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If V_0 is then averaged over the entire lattice, it is found that

$$V_0 = V_1 - [2n_\alpha n_\beta / N^2](V_1 - V_2). \qquad (3)$$

The order parameter is defined as

$$\sigma = (n_\alpha - n_\beta)/N, \qquad (4)$$

which, when substituted in Eq. (3), gives

$$V_0(\sigma) = V_1 - (1 - \sigma^2)(V_1/2 - V_2/2). \qquad (5)$$

Although V_1 is the energy difference of a molecule in the ordered state, $V_0(1)$, it must be remarked that complete disorder results in a molecule having on the average three α and three β nearest neighbors. For this disordered state, then, $V_0(0) = \frac{1}{2}(V_1 + V_2)$. Defining ΔV as $V_0(1) - V_0(0)$, Eq. (5) becomes

$$V_0(\sigma) = V_0(1) - (1 - \sigma^2)\Delta V, \qquad (6)$$

which is the required form.

The Molecular Structure of 1,2-Dichloropropane

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Under the assumption of $V(\varphi) = V_0[1 - \cos(\varphi - \varphi_0)]/2$ for the potential hindering internal rotation, visual interpretation of the electron-diffraction pattern leads to the results (best values and estimated limits of error): C—Cl, 1.79±0.035A; C···Cl, 2.715±0.025A; C—C, 1.56A (range: 1.49–1.60A); $\angle$C—C—Cl, 108±4°; $|\varphi_0| \leqslant 30°$ (i.e., essentially *trans* in the chlorine atoms), with a small positive value of φ_0 (increasing CH$_3$···Cl$_{primary}$) most likely; $V_0 \geqslant 4$ kcal/mole. The best value for V_0 ranges from 10 kcal/mole for $\varphi_0 = 0°$ to 30–40 kcal/mole for $\varphi_0 = 25°$. The diffraction pattern is almost indifferently compatible with fractions ranging up to 50 percent of a *skew*-isomer with $\varphi_0 \sim 120°$ and a sufficiently low value of V_0, but consideration of dipole moment data provides some further evidence on its structure while showing the fraction present to be about 20 percent with an upper limit of about 30 percent.

THE present investigation of propylene chloride was undertaken primarily to obtain structural information needed for an application[1] of Kirkwood's theory of optical activity,[2] which in this case predicts a strong dependence of the optical activity upon internal rotation quite different from that of the conspicuous aspects of the diffraction pattern. Our electron-diffraction data alone were accordingly inadequate, but dipole moment data were fortunately made available which made possible a fairly complete structure determination.

In an x-ray diffraction study of the gas Berger found satisfactory agreement[3] on the assumption of reasonable values for the bond distances, tetrahedral bond angles, and the potential function $V(\varphi) = V_0(1 - \cos\varphi)/2$, with $V_0 = 0.88$ kcal/mole, for the dihedral angle of displacement φ of the Cl—C$_1$—C$_2$ and C$_1$—C$_2$—Cl planes from the *trans*-orientation. The structure of the related molecule, 1,2-dibromopropane, has been investigated by electron diffraction by Schomaker and Stevenson,[4] who reported normal values for the bond distances and bond angles and a root-mean-square torsional vibration of ±20° around the *trans*-position, again with no indica-tion of the possible occurrence of other internal-rotation isomers.

THE ELECTRON DIFFRACTION INVESTIGATION

Experimental

Two sets of photographs were prepared, the first at the 11-cm camera distance from some of the commercial Paragon product that had been distilled through a 40-cm column packed with glass helices ($n_D{}^{25}$ 1.4367, b.p. on redistillation through a similar 60-cm column 95.6–96.4°) and the second, partly at 11 cm and partly at 20 cm, from an independent sample prepared from propylene glycol by Dr. H. K. Garner (b.p. 96.2–96.5°, $n_D{}^{25}$ 1.4368; see lit.[5]: b.p. 96.2°, $n_D{}^{25}$ 1.43638), in the apparatus described by Brockway.[6] For the photographs actually used the sample temperature was about 25°.

The Photographs

Curve V_1 was drawn from the appearance and measurements of the photographs of the first set, the shape and height of the central maximum being guessed from past experience, while V_2, which was drawn after

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[1] Wood, Fickett, and Kirkwood, J. Chem. Phys. **20**, 561 (1951).

[2] J. G. Kirkwood, J. Chem. Phys. **5**, 479 (1937).

[3] H. Berger, Physik. Z. **38**, 370 (1937). Berger's data extended to only $q = (40/\lambda) \sin\vartheta/2 = 22$, however.

[4] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **62**, 2423 (1940).

[5] R. R. Dreisbach and R. A. Martin, Ind. Eng. Chem. **41**, 2875 (1949).

[6] L. O. Brockway, Revs. Modern Phys. **8**, 231 (1936). The wavelength, about 0.06A, was determined from ZnO photographs (C. S. Lu and E. W. Malmberg, Rev. Sci. Instr. **14**, 271 (1943): $a = 3.2492A$, $c = 5.20353A$). Corrections were made for film expansion.

