed conformer ratio. A more detailed discussion of electrostatic interactions will appear shortly.[19]

Acknowledgment. This work was supported by the National Science Foundation under grant CHE95-23581 to Oregon State University and CHE97-07677 to Yale University.

Supporting Information Available: Tables of the experimental scattered intensity data and Cartesian coordinates of the two conformers of model A. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Atkinson, V. A.; Hassel, O. *Acta Chem. Scand*. **1959**, *13*, 1737.

(2) Bugay, D. E.; Bushwell, C. H.; Danehey, C. T., Jr.; Hoogasian, S.; Blersch, J. A.; Leenstra, W. R. *J. Phys. Chem*. **1989**, *93*, 3908.

(3) Eliel, E. L.; Kandasamy, D. *J. Org. Chem*. **1976**, *44*, 3899.

(4) Abraham, R. J.; Rossetti, Z. L. *Tetrahedron Lett*. **1972**, 4965.

(5) *Gaussian94*, Revision D.4; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(6) Hedberg, L. Abstract, Fifteenth Austin Symposium on Molecular Structure, Austin, TX, March 1994. For a description of the first version of the program see: Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc*. **1993**, *160*, 117.

(7) Richardson, A.; Hedberg, K., to be published.

(8) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(9) Hedberg, L. Abstracts, Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, 1974, No. 37.

(10) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables of Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. 4, p 245.

(11) Hedberg, K.; Iwasaki, M. *Acta Crystallogr*. **1964**, *17*, 529.

(12) Bartell, L. S. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports; The Chemical Society; London, 1975; Vol. 5, Chapter 4.

(13) Shen, Q.; Peloquin, J. N. *Acta Chem. Scand*. **1988**, *A 42*, 367.

(14) Wiberg, K. B.; Hammer, J. D.; Castejon, H.; Bailey, W. F.; DeLeon, E. L.; Jarret, R. M. *J. Org. Chem*. **1999**, *64*, 2085.

(15) Wiberg, K. B., unpublished results.

(16) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem*. **1990**, *11*, 361.

(17) See Severance, D. L.; Jorgensen, W. L. *J. Am. Chem. Soc*. **1992**, *114*, 10966.

(18) Eucken, A. *Angew. Chem*. **1932**, *45*, 203.

(19) Wiberg, K. B. *J. Org. Chem*. **1999**, *64*, 6387.