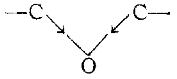
spectrum of dihydrotigogenin diacetate (VIII) is compared with the spectrum of androstanol-3β acetate. All of the characteristic side chain bands are lost and if allowance is made for the absorption of the terminal acetate group it is clear that the five-membered oxide ring contributes little to the spectrum.

Conclusions

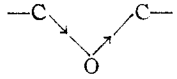
It is evident from the foregoing analysis, that provided the steroid ring is substituted only at position 3, the absorption of these compounds between 850 and 1350 cm.$^{-1}$ can be treated in quite good approximation as the sum of two independent absorbing systems; one is associated with the A ring and is determined by the nature of the substituent at C_3 and the stereochemical configuration at C_3 and C_5; the second, predominating, system is centered in the spiroketal side chain and is determined by the stereochemistry at the spirane ring junction.

On the introduction of addition hydroxyl, acetoxy or ketone groups small but significant changes are noted. The spectra can no longer be reconciled with the above hypothesis and some interaction effects involving the two centers of absorption apparently occur. The effect is more notable for the 12-ketones than for the sapogenins containing acetate or hydroxyl groups at 2, 6, 12 or 16. Even in these more highly substituted sapogenins, however, the interaction effects are comparatively small and the more prominent characteristic side chain bands (N, Q, T, U) are little affected.

The association of the side chain bands α–ω and A–U with specific modes of vibration in the spiroketal ring system cannot be made at present. It may be surmised that some of the stronger bands arise from symmetrical and antisymmetrical stretching vibrations of the C–O bonds (IX, X) since these motions should be associated with fairly large changes in dipole moment. From the fact that these bands all disappear in the spectra of the dihydrosapogenins it seems that the six-membered oxide ring rather than the five-membered oxide ring is most concerned in the active vibrations.



IX



X

Acknowledgments.—The authors wish to thank Professor R. E. Marker and the other investigators, listed individually in a footnote to Table III, who provided the compounds on which this study is based. The technical assistance of Mr. D. S. Keir of the National Research Council of Canada and Mr. R. Cohen, Miss F. Herling, and Miss Rita Conolly of the Sloan–Kettering Institute is also gratefully acknowledged.

The investigation was aided by grants from The American Cancer Society (upon recommendation of the Committee on Growth of the (U.S.) National Research Council), the Commonwealth Fund, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

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Molecular Structures of *trans*-1,4-Dihalogenocyclohexanes

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RECEIVED JULY 11, 1952

From the studies on the Raman spectra of *trans*-1,4-dihalogenocyclohexanes in various states, it has been concluded: (1) that they stand in the dynamic equilibrium of the two isomers (1p,4p) $\rightleftarrows$ (1e,4e) in solutions; (2) that the molecules, which have the structure (1e,4e), become more stable in the dilute carbon tetrachloride or cyclohexane solution than in the dilute benzene, ethyl alcohol or diethyl ether solution; and (3) that in the solid state, they take only the configuration (1e, 4e). The differences in the potential energy of the both configurations in various solvents were approximately estimated by measuring the relative intensities of the Raman lines.

It has been well established by means of various methods that the only form of the molecule of cyclohexane is the "chair-form" of D_{3d} symmetry. Hence, investigation of the molecular structure of these derivatives has now become a very interesting subject of study.

Supposing the valency angle of each carbon atom of the cyclohexane ring to be tetrahedral, one of the two remaining bonds of each carbon atom of the ring runs parallel to the threefold axis of symmetry and the other bond is not very far from being horizontal to the ring. According to the designation proposed by Pitzer, *et al.*,[1] the position of atoms combined with the former bonds was called p and that of those combined with the latter was called e. Using this designation and numbering the carbon atoms as usual from 1 to 6, a full and yet concise description of halogen derivatives can be given by symbols which indicate positions of only the halogen atoms combined to the ring.