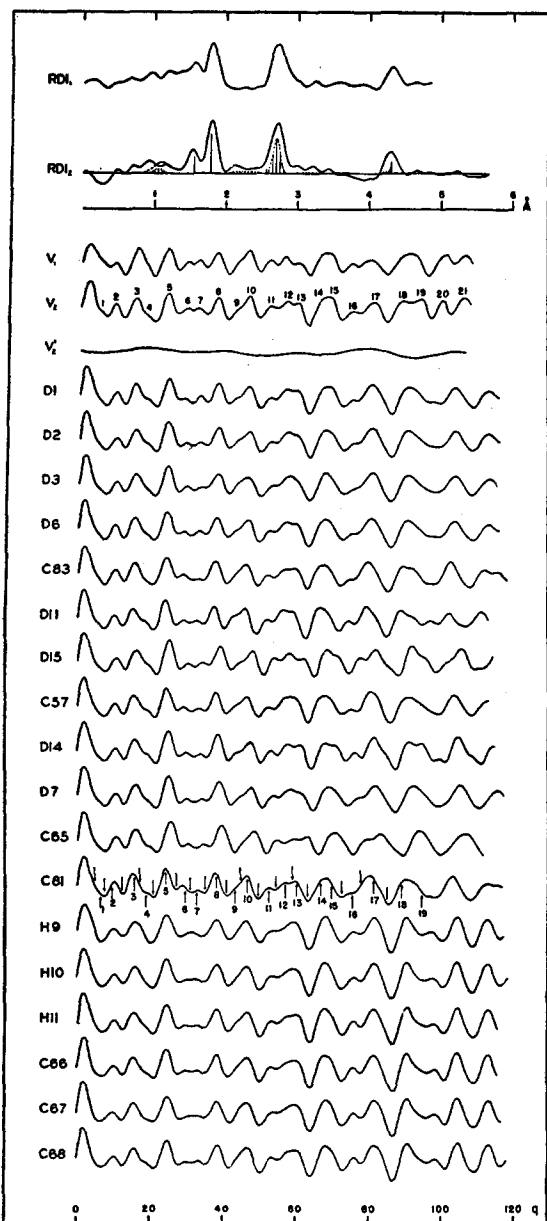Fig. 1. Radial distribution and visual curves. Intensity curves for models defined in Table I and the text.

Radial Distribution Curves

Curves RDI_1 and RDI_2 were calculated[8,9] respectively from V_1 and V_2 according to the equation

$$rD(r) = \sum_{q=1, 2, \cdots}^{q_{max}} V(q) \exp(-aq^2) \sin\pi qr/10, \quad (1)$$

with $q = 10s/\pi = (40/\lambda)\sin\vartheta/2$, ϑ the scattering angle, and a chosen to make the convergence factor $\exp(-aq^2)$ equal to 0.10 at $q=100$. The interpretation of the main peaks is clear in terms of a molecule approximately *trans* with respect to the chlorine atoms: 4.32A in RDI_1 and 4.30A in RDI_2, $Cl\cdots Cl$ (somewhat broad); 2.73 and 2.72, $C\cdots Cl$ (width indicates temperature factor with $a_{Cl\cdots Cl}=10^{-4}$ or a symmetrical splitting of the three nonequivalent $C\cdots Cl$ distances, with separations of about 0.05); 1.82 and 1.81, $C-Cl$; and 1.56 and 1.53, $C-C$ (poorly resolved). The more important remaining terms, some probably negligible and all weak, are the following: 2.16 and 2.45, $C\cdots H$ and $Cl\cdots H$ pairs having a common ligand (moderately heavy a); 2.52, $C\cdots C$; 2.8–3.5 (if $|\varphi|<30°$), rotation dependent $C\cdots Cl$ (large a); and 1.09, $C-H$. Agreement for these is fair, at least with RDI_2, but there are evidently errors, especially at low r and extending into the $C-H$ peak.[10]

TABLE I. Models of propylene chloride represented in Fig. 1.

Model[a]	C—Cl, A	C···Cl, A[b]	V_0, kcal/mole	φ_0, deg	$a_{Cl\cdots Cl}$[b]	$a_{Cl\cdots Cl}$
D1	1.79	2.70	30	10	0.00010	0.00010
D2	1.79	2.70	30	20	0.00010	0.00010
D3	1.79	2.70	30	30	0.00010	0.00010
D6	1.79	2.70	10	0	0.00010	0.00010
C83	1.80	2.73	4	0	0.00010	0
D11	1.82	2.74	60	25	0.00010	0
D15	1.76	2.64	60	20	0.00010	0
C57	1.79	2.72	30	20	0.00010	0.00010
D14	1.76	2.68	60	15	0.00010	0
D7	1.76	2.66	30	20	0.00010	0.00010
C65	1.73	2.60	30	15	0.00010	0.00010
C81[a]	1.80	2.73	10	0	0.00010	0.00010
H9[c]	1.79	2.70	30	20	0	0
H10[c]	1.79	2.70	30	20	0	0
H11[c]	1.79	2.70	30	20	0	0
C66[c]	1.79	2.70	···	···	0	0
C67[c]	1.79	2.70	···	···	0	0
C68[c]	1.79	2.70	···	···	0	0

