sistent with the assumption that there is little or no ionization of the acid in dioxane.

The diffusion coefficient decreases rapidly as the dioxane content of the solvent changes from zero to 20 mole per cent. From this point on to pure dioxane, D decreases slowly even though the dielectric constant decreases rapidly.[8] The values in the last column of Table V represent diffusion coefficients corrected to the viscosity of pure dioxane so as to provide a uniform basis for comparison. The correction factor equals the quotient of the viscosity of the mixture by the viscosity of pure dioxane (η/η_0). This correction is necessary because the viscosity of water–dioxane mixtures varies with concentration and passes through a maximum at 20 mole per cent. dioxane.[8]

Conductance measurements likewise give the expected evidence that there is little ionization of polyacrylic acid in dioxane. The data of Table VI show that the specific conductance of polyacrylic acid in dioxane–water mixtures exhibits the same type behavior as the diffusion coefficient. The conductance data also have been corrected to the viscosity of pure dioxane.

The partial specific volume and the sedimentation constant of polyacrylic acid in dioxane were also measured. The values were 0.69 ml. and 4.03

(8) H. Hartmann, Z. physik. Chem., A191, 197 (1942).

TABLE VI

SPECIFIC CONDUCTANCE, λ, OF POLYACRYLIC ACID IN DIOXANE–WATER MIXTURES

Mole % of dioxane in solvent	Weight % polyacrylic acid	$\lambda \times 10^6$	$\lambda \, \eta/\eta_0 \times 10^6$
0.0	0.845	555	420.7
2.29	.850	322.3	296.6
5.0	.852	174.7	191.7
8.22	.842	89.7	115.1
12.20	.838	42.1	62.3
17.22	.837	18.0	29.0
23.62	.832	4.0	6.7

$\times 10^{-13}$ sec., respectively. The molecular weight calculated from these data combined with the diffusion coefficient is 1.6×10^5 which is to be compared with a light scattering value of 2.3×10^5, also measured in this Laboratory. Since different kinds of averages of the molecular weights are involved, the agreement is satisfactory.

Experiments also have been carried out on other polymers such as fractions of polystyrene and fractions of polyisobutylene. The results will not be reported at this time, however, since the measurements were made at one concentration only. The expected dependence in molecular weight was observed for both materials.

URBANA, ILLINOIS

The Dipole Moments and Structures of *cis*- and *trans*-1,2-Dichlorocyclohexane[1,2]

BY A. TULINSKIE, A. DI GIACOMO[3] AND C. P. SMYTH

The dipole moments of *cis*- and *trans*-1,2-dichlorocyclohexane have been measured in the vapor state and in benzene solution. The values obtained for the *cis* isomer correspond closely to a 1e,2p configuration, while those for the *trans* show the substance to be an equilibrium mixture of 1e,2e and 1p,2p configurations. The energy difference between the two configurations is calculated and the effect of the solvent upon the energy of the polar configuration is shown.

Pure samples of *cis*- and *trans*-1,2-dichlorocyclohexane prepared[4] by Dr. Henry C. Stevens and Professor Oliver Grummitt of Western Reserve University and sent to us for dipole moment determinations have made possible an investigation of the structure and relative stabilities of the different molecular forms of these compounds.

Experimental Methods and Results

The dipole moments of the molecules were measured in benzene solution and in the vapor state. The refractive indices n^{20}D reported[4] for the two 1,2-dichlorocyclohexanes were *cis*, 1.4968; *trans*, 1.4904. Our values were *cis*, 1.49684; *trans*, 1.49039. Benzene purified as in earlier work[5] boiled at 80.2° (765 mm.) and had a refractive index,

n^{20}D, 1.50132. The measurements of the dielectric constants and densities of the solutions in benzene were made by methods previously employed in this Laboratory,[5,6] as were the measurements on the vapors,[7] which, because of the high boiling points of the liquids, were made at only one temperature. Six or seven solutions of each substance were measured at concentrations from 0.0008 to 0.006 mole fraction of polar component. The polarizations $P\infty$ at infinite dilution were calculated by the Debye method and by that of Halverstadt and Kumler[8] from the constants of the equations for the dielectric constants ϵ_{12} and the specific volumes v_{12} as linear functions of the weight fractions w_2 of the solute

$$\epsilon_{12} = \epsilon_1 + \alpha w_2; \qquad v_{12} = v_1 + \beta w_2$$

The dipole moments were calculated by means of the usual equation

$$\mu = 0.01281 \times 10^{-18}[(P_\infty - R_D)T]^{1/2}$$

in which R_D is the molar refraction for the D sodium line and T, the absolute temperature. The experimental results are given in Table I.