At first sight it would seem that because of the difference in position of the halogens combined to the ring 1,4-dihalogenocyclohexane has the four configurations represented by the following symbols: (1p, 4p), (1p, 4e), (1e, 4p) and (1e, 4e). However, since (1p, 4e) and (1e, 4p) represent the same configuration, three configurations remain to be considered. If by the torsional and deformation vibration in the ring, one chair configuration is converted into the other chair configuration—which is identical, so far as the carbon ring is con-

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(1) K. S. Pitzer and C. W. Beckett, THIS JOURNAL, **69**, 977 (1947).

cerned, with the configuration which would be formed by rotating the former 60° around the threefold axis of the ring (although the position of p is converted to e and *vice versa* by this conversion)—the configurations (1e, 4e) and (1p, 4p) might be mutually convertible. The two isomers, which are interconvertible by such a motion, may be called "inverted isomers" according to Morino's notation[2] instead of "geometrical tautomers" proposed by Pitzer, *et al.*[3] The compound which is capable of having the inverted isomer (1p, 4p) $\rightleftarrows$ (1e, 4e) will be called *trans*-geometrical isomer, while the compound which has the configuration (1p, 4e) will be called *cis*-geometrical isomer.

Hassel's investigation[4] based on electron diffraction has indicated the existence of the inverted isomer only in the case of *trans*-1,2-dibromocyclohexane in the vapor state. By use of the same method and X-ray diffraction, however, he concluded that in the case of *trans*-1,4-dihalogenocyclohexanes the molecules have only the configuration (1e, 4e) in either vapor[5] or solid state.[6] But the results mentioned above do not exclude the possibility that in the liquid state the inverted isomers of the *trans*-1,4-dihalogenocyclohexanes stand in equilibrium. In order to clarify this point we carried out the following research.

Experimental

Preparation and Purification of Compounds.—In order to obtain *trans*-1,4-dihalogenocyclohexanes, we first prepared 1,4-cyclohexanediol by the hydrogenation of hydroquinone using Raney nickel as catalyst at 100° and at several atmospheres. 1,4-Cyclohexanediol thus obtained was heated at 100° in the sealed glass tube with concentrated hydrochloric acid or hydrobromic acid according to whether the compounds desired are chlorine or bromine derivatives. In both cases by distilling the oily substance separated in the sealed tube *in vacuo*, crystals solidified from the distillate. After repeated recrystallization, these crystals were thoroughly dried. The melting point of the crystals in the case of the chlorine derivative is 102° and that of bromine derivative is 112°. These data were found to agree with values already reported for the melting points of *trans*-1,4-dihalogenocyclohexanes.[7]

Electric Dipole Moments.—The dipole moments of these compounds have already been measured in the dilute benzene solution alone by Hassel, *et al.*[8] However, because benzene behaves occasionally as an abnormal solvent, we studied the moment in carbon tetrachloride solution.

Dielectric constants were measured as usual by heterodyne beat method at a wave length of 100 m. In order to make more accurate the measurements of the differences between the dielectric constant of solvent and that of solutions, we used a variable precision condenser which was constructed from a micrometer and a metallic cylinder.

The results obtained are shown in Tables I and II, where f and P_2 denote the mole fraction and the molar polarization, respectively. Other notations have their usual significances.

The concentrations at which the measurements were made are so dilute that the measured values of P_2 in both cases are almost independent of concentration. Therefore, the value of $P_{2\infty}$ is taken as the mean value of P_2 in either of the cases. Regarding both data the molar polarization, $P_{2\infty}$ is nearly equal to the molecular refraction R_D for the D-line calculated from the atomic refractions of constituent atoms. Therefore, we come to the conclusion that the dipole moments of these compounds are zero or nearly zero.

TABLE I

MOLAR POLARIZATION OF *trans*-1,4-DICHLOROCYCLOHEXANE

$t = 25°$, $R_D = 37.4$, $P_{2\infty} = 41.9$

f	ϵ	d	P_2
0.0000	2.2305	1.5842	
.01786	2.2360	1.5752	42.0
.03635	2.2416	1.5673	42.0
.04842	2.2453	1.5611	41.8

TABLE II

MOLAR POLARIZATION OF *trans*-1,4-DIBROMOCYCLOHEXANE

$t = 25°$, $R_D = 43.2$, $P_{2\infty} = 46.5$

f	ϵ	d	P_2
0.0000	2.2305	1.5842	
.03158	2.2444	1.5931	46.6
.03599	2.2483	1.5963	46.5
.03862	2.2492	1.5977	46.3

Raman Spectra.—We built the spectrograph which was used to obtain the Raman spectra, using 60° prisms of height 14 cm. and two lenses of 12 cm. diameter and 60 cm. focal length. At 4358 Å. the reciprocal dispersion at the film is 14.6 Å./mm.