[a] C—C, 1.54A and C—H, 1.09A, except that C81 has C—C, 1.57A and C—H, 1.06A.
[b] The three rotation-independent terms.
[c] Mixtures of *skew* and *trans*: see text.

comparisons with a number of theoretical curves had shown persistent discrepancies suggestive of errors in V_1, incorporates changes based upon the second set of photographs and observations by Dr. Kenneth Hedberg, who had no knowledge of the nature of the discrepancies. (See Fig. 1 and Table I.) (The second set shows no significant differences from the first but is much more distinct, especially at the triplet 11–12–13.) We have used both curves, emphasizing V_2, however, where the differences between them[7] are significant.

an average of the observers' differing opinions. The relative heights of maxima 11, 12, and 13, and the shape and positions of maxima 17 and 18–19 and minima 18, 20, and 21 show changes from V_1 based on the second set of pictures. (Beyond $q\approx 90$ both sets are unclear and the film edge is close enough to be bothersome.)

[8] R. Spurr and V. Schomaker, J. Am. Chem. Soc. 64, 2693 (1942).
[9] Shaffer, Schomaker, and Pauling, J. Chem. Phys. 14, 648, 659 (1946).
[10] Not unusual for complicated molecules and ordinarily corresponding to inconsequential low frequency errors in the visual curve. It here became necessary, however, to attempt direct comparisons of the intensities of rather widely separated features of the pattern and in the comparisons to allow for these errors which had been made obvious by the radial distribution curves.

[7] In V_2 the depth of min 2 *vs* min 3, the height of max 2 *vs* max 3, the position of shelf 4 on max 3, and the position of shelf 9 on max 10 reflect reinterpretations in agreement with Dr. Hedberg. The depth of min 6 *vs* min 8 is difficult to determine and represents

Altogether, the indication was that except for these errors the diffraction pattern could be accounted for with a model having conventional distances and angles with the possible exception of $C-Cl$, which might be 0.04A longer than usual, and only a small amplitude of libration about the *trans*-orientation $\varphi=0$.[11]

Theoretical Intensity Curves

As the appropriate simplified intensity function we have taken

$$I(q)=\{\sum_i (Z-f)_i^2\}^{-1} \sum_{ij}{}' (Z-f)_i(Z-f)_j r_{ij}^{-1}$$
$$\times \exp(-a_{ij}q^2) \sin\pi r_{ij}q/10 \quad (2)$$

with $a_{ij}=\frac{1}{2}(\pi/10)^2\langle\delta r_{ij}^2\rangle_{Av}$, omitting the form factors f_i, however (trial calculations showed them to be unimportant in this case), and, whenever necessary for the internal-rotation dependent terms, replacing the factors $r_{ij}^{-1} \exp(-a_{ij}q^2) \sin\pi r_{ij}q/10$ by adequate explicit approximations to the integrals[9] $\int r D_{ij}'(r) \sin\pi rq/10 dr$ over the distribution functions $r^2 D_{ij}'(r)$ as defined by the assumed potential function and classical statistics. The effective value of Z_H was taken as 1.25. Except where otherwise stated the following special assumptions were made: all bonded $C-C$, bonded $C-Cl$, and next-to-bonded $C\cdots Cl$ distances respectively equal; $\angle C-C-C$ and all bond angles involving hydrogen atoms tetrahedral; $a_{C-H}=0.00016$; $a_{C\cdots H}=a_{Cl\cdots H}=0.00030$; and all hydrogen terms except $C-H$ and next-to-bonded $X-H$ negligible, as was verified by test calculations.

The remaining shape parameters were taken (holding $C-C$ constant), as (1) $C-H$, (2) $C-Cl$, (3) $C\cdots Cl$, (4) the positions of the minima of the potential hindering internal rotation around the C_1-C_2 bond, (5) the shape of the potential barrier in the neighborhood of the

minima,[12] and (6) the skeletal vibrational temperature factors. The number of these parameters and the complex nature of the ones most important for us prolonged and complicated the work, while making impracticable systematic investigation; we can only summarize, showing a few of the theoretical curves.

Assumption of a Single Potential Minimum

At first the potential $V(\varphi)=V_0[1-\cos(\varphi-\varphi_0)]/2$ was assumed. (*We quote V_0 in kcal/mole throughout. A positive displacement of φ, at $\varphi=0$, increases $CH_3\cdots Cl_{primary}$.*)

It was not found possible to get general agreement including maxima 11–12–13 and 18–19 without widening the $C\cdots Cl$ distribution about as indicated by the RDI's. For most of the later curves, therefore, a temperature factor with $a_{C\cdots Cl}=10^{-4}$ was used, there being no apparent reason for the three nonequivalent distances to be significantly different, whereas considerations of the probable amplitudes of vibration seemed to justify an even greater a value.[13,14] The same considerations seemed to require a vibrational a of about 10^{-4} for $Cl\cdots Cl$ also. For the long $C\cdots Cl$ term, finally, a considerably more severe factor would be reasonable but none was used, since its effect would be small compared to the librational attenuation.