Discussion of Results

A considerable amount of evidence[9] based on

(1) This research has been supported in part by the office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work to be submitted by Mr. A. Tulinskie to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Procter and Gamble Fellow in Chemistry.

(4) H. C. Stevens and O. Grummitt, THIS JOURNAL, 74, 4876 (1952).

(5) L. M. Kushner and C. P. Smyth, ibid., 71, 1401 (1949).

(6) G. L. Lewis and C. P. Smyth, ibid., 61, 3063 (1939).

(7) J. H. Gibbs and C. P. Smyth, ibid., 73, 5115 (1951).

(8) I. F. Halverstadt and W. D. Kumler, ibid., 64, 2988 (1942).

(9) O. Hassel, Research, 3, 504 (1950).

TABLE I

EMPIRICAL CONSTANTS, POLARIZATIONS, REFRACTIONS AND
DIPOLE MOMENTS OF 1,2-DICHLOROCYCLOHEXANES

	T, °C.	ϵ_1	v_1	α	β	P_∞(cc.)	R_D(cc.)	$\times 10^1$
cis	40	2.2475	1.1671	6.428	−0.3474	227.8	37.18	3.13
cis	236		Vapor			152.8		3.11
trans	40	2.2496	1.1666	4.600	−0.3115	171.8	37.39	2.66
trans	239		Vapor			101.1		2.31

electron diffraction,[10] Raman[11] and infrared[12] spectra and thermal studies[13] indicates that the chair form of the cyclohexane ring is much more stable than the boat form. If the principal axis of the carbon ring of the chair form is taken as vertical,[9] three of the six C–H bonds parallel to it will point upward and three downward (Fig. 1), the positions on these bonds being designated as polar (p). The remaining six C–H bonds, which make angles of about 110° or 180° − 110° = 70° with the principal axis, are designated as equatorial (e). If the six carbon atoms pass through a single plane by torsional vibration, the original polar positions become equatorial, and *vice versa*. To calculate the dipole moments of the different possible structures a system of coördinate axes may be chosen with the z-axis parallel to the polar bonds. The moment of the molecule is calculated as the resultant of the components, m_x, m_y and m_z, of the moments, m, associated with the two C–Cl bonds and their environments. The moment values reported[14,15] for chlorocyclohexane vary from 2.07 to 2.3. Since these values are, probably, increased somewhat by inductive effects, which partially cancel each other and also lower the C–Cl bond moments when these are close together in the 1,2-dichlorocyclohexanes, a somewhat lower value, 1.9, has been used for m in the moment calculations.

The two possible configurations of the chair form of *cis*-1,2-dichlorocyclohexane, 1e,2p and 1p,2e, which might be formed from each other by torsional vibration, are obviously equivalent to each other in energy and dipole moment. The latter has been calculated from m_x = 1.9 cos 20° cos 60°, m_y = 1.9 cos 20° cos 30°, m_z = 1.9 (1 + cos 70°) as μ = 3.1, in closer agreement with the observed moment values in Table I than is warranted by the accuracy of the value m = 1.9. However, the agreement supports the correctness of the structure attributed to the molecule. The absence of difference between the moment value in benzene solution at 40° and in the vapor state at 236° indicates the absence of any appreciable shift to another form of different moment with change of temperature and molecular environment.

Two forms of *trans*-1,2-dichlorocyclohexane are possible, 1e,2e and 1p,2p. The moment of the 1p,2p form is obviously zero, while, for the 1e,2e form, m_x = 0, m_y = 2 × 1.9 cos 20° cos 30°, m_z = 0, giving μ = 3.1, identical with the value calculated for 1e,2p and observed for *cis*-1,2-dichloro-

cyclohexane. The observed values, 2.66 in benzene solution at 40° and 2.31 in the vapor at 239°, indicate that the substance is an equilibrium mixture of the two forms. The mean square moment observed for the mixture is given by the equation