The Raman spectra of these compounds were observed in the solid state and also in various solutions. The results of wave number readings are shown in Tables III and IV, together with the relative intensities obtained by the visual measurements.

TABLE III

RAMAN SPECTRA OF *trans*-1,4-DICHLOROCYCLOHEXANE AND THEIR INTERPRETATION

Raman spectra, cm.$^{-1}$		Configurations determined by		
Solution	Solid	Experiments	Calculation	Modes of vibration
	50 (1)			
	80 (1)			
167 (4)				
279 (7)	280 (2)	e,e	e,e	Deform. vib. Ag
533 (7)		p,p	p,p	Deform. vib. Ag
645 (9)		p,p	p,p	C–Cl stretch. Ag
724 (9)	715 (5)	e,e	e,e	C–Cl stretch. Ag
812 (6)			p,p	C–C stretch. Ag
838 (6)			e,e	C–C stretch. Ag
1006 (6)	1008 (1)	e,e	e,e	C–C stretch. Ag
1029 (6)			p,p	C–C stretch. Ag
1236 (6)				
1256 (1)				
1272 (1)				
1331 (4)	1333 (0)	e,e		
1425 (4)				
1440 (4)				
1461 (1)	1483 (1)	e,e		
2861 (6b)				
2912 (10b)	2914 (3b)			
2960 (10b)	2961 (4b)			

As the wave numbers of Raman spectra of both compounds do not change with solvent, only the data concerning carbon tetrachloride are described in these tables. As shown in these tables, some of the Raman spectra obtained in the liquid phase disappear in the solid state. At first sight, however, it might seem that experimental difficulties involved in obtaining Raman spectra of solids limit the completeness of the spectrum and only strong

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(2) Y. Morino, I. Miyagawa and T. Oiwa, *Botyu-Kagaku*, **15**, 181 (1950).

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

(4) O. Bastiansen and O. Hassel, *Tids. Kjemi, bergvesen Met.*, **8**, 96 (1946).

(5) J. G. Gudmundsen and O. Hassel, *Z. physik. Chem.*, **B40**, 326 (1938).

(6) E. Halmöy and O. Hassel, *ibid.*, **B16**, 234 (1932).

(7) M. B. Rothstein, *Ann. chim.*, **14**, 461 (1930).

(8) E. Halmöy and O. Hassel, *Z. physik. Chem.*, **B15**, 472 (1932).

TABLE IV

RAMAN SPECTRA OF *trans*-1,4-DIBROMOCYCLOHEXANE AND THEIR INTERPRETATION

Raman spectra, cm.$^{-1}$ Solution	Solid	Configurations determined by Experiments	Calculation	Modes of vibration
121 (6)				
173 (10)	170 (10)	e,e	e,e	Deform. vib. Ag
	241 (1)	e,e	e,e	Deform. vib. Ag
261 (1)	265 (1)	e,e	e,e	Deform. vib. Bg
351 (8)		p,p	p,p	Deform. vib. Ag
430 (2)	432 (0)	e,e	e,e	Deform. vib. Ag
485 (12)		p,p	p,p	Deform. vib. Ag
607 (8)		p,p	p,p	C–Br stretch. Ag
670 (10)	660 (10)	e,e	e,e	C–Br stretch. Ag
806 (6)		p,p	p,p	C–C stretch. Ag
823 (0)	817 (2)	e,e	e,e	C–C stretch. Ag
999 (6)	999 (7)	e,e	e,e	C–C stretch. Ag
1028 (6)		p,p	p,p	C–C stretch. Ag
1201 (8b)	1209 (2b)	e,e		
1255 (3)	1249 (2b)	e,e		
1274 (2)				
1333 (4)	1332 (2b)	e,e		
1424 (1)				
1438 (2)				
2864 (?)	2864 (?)			
2908 (8b)	2918 (4b)			
2959 (8b)	2959 (4b)			