A best value of φ_0 is easily chosen if the other parameters, including V_0, are arbitrarily fixed. This is illustrated by Curves $D1$, $D2$, and $D3$; $D1$ and $D3$ we regard as unacceptable, in relative amplitude of maxima 6 and 7 particularly, whereas $D2$ is quite good. There is, however, already a strong interaction of the parameters V_0 and φ_0. This arises (1) from the increase of $|dr_{Cl\cdots Cl}/d\varphi|$ with $|\varphi|$, so that even at constant V_0 the attenuation of the $Cl\cdots Cl$ term increases with $|\varphi_0|$ in the way shown by the series $D1-D2-D3$, and (2) directly from the variation of

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The expected $C-H$ peak was joined onto RDI_2 as shown by the dashed line. The difference between RDI_2 so modified and RDI_2 itself was then Fourier-inverted, adjusted to allow for the use of a convergence factor in the inversion, and taken as a correction (V_2') to be added to V_2: the hump at $q\approx 18$ points to an unimportant mistake but the wave with node at $q\approx 85$ is interesting, since the correction serves to raise max 17 above the line of max 14–15 and max 18–19, as is required by all otherwise acceptable theoretical intensity curves. Even though all observers were here in agreement, therefore, V_2 must be in error in this respect.

[11] For asymmetric components of the distribution function the relation $rD(r) \propto \int_{-\infty}^{\infty} r'D'(r')\{\exp[-(r-r')^2/4a] +\exp[-(r+r')^2/4a]\}dr'$ (with $rD(r) \propto \int_0^{s_{max}} I(s)\exp(-as^2)\sin rsds$ and $rD'(r) \propto \int_0^{\infty} I(s) \sin rsds$) between the true distribution function $r^2D'(r)$ and the one, $r^2D(r)$, corresponding to Eq. (1) is rather complex. In particular, the positions of the maxima do not coincide: for the *trans* $Cl\cdots Cl$ distance in propylene chloride, for example, reasonable amplitudes of libration could cause differences of 0.05A or more. This circumstance, the uncertainty in the pertinent $C-C$ distance, and the fact that the maximum of the angular distribution does not necessarily occur at the angle corresponding to the maximum of the distance distribution prevent an immediate reliable determination of φ.

In the earlier study of propylene bromide (see reference 4) neither these circumstances nor, in the calculation of theoretical curves, even the variation of $Br\cdots Br$ with the amplitude of φ, at $\bar\varphi=0$, were considered. Since the $C-Br$, $C\cdots Br$, and $Br\cdots Br$ terms predominate in this molecule, the situation may be interpreted merely as indicating somewhat different values of $C-C$ and $\angle C-C-Br$ than were reported.

[12] The temperature of the vapor was assumed to be 300°K but was not actually known and may possibly have been significantly lower.

[13] Extension of the normal coordinate analysis of ethylene chloride (S. Mizushima and Y. Morino, Sci. Papers I. P. C. R. (Tokyo) 26, 1 (1934); Bull. Chem. Soc. Japan 13, 189 (1938); we used the same force constants and frequencies, and neglected the motions of the hydrogen atoms as in the first paper) leads to the following mean-square displacements: $C-Cl$, 0.0030A^2; $C-C$, 0.0026A^2; $C\cdots Cl$, 0.0063A^2; $Cl\cdots Cl$, 0.0070A^2. Referred to $a_{C-C}=0$, the resulting a's are: for $C-Cl$, ~ 0; $C\cdots Cl$, 0.00018; $Cl\cdots Cl$, 0.00020. Also, the frequencies and diagrams of the normal modes given by P. C. Cross and J. H. Van Vleck (J. Chem. Phys. 1, 350 (1933)) for the skeletal motions of ethyl chloride lead to the values, roughly estimated, $a_{C-Cl}\approx 0$ and $a_{C\cdots Cl}\approx 0.00027$, again referred to $a_{C-C}=0$. These estimates are uncertain in that the valence-force potential functions assumed are not necessarily correct, but they at least suggest the assumption of considerable vibrational amplitudes for $C\cdots Cl$ and $Cl\cdots Cl$ in propylene chloride.

[14] It has been usual to assume a rigid heavy-atom skeleton (excepting internal rotations) unless large amplitudes of vibration were obviously to be expected or unless it was found impossible or seemed unreasonable (as for $C\cdots Cl$ here) to obtain a fit otherwise. But the possibility of getting agreement with a rigid skeleton does not guarantee the results so obtained—compare the possible conclusion for propylene chloride that the three $C\cdots Cl$ distances were significantly split. Moreover, the simultaneous contributions of vibrations and libration can become important in the same sense, particularly at *trans*, where the resulting attenuations may well be comparable. To be sure, the finer effects do differ, notably the variation with q of the effective value of r in the case of libration.

The value 0.004 reported for $a_{Br\cdots Br}$ (s scale) in reference 4 corresponds to a torsional amplitude greater than the reported $\pm 20°$, unless allowance, not mentioned in the article, is made for a vibrational contribution.

TABLE II. Comparison of observed and calculated q values Model $C81$.