$$\mu^2 = \frac{N_e\mu_e^2 + N_p\mu_p^2}{N_e + N_p}$$

where N_e is the number of molecules in the 1e,2e form, N_p is the number in the 1p,2p form, and μ_e and μ_p are the molecular moments of the two forms. Substitution of the observed values for μ and the values calculated above for μ_e and μ_p gives the mole fraction c_e = $N_e/(N_e + N_p)$ of the 1e,2e form as 0.56 in the vapor at 239° and 0.72 in benzene solution at 40°. The indication of nearly equal concentrations of the two forms in the vapor at 239° parallels that of electron diffraction[9,16] for the vapor of the dibromo compound.
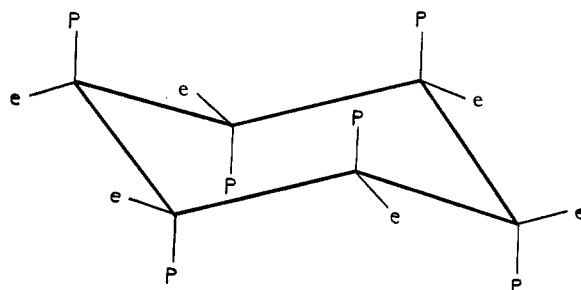
Fig. 1.—Chair form of cyclohexane molecule.

The energy difference ΔE between the 1p,2p form and the 1e,2e form can be calculated by combination of the above expression for the mean square moment observed for the mixture with the Boltzmann relation

$$N_p/N_e = (f_p/f_e)\, e^{-\Delta E/RT}$$

in which the ratio of the partition functions for the two forms, f_p/f_e, is taken as 1. The energy of the 1p,2p form is thus calculated to be 0.1 kcal./mole greater than that of the 1e,2e form in the vapor at 239° and 0.3 greater in benzene solution at 40°. The energy differences are of the same magnitude as those calculated[11] from Raman spectra intensities for 1p,4p and 1e,4e forms of *trans*-1,4-dichlorocyclohexane. The energy difference 0.3 -- 0.1 = 0.2 can be accounted for by the effect of the solvent upon the energy of the polar molecules immersed in it. When a molecule of radius a with a dipole of moment μ at its center is transferred from a medium of dielectric constant 1 to one of dielectric constant ϵ, the energy is decreased by an amount[17]

$$E = 2(\epsilon - 1)\mu^2/(2\epsilon + 1)a^3 \text{ kcal./mole}$$

(10) O. Hassel, *Tids. Kjemi Bergvesen*, **3**, 32 (1943).

(11) K. Kozima and T. Yoshino, THIS JOURNAL, **75**, 166 (1953).

(12) R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943).

(13) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

(14) J. W. Williams, THIS JOURNAL, **52**, 1831, 1838 (1930).

(15) O. Hassel and E. Naeshagen, *Z. physik. Chem.*, **B15**, 373 (1932); *ibid.*, **19**, 434 (1932).

(16) O. Bastiansen and O. Hassel, *Tidsskr. Kjemi Bergv. Met.*, **6**, 96 (1946).

(17) S. Mizushima and H. Okazaki, THIS JOURNAL, **71**, 3411 (1949).

With ϵ taken as 2.3 for the benzene solutions and a as 2.5 Å., ΔE is calculated as 0.3 for the 1e,2e molecules and zero for the 1p,2p, which means that the energy difference between the two forms should be about 0.3 greater in benzene solution than in the vapor, as compared to the observed difference 0.2, an agreement as good as could be hoped for with the approximations involved in the calculation. It is evident that the dipole moment values observed for the isomers of 1,2-dichlorocyclohexane are consistent with the existence of the molecules entirely in the chair form, but this fact is not inconsistent with the existence of a tautomeric equilibrium between the chair form and a small amount of the boat form as indicated by thermodynamic evidence.[18]

PRINCETON, NEW JERSEY

The Reaction of Osmium Tetroxide with Thiourea

BY R. D. SAUERBRUNN[1] AND E. B. SANDELL

The red complex formed by the reaction of thiourea with osmium tetroxide in acidic medium contains trivalent osmium and has the composition $[Os(NH_2CSNH_2)_6]^{+++}$ in solution. Osmium in this compound can be reduced to the divalent state with chromous chloride. In the presence of much chloride, yellow-brown mixed chlorothiourea complexes of Os(III) can be formed. $[OsO_2(NH_2CSNH_2)_4]^{++}$ is an intermediate product in the osmium tetroxide–thiourea reaction and can be isolated as the slightly soluble sulfate.

The composition of the soluble red product formed by the reaction of excess thiourea with osmium tetroxide or chloroösmate in acidic medium is uncertain. Chugaev crystallized a red solid from the reaction mixture, which on analysis gave a percentage composition interpretable as corresponding to either $[Os(NH_2CSNH_2)_6]Cl_3 \cdot H_2O$ or $[Os(NH_2CSNH_2)_6]OHCl_3$. In his early paper on the subject, Chugaev[2] accepted the first formula, but later[3] rejected it in favor of the second formula, thus assigning osmium a valency of +4 in the complex. Sidgwick[4] accepts the quadrivalency of osmium in the compound, but writes the formula as $[Os(NH_2CSNH_2)_6]Cl_4 \cdot 4H_2O$, apparently without new experimental evidence.