lines may be obtained. But, this is not the case, because the strong lines observed in the liquid phase disappear in the solid spectrum whereas the weak lines remain in the solid spectrum. This disappearance can be explained reasonably by considering the existence of the two isomers, of which only one isomer persists in the solid state. Concerning both compounds, furthermore, remarkable phenomena were observed in that relative intensities of the Raman spectra in the liquid states change markedly with solvent. It is very interesting that by visual intensity measurements the liquid spectra are easily divided into two groups, according to whether the relative intensities of the Raman lines are strengthened in the carbon tetrachloride or in the benzene solvent. One of the two groups of the Raman lines, the intensities of which are strengthened in the benzene solution, remains in the solid spectrum.

As for the dichloro derivative the relative intensities of the lines at 724 cm.$^{-1}$ and at 645 cm.$^{-1}$, which correspond to the stretching vibrations of the C–Cl bonds of the configuration (1e, 4e) and (1p, 4p), respectively, as shown by the calculation of the skeletal modes of vibration, were exactly measured in the various solutions by the photographic method by the use of microphotometer and optical wedge.[9] Namely, the densities of the Raman lines and of their corresponding backgrounds are first determined. The densities are converted to relative intensities by means of the density–intensity curve. Background intensities are subtracted from total intensities. Corrections are made for the variation of sensitivity of the films with wave length. The results are shown in Table V.

TABLE V

THE VARIATIONS OF THE RATIOS OF RELATIVE INTENSITIES CAUSED BY CHANGING THE SOLVENTS

Solvents	I_e/I_p	Solvent	I_e/I_p
Carbon tetrachloride	0.65	Ethyl alcohol	1.62
Cyclohexane	0.88	Diethyl ether	1.65
n-Heptane	1.18	Benzene	1.70

Mixed solvents	I_e/I_p	Molar fraction of ether
Cyclohexane–ether I	0.97	0.15
Cyclohexane–ether II	1.06	.32
Cyclohexane–ether III	1.23	.47
Cyclohexane–ether IV	1.38	.67

It is desirable to use as concentrated a solution as possible to obtain the Raman spectra of these compounds in the solutions as shown in the first column of Tables III and IV. However, in order to obtain the relative intensities of the strong Raman lines, it is rather expedient to use the dilute solutions. Therefore, the concentration of all the solutions in this case is taken to be 0.71 mole/l.

The ratios I_e/I_p of the intensity of the Raman line at 724 cm.$^{-1}$ (I_e) and that of the line at 645 cm.$^{-1}$ (I_p) are shown in the second column of Table V. The ratios of the relative intensities change markedly when changes are made in the solvents or concentration of the solutes. For the mixed solvents the mole fractions of the solvents are indicated in the last column of the table.

Regarding the dibromo derivative the analogous measurements were also made by the visual method. The results are shown in Table VI. The mole fraction of the solute in the carbon tetrachloride is 0.10 and that of the solute in the acetone solution is 0.064.

TABLE VI

Solvents	I_e/I_p
Carbon tetrachloride	10/8
Acetone	10/3

Discussion of the Results

It is not immediately clear that the dihalogenocyclohexanes prepared from 1,4-cyclohexanediol, as described above, are 1,4-dihalogenocyclohexanes. However, from the fact that the dipole moments of these compounds are zero or nearly zero, there can be only the following two possibilities. The compounds may be either (1) *trans*-1,4-dihalogenocyclohexanes or (2) *trans*-1,2-dihalogenocyclohexanes in the hypothetical case in which they had only the configuration (1p, 2p) in the dilute solutions. The latter is not the case, however, because we have recently found that *trans*-1,2-dihalogenocyclohexanes are different compounds and in the solution they stand in the dynamic equilibrium (1p, 2p) $\rightleftarrows$ (1e, 2e). As for the 1,2-dihalogeno derivatives we shall report in detail sometime in the future. Therefore, these compounds must be *trans*-1,4-dihalogenocyclohexanes. Furthermore, the same conclusion is supported by the investigations based on electron and X-ray diffraction, as reported by Hassel, *et al.*[5,6]

From the fact that the Raman spectra of these compounds are capable of dividing into two groups, we came to the conclusion that one group of the

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[9] Within the accuracy of the technique for obtaining intensities it was found that peak intensities could be used instead of areas. As a result the intensities given in Table V and IX are all peak intensities.