Max	Min	$q_0{}^a$	q_c/q_0	Max	Min	$q_0{}^a$	q_c/q_0
	1	4.6	(0.913)		12	54.8	0.994
1		6.2	(0.935)	12		57.5	0.995
	2	7.4	(1.000)		13	59.4	0.988
2		9.5	(1.063)	13		60.6	0.998
	3	12.2	(1.033)		14	63.6	1.003
3		15.6	0.987	14		67.3	0.992
	4	17.2	(1.058)		15	68.8	0.993
4		19.0	(1.042)	15		70.2	0.994
	5	20.9	1.005		16	73.0	1.000
5		24.3	1.004	16		76.0	0.993
	6	27.3	1.004		17	78.3	0.983
6		29.9	0.970	17		81.8	0.980
	7	31.2	1.013		18	85.6	1.008
7		33.0	1.012	18		89.6	(1.003)
	8	35.3	0.992		19	92.4	(0.990)
8		38.4	0.971	19		95.2	(0.978)
	9	41.2	1.005				
9		43.7	0.986	Average, 28 terms^b			0.995
	10	45.1	0.989	Average deviation			0.008
10		47.0	0.998	Scale factor^c			0.993
	11	50.0	1.000				
11		53.0	0.992				

^{a} Weighted averages from both sets of photographs.
^{b} Excluding unreliable values in parentheses.
^{c} Corrected for change in λ from tentative value 0.0608A used for q_0 to calibration value 0.0606$_5$A.

$r_{\text{Cl}\cdots\text{Cl}}$ with φ and the consequent dependence of the effective value of $r_{\text{Cl}\cdots\text{Cl}}$ on both φ_0 and V_0 (as well as q^{13}), so that, for example, the combination $V_0 = 30$, $\varphi_0 = 10°$ ($D1$) is unsatisfactory in a way that could be corrected by making $|\varphi_0|$ greater, whereas $V_0 = 10$, $\varphi_0 = 0°$ ($D6$) is acceptable. Curve $C83$, with $V_0 = 4$ and $\varphi_0 = 0°$, is again unacceptable, but here other parameter variations are also involved.

Further investigation indicated more generally that for $|\varphi_0| > 30°$ no satisfactory curves exist, that for $|\varphi_0| \approx 20°$, $V_0 = 30$ is satisfactory, and that for the *trans*-position $\varphi_0 = 0$, $V_0 \approx 10$ is required.[15] Curves $D11 \cdots D65$ illustrate several combinations of C–Cl and C$\cdots$Cl, each for its best φ_0 and a roughly corresponding V_0. If, as in $C65$, C–Cl is 1.73A and C$\cdots$Cl is selected for shape of max 18–19, there is no φ_0 which makes satisfactory the inner features, particularly maxima 6 and 7, whereas with a longer C$\cdots$Cl distance the situation is reversed: there seems to be no satisfactory choice with C–Cl this small. For C–Cl $\geq$ 1.82A, on the other hand, the height of max 18–19 decreases while further deviations occur, notably degeneration of the triplet into an excessively strong[16] doublet and a weak, too well separated, inside member (see $D11$) and, for C–Cl = 1.85A, excessive growth of max 13 *vs* max 12. Our use of max 18–19 is illustrated by $D2$, $D11$, and $D15$ (not symmetrically doubled: component 19 too weak), $C57$ (too weak, but shape acceptable), and $D14$ (both shape and height somewhat improved).

All curves so far called acceptable have certain deficiencies associated with the height of max 10 *vs* maxima 8 and 11–12–13, the depth of min 9 *vs* minima 8 and 11, and the depth of min 11 *vs*

minima 9 and 14. Dr. Hedberg agreed that the pictures seem to require max 10 to be higher, min 9 deeper, and min 11 shallower than the respective lines joining the mentioned adjacent features, but tangency of line and feature was finally deemed acceptable for each.[17] We find $C44$, $D6$, $D11$, and $D15$ barely acceptable at max 10 and $D2$, $D11$, and $C57$ unacceptable; $D2$, $D7$, $D11$, $C44$, $C57$, $D14$, and $C65$ barely acceptable or acceptable at minima 9 and 11; and $D15$ unacceptable at min 11 and doubtful at min 9. None is everywhere satisfactory; $D11$, for example, fails at max 18–19, while similar models having longer C$\cdots$Cl (2.76A, say), although even better as regards max 10 and the shape of max 18–19, make the latter feature rather too weak (even on allowing the correction V_2') while showing the deterioration of the triplet. Shortening C–H to about 1.04A ameliorates the relations at max 10 but not at minima 9 and 11.