We have established the composition of the red compound in solution by obtaining the valency of osmium and the osmium–thiourea ratio. The complex is found to be the hexathioureaosmium-(III) cation. In the course of this work a thiourea complex of hexavalent osmium was prepared, and observations were made on the reaction of thiourea with Os(VIII) and Os(IV) at high chloride concentrations.

Experimental

Apparatus and Materials.—A Beckman model B spectrophotometer with 1-cm. Pyrex cells was used for absorbance measurements.

Solutions of osmium tetroxide were standardized by the Klobbie iodometric method with starch as external indicator. Thiourea (Eastman Kodak Co., white label) was recrystallized from water. Chromous chloride solution was prepared and standardized by customary methods.

Valence of Osmium in the Red Complex.—This was obtained by potentiometric titration with chromous chloride. Five ml. of 0.0154 M osmium tetroxide solution was treated with 5 ml. of concentrated hydrochloric acid and 5 ml. of 2% thiourea solution in a titration cell. Oxygen was removed by bubbling nitrogen through the solution and the

titration was made with 0.0508 M chromous chloride solution. Both a platinum and a mercury electrode were used as indicator electrodes. After addition of 7.65 ml. of chromous chloride, both electrodes showed a sharp break in potential (Fig. 1), but the solution retained its intense red color. Further addition of chromous chloride resulted in another break (mercury electrode) at 9.20 ml. total, at which the red color disappeared. The two breaks in this, and replicate, titrations, correspond to the following ratios of moles Cr(II) oxidized to moles Os present: first, 5.05, 4.95, 5.02; second, 6.07, 5.98, 6.03.

In the next series of experiments, a solution of the red complex formed as before was reduced with an excess of chromous chloride and air was then bubbled through for 20 minutes to oxidize all Cr(II) and restore osmium to its original valence in the red complex. After removal of oxygen, the solution was titrated with chromous chloride. The end-point in duplicate titrations, with the mercury electrode as indicator electrode, corresponded to the addition of 0.995 and 1.010 moles of Cr(II) per mole of osmium present.

Ratio of Thiourea to Osmium in the Red Complex.—Constant amounts of osmium tetroxide at a final concentration of 1.01×10^{-4} M in 0.25 M sulfuric acid were treated with varying amounts of thiourea and the transmittancy of the solutions was determined at 480 mμ after attainment of constant readings, which for low ratios of thiourea to osmium required an hour. The data are shown in Fig. 2.

Reaction of Thiourea with Osmium Tetroxide in the Presence of Much Chloride.—Thiourea was added to acidified osmium tetroxide solutions in the molar ratio 11.14:1 (approximately 1% in excess of the amount required to form the red complex) in the presence of various amounts of chloride. After 24 hours standing, when at least an approach to equilibrium had been attained, the absorbance curves recorded in Fig. 3 were obtained. No attempt was made to isolate a solid phase.

Preparation and Analysis of Tetrathioureadioxoösmium (VI) Sulfate.—Five ml. of 5% thiourea solution was added to 25 ml. of 0.015 M osmium tetroxide solution in 0.3 M sulfuric acid. The brown precipitate soon forming was filtered off, washed with 0.01 M sulfuric acid and finally with small portions of cold water. The crystalline product was dried at room temperature over anhydrous magnesium perchlorate. The yield was 80%.

Analysis of the compound was carried out as follows: osmium by dissolving in a dilute sulfuric acid solution of thiourea and measuring the optical density of the red solution; sulfate by dissolving in dilute hydrochloric acid, precipitating and weighing as barium sulfate; thiourea by determination of nitrogen by the Dumas method, and also from the total sulfur content found after decomposing the sample with concentrated nitric acid. These analyses were made on the semi-micro scale. The percentage composition

(1) From the Ph.D. thesis of R. D. Sauerbrunn, 1952.

(2) L. A. Chugaev, *Bull. soc. chim.*, **23**, 377 (1918); *Compt. rend.*, **167**, 235 (1918).

(3) L. A. Chugaev, *Z. anorg. allgem. Chem.*, **145**, 65 (1925).

(4) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, 1950, p. 1495.