Raman lines is due to the one of the two configurations which *trans*-1,4-dihalogenocyclohexanes possess, and the other group is due to the other configuration. Then, the question is how to assign the two groups of the Raman lines to two different configurations. As for the dibromo derivative the answer to this question is given by the fact that the molecules have only the configuration (1e, 4e) in the solid state, as shown by the investigation of Hassel, *et al.*,[6] based on X-ray diffraction. By use of the fact mentioned above and by the comparison of the Raman spectra of both compounds obtained in the solid and solution states, it is known that the configuration of *trans*-1,4-dichlorocyclohexane persisted in the solid state is probably also (1e, 4e). It is concluded, therefore, that the group of the Raman lines which remain in the solid spectrum and the intensities of which are strengthened in the spectrum of benzene solution in comparison with that of carbon tetrachloride solution is attributed to the configuration (1e, 4e) and the other group to the configuration (1p, 4p), and that in the solutions they stand in the dynamic equilibrium between the configuration (1e, 4e) and (1p, 4p). According to these conclusions the configurations by which each of the Raman lines is to be scattered are shown in the third column of Table III and IV.

To confirm the conclusions stated above we have calculated the skeletal frequencies of these molecules. To do this we have first to determine the force constants in cyclohexane molecule, the parent molecule of cyclohexane derivatives. Fortunately, however, Shimanouchi and one of the present authors[10] have recently studied the skeletal modes of vibration of cyclohexane molecule by Wilson's method[11] assuming the Urey–Bradley field,[12] in the same way in which Shimanouchi[13] frequently studied the normal or skeletal frequencies of vibration of various molecules with success.

As this molecule has the symmetry of D_{3d}, the force constants are almost unambiguously determined. The force constants obtained are

$$K = 3.55 \times 10^5 \text{ dyne/cm.} \quad H = 0.35 \times 10^5 \text{ dyne/cm.}$$
$$F = 0.20 \times 10^5 \text{ dyne/cm.} \quad F' = 0.0 \times 10^5 \text{ dyne/cm.}$$

where K is the force constant of stretching vibration of CH_2–CH_2, H is that of deformation vibration of CH_2–CH_2–CH_2, and F and F' are the repulsive force constants between the non-bonded and nearest CH groups. As these notations are the same as those used by Shimanouchi, no detailed explanations will be necessary.

The assignments determined by our results thus obtained nearly agree with those determined by Pitzer, *et al.*[3] However, our assignments differ in the following two points from those of Pitzer, *et al.*, *viz.*, the infrared active deformation vibration in class A_u can be confidently assigned by us to the 676 cm.$^{-1}$ band, and the infrared active stretching vibration in class E_u to the 907 cm.$^{-1}$ band, whereas according to Pitzer, *et al.*, the former is assigned to 522 cm.$^{-1}$ and the latter to 864 cm.$^{-1}$. In these calculations we found that it is almost impossible to determine the force constants in such a way as to make the assignments agree with those by Pitzer, *et al.* It is highly probable that the weak infrared band at 522 cm.$^{-1}$ is the combination tone of 907—382 cm.$^{-1}$. After this calculation had been done, we learned that the analogous calculation for cyclohexane molecule had been done by Ramsay and Sutherland[14] by a quite different method. The force constants obtained by them are somewhat different from those obtained by us. However, their assignments completely agree with ours.

Subsequently, we calculated the skeletal modes of vibration of *trans*-1,4-dihalogenocyclohexanes by the same method as mentioned before, on the assumption that the force constants obtained above are adequate for cyclohexane ring. The force constants regarding halogen atoms in these molecules are approximately estimated from those of 1,2-dichloroethane[15] and carbon tetrabromide[16] as

$$K_{Cl} = 2.30 \times 10^5 \text{ dyne/cm.}$$
$$F_{Cl} = 0.48 \times 10^5 \text{ dyne/cm.}$$
$$H_{Cl} = 0.30 \times 10^5 \text{ dyne/cm.}$$
$$F'_{Cl} = 0.0 \times 10^5 \text{ dyne/cm.}$$

and

$$K_{Br} = 2.26 \times 10^5 \text{ dyne/cm.}$$
$$F_{Br} = 0.35 \times 10^5 \text{ dyne/cm.}$$
$$H_{Br} = 0.20 \times 10^5 \text{ dyne/cm.}$$
$$F'_{Br} = 0.0 \times 10^5 \text{ dyne/cm.}$$

The meaning of these notations will be clear.