Altogether, model $C81$ has about the optimum shape. The scale determination for it (Table II) together with the range of qualitative acceptability of the intensity curves and the estimated scale uncertainty (both direct and as consequence of the uncertainty in shape) leads to the following parameter values and approximate limits of error for the single-minimum model: C–H, (1.05A);[18] C–C, 1.56A (1.49–1.60A); C–Cl, 1.79±0.035A; C$\cdots$Cl, 2.715±0.025A; $\angle$C–C–Cl, 108±4°; and $V_0 \geq 4$ (upper limit not determined)[14] and $|\varphi_0| \leqslant 30°$, with best values not separately determined but only related as indicated by the pairs $\varphi_0 = 0°$, $V_0 = 10$ and $\varphi_0 = 25°$, $V_0 = 30 – 40$. The sign of φ_0 remains somewhat uncertain: librational attenuation renders the odd C$\cdots$Cl, the only pertinent term, unimportant despite its having half the weight of Cl$\cdots$Cl. For the larger values of $|\varphi_0|$, however, V_0 has to be so large as to diminish this attenuation considerably (for $V_0 = 30$ and $\varphi_0 = 0°$, as would correspond roughly to the best models with $\varphi_0 = \pm20°$, the term retains a quarter of its initial amplitude at $q = 35$), and positive φ_0 gives the better agreement. This is satisfactory, since the approximate equality of van der Waal's radii for methyl and chlorine suggests that the value 10° reported[19] for 1,1,2-trichloroethane might hold approximately here also.

Consideration of Other Conformations

The steric similarity of chloro and methyl groups and the analogy to trichloroethane,[19] as well as the existence of internal-rotation isomers even in ethylene chloride,[20] suggest that for propylene chloride there may be a significant population of *skew*-molecules with $\varphi_0 \approx 120°$, i.e., with $-\text{CH}_3$ rather than $-\text{Cl}$ *trans* to the primary

[15] The question of an upper limit of V_0 was not investigated, because the optical activity does not depend critically on it. Discrepancies do appear for very large V_0, due to the too-long persistence of the libration-dependent terms; but this indication is unreliable, since more severe vibrational a's than were used would not be unreasonable. For the larger values of V_0 (and $|\varphi_0|$) the factor for Cl$\cdots$Cl (with $a = 0.00010$) tends to eliminate an otherwise bad hump on the outside of max 17, while causing a not unsatisfactory coalescence of maxima 18 and 19 into a single broad feature, but for low values of V_0 its inclusion has little effect on the curves or the optimum for the other parameters. For many of the curves it was omitted.

[16] The following doublet (14–15) appears *much* the stronger, but this may be only a visual consequence of the greater width of the triplet.

[17] Curves V_1 and V_2 would imply more stringent requirements on the relative amplitudes of *pairs* of adjacent features in this series: e.g., max 10 higher than max 8. We have been forced to discount these judgments, as is reasonable in view of the difficulty of estimating and allowing for the slope of the apparent background, and have emphasized the presumably more reliable comparisons of *triples* of adjacent features.

[18] The small weight, severe temperature factor, and evidently large corresponding error in the radial distributions justify regarding C–H as *assumed* (relative to C–C), even though it was chosen in the effort to improve max 10. Use of the more likely value 1.09A leaves the other shape parameters and the scale determination essentially unchanged.

[19] A. Turkevitch and J. Y. Beach, J. Am. Chem. Soc. **61**, 3127 (1939).

[20] W. D. Gwinn and K. S. Pitzer, J. Chem. Phys. **16**, 303 (1948).

chlorine atom.[21] Since the. calculated optical activity[1] depends critically on internal rotation, being of comparable magnitude but different sign for the *trans*- and *skew*-isomers, a limiting estimate of the fraction of *skew* is essential, even though the photographs give no clear indication that any is present. For reasonable hindering potentials, we find that 25 percent of *skew* is equally acceptable with pure *trans* while 50 percent or more is unacceptable; the diffraction data do not afford a much lower limit. On the other hand, a fraction somewhere between the half-fractions $\frac{1}{10}$ and $\frac{1}{2}$ for ethylene chloride[20] and trichloroethane[21] would correspond to the plausible sequence of steric effectiveness $-H < -CH_3 < -Cl$.

Sums of *skew*- and *trans*-curves in various proportions were examined, taking D2 without the $C\cdots Cl$ and $Cl\cdots Cl$ temperature factors for *trans*,[22] and the same basic model for *skew*, with various values V_{0s} and φ_{0s} for the constants of the assumed onefold cosinusoidal potential. For Curves H9, H10, and H11 the further assumption was made that V_{0s} is sufficiently low to wash out completely the contribution of the rotation-dependent *skew*-terms, as is reasonable for $Cl\cdots Cl$, which now varies rapidly with φ, and not too unsatisfactory for $C\cdots Cl$, which, although at about its maximum distance in any *skew*-model, has low weight. Curve H9 (75 percent *skew*) is out of the question, H10 (50 percent *skew*) is doubtful, and H11 (25 percent *skew*) is as good as D2, i.e., as 100 percent *trans*. The results obtained on including specific *skew*-terms are illustrated by the last three curves. Curve 66 (25 percent *skew*, $V_{0s}=30$, $\varphi_{0s}=120°$) is similar to H11 (justifying the preceding special assumption) and acceptable, C67 (50 percent *skew*, $V_{0s}=30$, $\varphi_{0s}=120°$) is at least as poor as H10, and C68 (25 percent *skew*, $V_{0s}=80$, $\varphi_{0s}=120°$) is satisfactory for moderate ·q[22] except possibly in showing max 7° higher than max 6 (see V_2), a difficulty improvable either by slightly increasing φ_{0t} or (as would be structurally reasonable) decreasing φ_{0s}. Other variations of the *skew*-structure were tried, also after the *trans*-parameters had been frozen, but none were successful. More nearly quantitative intensity data than can be got by the visual method would no doubt better define the diffuse $Cl\cdots Cl$ term and abundance of the *skew*-isomer as well as the diffuse $C\cdots Cl$ term of the *trans*.

THE DIPOLE MOMENT BEHAVIOR

For the interpretation of the moment values (Table III), from the work of Oriani and Smyth,[23] we have used the expression $\mu(\varphi)=2\mu_\perp \sin\varphi/2 = 2\mu_0 \sin\angle C-C-Cl \sin\varphi/2$, assuming the molecular dipole moment $\mu(\varphi)$ to be the sum of $-CH_2Cl$ and $-CH(CH_3)Cl$ group moments of equal magnitude μ_0 which lie along the respective $C-Cl$ lines at equal angles to the connecting $C-C$ bond, all independent of the angle of internal rotation φ.[24] Two sets of calculations were made, the first on the further assumption that effectively there is simply an equilibrium between *trans*- and *skew*-species, each with temperature-independent characteristics, and the second with the explicit use of various possible forms of the hindering potential.

In the first case the equation

$$\langle\mu^2(T)\rangle_{Av}=\{\mu_t^2+\mu_s^2 a \exp(-\Delta E/RT)\}/ \{1+a \exp(-\Delta E/RT)\} \quad (3)$$

is an appropriate approximation, μ_t and μ_s being the moments of *trans* and *skew*, a the ratio of partition functions referred to the separate origins $\bar{E}_s$ and $\bar{E}_t$ (or, roughly, the ratio of torsional vibration periods), and ΔE the difference $\bar{E}_s-\bar{E}_t$ in average energy.[25] Least-squares fits to this equation in the logarithmic form (Mizushima and Morino)[13]

$$\ln\{\mu_s^2-\mu^2(T)\}-\ln\{\mu^2(T)-\mu_t^2\}=-\ln a+\Delta E/RT \quad (4)$$

with plausible assumed values of φ_t, φ_s, and $\mu_\perp$ are all good, and about equally good, as perhaps can be seen from the small, relatively nearly constant standard errors (estimated from the residuals) of the derived values of a and ΔE (Table IV).[26] Nevertheless, the insensitivity of ΔE and the rapid variation of a with $\mu_\perp$ and φ_s, i.e., with the moment of the *skew*-molecule, taken together with inferences from related molecules, do limit φ_s and the fraction of *skew* at room temperature fairly well: $\mu_\perp$ will surely be close to the $1.59D$ found by Gwinn and Pitzer for ethylene chloride[20] or some-

TABLE III. Dipole moment of propylene chloride according to two treatments of the atom polarization.

T, °K	$\mu \times 10^{18}$, e.s.u.	
344.7	1.46[a]	1.40[b]
381.7	1.50	1.44
393.8	1.53	1.47
432.2	1.59	1.52
465.6	1.63	1.56
505.7	1.68	1.61

[a] On the assumption $P_A+P_E=M_D$. (See reference 23.)
[b] Recalculated on the assumption $P_A=P_E/10$, with P_E set equal to the mole refraction as extrapolated from M_R to infinite wavelength by analogy to the known behavior for ethylene chloride. The second set of moment values is used here, the nearly constant differences between the two sets corresponding essentially to a negligible difference in the value of the group moment.

[21] Only the "staggered" conformations are at all likely, and of these the third, with $\varphi_0 \sim -120°$ (tertiary $-H$ *trans* to primary $-Cl$), is probably about as unstable, relatively, as in 1,1,2-trichloroethane ($\Delta E>2.5$: J. R. Thomas and W. D. Gwinn, J. Am. Chem. Soc. **71**, 2785 (1949)) and therefore negligible for ordinary temperatures.

[22] Not the best *trans*-model, but good enough except at large q (see reference 14). Omission of the $Cl\cdots Cl$ temperature factor partly compensates for the inclusion of *skew* and so tends to keep conservative our estimate of the upper limit of *skew*.

[23] R. A. Oriani and C. P. Smyth, J. Chem. Phys. **17**, 1174 (1949).

[24] We are confident the inaccuracies of these assumptions will not vitiate the essential conclusions to be drawn.

Since most of the average dipole moment is due to the *skew*-isomer, the value of $\mu_\perp$ will refer essentially to it.

[25] K. S. Pitzer (J. Chem. Phys. **14**, 239 (1946)) has shown that in the classical partition function the effects of the dependence on φ of the vibrational frequencies and of the external moments of inertia cancel, if the potential energy is free of cross terms between φ and the vibrational coordinates, so that the simple factor $a \exp(-\Delta E/RT)$ may be used to weight classical averages over φ. For ethylene chloride, furthermore, Gwinn and Pitzer (see reference 20) were able to show in detail that the same is true of the quantum-mechanical averages.