The predictions of group theory concerning the symmetry properties of the skeletal modes of vibration of these molecules which have the symmetry of C_{2h} are given in Table VII. Therefore, though the vibrational secular determinants (constructed by Wilson's method) corresponding to the configuration (1e, 4e) and (1p, 4p) are eighteen orders, respectively, the determinant can be broken up at once, if one uses the generalized coördinates with the proper symmetry, into the following orders: six of A_g, three of B_g, four of A_u and five of B_u. Since we are concerned only with the Raman spectra, we have only to solve the secular determinants of six orders and three orders as regards both configurations of these compounds. As our purpose is to assign the observed Raman spectra we do not intend to determine the force constants in such a way as to make the calculated frequencies completely agree with the observed ones by repeated calculations. The calculated frequencies are used then as a satisfactory guide in assigning

TABLE VII

	The number of skeletal modes of vibration	Selection rule
A_g	6	Raman active
B_g	3	Raman active
A_u	4	Infrared active
B_u	5	Infrared active

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[10] T. Shimanouchi and K. Kozima, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 468 (1951) (in Japanese).

[11] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[12] H. C. Urey and C. A. Bradley, *Phys. Rev.*, **38**, 1969 (1931).

[13] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

[14] D. A. Ramsay and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A190**, 245 (1947).

[15] S. Mizushima, Y. Morino and T. Shimanouchi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **40**, 87 (1942).

[16] T. Shimanouchi, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **21**, 834 (1942).

the observed frequencies to their respective configurations. The assignments thus made completely agree with those obtained by the experiments as shown in the fourth column of Table III and IV. As far as the skeletal modes of vibration are concerned, the Raman spectra are almost completely assigned to only A_g as shown in the fifth column of the tables.

In the next place, to determine which of these two configurations predominates in the solution state seemed to be of considerable interest. To do this, first making the usual assumption that the relative intensity of Raman line of each component in solutions is proportional to the concentration as in equation (1), and using the results of the variations of the relative intensity with solvents as shown in Table V, we tentatively estimated the variations of the difference of the potential energy between the configuration (1e, 4e) and (1p, 4p) of *trans*-1,4-dichlorocyclohexane with solvents. Namely, on the assumption stated above we may write the equation

$$I_e/I_p = S_eN_e/S_pN_p \qquad (1)$$

where N_e or N_p is the number of molecules, which have the configuration (1e, 4e) or (1p, 4p), and S_e/S_p is the ratio of the two intensities, each of which is due to the one molecule of each configuration shown by the suffixes, respectively. It is evident that the abundance ratio N_e/N_p is given by equation (2)

$$N_e/N_p = f_e/f_p \exp(-\Delta U/RT) \qquad (2)$$

where f_e and f_p are, respectively, the partition function of each of the configurations shown by the suffixes, ΔU is the difference of the potential energy between the two forms, R is the gas constant, and T the absolute temperature. By combining equations (1) and (2) and on the assumption that the relation $f_e = f_p$ is approximately satisfied in this case, we then obtain equation (3)

$$I_e/I_p = S_e/S_p \exp(-\Delta U/RT) \qquad (3)$$

By the application of equation (3) to any two of the solutions as listed in Table V, we may write

$$I'_e/I'_p = S_e/S_p \exp(-\Delta U'/RT)$$
$$I''_e/I''_p = S_e/S_p \exp(-\Delta U''/RT)$$

From these equations we obtain

$$\frac{I'_e}{I'_p}\Big/\frac{I''_e}{I''_p} = \exp(-(\Delta U' - \Delta U'')/RT) \qquad (4)$$

By the use of equation (4) and the data of the relative intensities as shown in Table V, we may calculate the variations of ΔU with the solvents. For instance, by calculations concerning the dilute carbon tetrachloride and benzene solutions it may be shown that the (1p, 4p) form of *trans*-1,4-dichlorocyclohexane becomes more stable in the former solvent than in the latter by about 0.58 kcal. per mole. Since from the foregoing, however, the value of S_e/S_p cannot be obtained, the value of ΔU itself in each solvent cannot be calculated. In order to obtain the value of ΔU the variations of the relative intensities with temperature have to be measured as reported before.[17,18] Therefore, intensity measurements of the Raman spectrum of this compound in solution were made in order to see whether there was any temperature dependence of the relative intensities of the Raman bands of the two forms. However, the intensity change was not large enough to allow us to estimate ΔU. Then we had to use another method. According to a method as described in the Appendix in detail, we were able to estimate S_e/S_p of the compound to be 2.0. Therefore, by the application of equation (3) with the value shown in Table V, we can obtain ΔU in each solvent as shown in Table VIII.

TABLE VIII

THE VALUES OF ΔU IN THE VARIOUS SOLVENTS

Solvents	Kcal./mole	Solvents	Kcal./mole
Carbon tetrachloride	0.67	Benzene	0.09
Cyclohexane	.49	Cyclohexane–ether I	.43
n-Heptane	.31	Cyclohexane–ether II	.37
Ethyl alcohol	.12	Cyclohexane–ether III	.28
Diethyl ether	.10	Cyclohexane–ether IV	.21

From Table VIII it is easily recognized that the (1p, 4p) form, as a rule, is more stable in the nonpolar solvents than in the polar solvents, with an exception of the benzene solvent. It seems to be one of the striking points emerging from these studies that the (1e, 4e) form of *trans*-1,4-dichlorocyclohexane is generally less stable in the various solvents, although in the solid state the (1e, 4e) form is more stable.

Acknowledgment.—The authors are grateful to Professor S. Mizushima, Professor Y. Morino and Dr. T. Shimanouchi, of Tokyo University, for their interest and kind advice during the course of the work.

Appendix

On the assumption as used in equation (1), we may write the following formulas concerning the benzene and benzene–cyclohexane solutions of *trans*-1,4-dichlorocyclohexane

$$\begin{aligned} I'_P/I'_B &= S_pN'_p/S_BN'_B,\ I'_e/I'_B = S_eN'_e/S_BN'_B, \\ I''_P/I''_B &= S_pN''_p/S_BN''_B,\ I''_e/I''_B = S_eN''_e/S_BN''_B, \end{aligned} \qquad (5)$$

where the notations have the same meaning as those used in equation (1); the notations with suffix B refer to benzene, and ′ or ″ is added to the notations depending on whether they refer to the former solution or the latter. If the relative intensities in the both solutions are calculated on the basis of 10 for the intensity of the band of benzene at 606 cm.$^{-1}$ we may write

$$N'_P/N''_P = I'_P N'_B/I''_PN''_B,\ N'_e/N''_e = I'_eN'_B/I''_eN''_B \qquad (6)$$

As our purpose was to estimate S_e/S_p by the application of equation (6), we carried out the following measurements. Namely, we measured in the benzene and the benzene–cyclohexane solution, at room temperature, the relative intensity of the band at 645 cm.$^{-1}$ of the (1p, 4p) form and that of the band at 724 cm.$^{-1}$ of the (1e, 4e) form, comparing with that of the band at 606 cm.$^{-1}$ of benzene. The results obtained are shown in Table IX.

TABLE IX

THE RELATIVE INTENSITIES MEASURED IN THE SOLUTIONS BOTH OF WHICH CONTAIN BENZENE

	Molar fractions			Relative intensities		
Solvents	*t*-1,4-$C_6H_{10}Cl_2$	C_6H_6	C_6H_{12}	I_P	I_e	I_B
Benzene	0.312	0.688	0.000	9.5	11.2	10.0
Benzene–cyclohexane	.091	.190	.719	11.6	11.7	10.0

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

(18) A. Langseth and H. J. Bernstein, *J. Chem. Phys.*, **8**, 410 (1940).