It may be seen that μ_t and μ_s can really be constant only if the minima of $V(\varphi)$ are very narrow; and a, only if the minima are fairly wide and suitably similar in shape, or so narrow as to make $a=1$, with only one torsional energy level occupied for each isomer. Rough estimates make it clear, however, that both conditions are probably satisfied.

[26] In both treatments the lowest-temperature point deviates badly, as if the observed moment were too high, and has been ignored in the calculations. It probably is in error.

TABLE IV. Equation (4) fitted to the dipole behavior.

$\frac{\mu_\perp}{D}$	Assumed φ_t, deg	φ_s, deg	a	Calculated ΔE kcal mole⁻¹	Fraction skew, 300°K
1.59	0	120	1.34±0.05	0.96±0.03	0.21
1.59	0	90	3.54±0.19	1.23±0.04	0.31
1.80	0	120	0.86±0.03	0.87±0.03	0.17
1.80	0	90	1.85±0.08	1.03±0.04	0.25
2.00	0	120	0.62±0.02	0.84±0.03	0.14
2.00	0	90	1.21±0.05	0.94±0.03	0.20
1.59	25	120	1.29±0.06	1.12±0.04	0.16
1.59	25	90	3.43±0.20	1.40±0.05	0.25

TABLE V. Various internal-rotation potentials and $\mu_\perp$ values adjusted to the dipole behavior.

$V(\varphi)$, kcal mole⁻¹	φ, deg	ΔE	$\mu_\perp, D$
1. $2.5[1-\cos\varphi]$	−40— 40	1.1	1.76
2.1	40— 70		
$\Delta E+2.5[1-\cos(\varphi-120°)]$	70—160		
∞	160—320		
2. $15[1-\cos(\varphi-20°)]$	−40— 50	1.3	1.52
2.09	50— 80		
$\Delta E+2.5[1-\cos(\varphi-120°)]$	80—160		
∞	160—320		
3. $15[1-\cos(\varphi-20°)]$	−40— 50	1.3	1.74
1.64	50— 60		
$\Delta E+2.5[1-\cos(\varphi-90°)]$	60—140		
∞	160—320		
4. $0.75[1-\cos\varphi]+0.22[1-\cos3\varphi]$	−30—150	(0.96)	1.83
∞	150—330		
5. $1.0[1-\cos\varphi]+1.1[1-\cos3\varphi]$	−60—180	(0.85)	1.62
∞	180—300		
6. 0	10— 30	1.3	1.29
2.1	30— 80		
ΔE	80—160		
∞	160—370		
7. 0	0— 40	1.1	1.42
2.1	40— 80		
ΔE	80—160		
∞	160—360		

what larger due to induction in the methyl group but, due to mutual induction of the two C−Cl dipoles, not so large as for ethyl chloride; a must be about unity, the corresponding ratio being about one for ethylene chloride and necessarily one for 1,1,2-trichloroethane; and φ_s is probably forced toward *trans* away from the ideal 120°, perhaps by less than the 10° reported for trichloroethane[19] or the somewhat smaller amount indicated by Gwinn and Pitzer's potential function for ethylene chloride. Increasing φ_t to about the upper limit permitted by the diffraction pattern, it will be noted, increases ΔE substantially and correspondingly decreases the fraction of *skew*.

The explicit potentials listed in Table V also afford satisfactory fits, the parameters ΔE and $\mu_\perp$ having been adjusted to fit the 432°K point exactly and the others, excepting the lowest temperature point,[26] as well as possible. In agreement with our first treatment, ΔE is about 1.0, at least for barriers of reasonable shape, with any implausibly high ratio of widths of the two minima (numbers 6, 7, and perhaps 2) again resulting in a too low value of $\mu_\perp$). Potential 5 and the onefold barrier $V(\varphi) = V_0(1-\cos\varphi)/2$ with $V_0 = 2.5$ originally fitted[23] to the moment values are both incompatible with our diffraction data, the *trans*-minimum of 5 being somewhat too narrow and that of the onefold barrier much too wide. This contradiction with the onefold barrier constitutes rather direct evidence favoring the existence of auxiliary potential minima.

Similar conclusions from the dipole data have been reached by Morino, Miyagawa, and Haga.‡

In summary, we believe that the above results should lead to fairly reliable estimates of averages over φ, with

‡ Morino, Miyagawa, and Haga, J. Chem. Phys. **19**, 791 (1951).

the *skew*-conformation perhaps conservatively overweighted in view of our concern with the optical activity. Knowledge of the Raman and infrared spectra of the vapor, and particularly their temperature dependence, would be very helpful, however.[27]

[27] The liquid spectra (K. W. F. Kohlrausch and Gr. Prin Ypsilanti, Z. physik. Chem. **B32**, 407 (1936); L. Kahovec and J. Wagner, Z. physik. Chem. **B47**, 48 (1940); H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London), **A184**, 21 (1945); temperature dependence not reported) do clearly indicate the presence of at least two isomers in the same way as has been noted for ethylene chloride (see Mizushima, Morino, Watanabe, Simanouti, and Yamaguchi, J. Chem. Phys. **17**, 591 (1949)).