If the volume of the former solution is V' and that of the latter is V'', it is evident that

$$N'_B = f'_B N_A/V',\ N''_B = f''_B N_A/V'',\ N'_P + N'_e = f'_t N_A/V',\ N''_P + N''_e = f''_t N_A/V'' \quad (7)$$

where f'_t and f'_B denote, respectively, the molar fraction of *trans*-1,4-dichlorocyclohexane and that of benzene in the former solution, f''_t and f''_B have, respectively, the same meaning concerning the latter, and N_A is the Avogadro number. By combining equations (6) and (7), we may write

$$X'_P/X''_P = I'_P f'_B f''_t / I''_P f''_B f_t \quad (8)$$

where X'_P and X''_P are given by the relations (9)

$$X'_P = N'_P/(N'_e + N'_P),\ X''_P = N''_P/(N''_e + N''_P) \quad (9)$$

Similarly, we may write

$$X'_e/X''_e = I'_e f'_B f''_t / I''_e f''_B f'_t \quad (10)$$

where X'_e and X''_e denote the similar fractions as represented in equation (9), and it is evident that

$$X_e + X'_P = X''_e + X''_P = 1 \quad (11)$$

From equations (8), (10) and (11) we can calculate the values for X'_e, X'_P, X''_e and X''_P. The values for X'_P and X''_P thus obtained are, respectively, 0.58 and 0.66. Therefore, by using equation (1) the value for S_e/S_p is estimated to be 2.0.

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Spectra of Azlactones. I. Azlactones Derived from Substituted Benzaldehydes and Hippuric and Nitrohippuric Acids

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RECEIVED FEBRUARY 20, 1952

The absorption spectra of a series of azlactones obtained by condensation of hippuric acid, *o*-, *m*- and *p*-nitrohippuric acids, with benzaldehyde and substituted benzaldehydes, have been determined in acetic acid solution up to 255 mμ. All the azlactones show a band of high intensity, each with a maximum varying with substitution, at 346–430 mμ. In some azlactones, a second, less intense band, with a maximum at 256–310 mμ is found. It is absent in azlactones where a nitro group is placed ortho or meta, in phenyls R_1 or R_2 (Formula I). Some correlations, between the position of the first maximum in the absorption spectra and the substituents, are described.

The azlactones, obtained by condensation of aromatic aldehydes with hippuric acid by the Plöchl–Erlenmeyer reaction, contain a conjugate system of two double bonds with two end phenyl nuclei, R_1 and R_2 (I). The fact that the azlactones can be easily prepared and that a wide variation of substitution in one or both phenyls is a possibility, makes this class of compounds particularly favorable for the study of the influence of substituents on the absorption spectra.

The first reports on the absorption spectra of the azlactones are those of Asahina[1] whose data are very difficult to interpret because in many cases the data are given only graphically. Recently, Carter and Hinman[2] reported the ultraviolet absorption spectrum of one azlactone, the 2-phenyl-4-*p*-methoxybenzal-5-oxazolone (No. 13), while Bennett and Niemann[3] reported the absorption spectra in the ultraviolet and the visible of 2-phenyl-4-*p*-fluorobenzal oxazolone and of 2-phenyl-4-*m*-fluorobenzal oxazolone. Both Asahina and Carter found a band with a maximum at about 250–260 mμ. At longer wave lengths Bennett and Niemann found a stronger band with a maximum at about 360–390 mμ. More recently Schueler and Wang[4] determined the absorption spectra of 28 azlactones and except for a few cases, found two maxima, at shorter wave lengths than other workers, one at about 220–232 mμ, the other at 284–323 mμ.

The authors have determined the absorption spectra for 71 azlactones in acetic acid solution (Table I, Part A) and for 5 of the above mentioned azlactones in absolute ethanol (Table I, Part B).

Unfortunately, owing to the instability of the azlactones derived from the nitrohippuric acids, in dilute ethanol solutions and to their insolubility in other less absorbing solvents, the authors determined the spectra of the azlactones studied in acetic acid solution, limiting the observations up to 255 mμ. The spectra of some of the azlactones derived from hippuric acid, in ethanol (No. 1, 13, 24, 28 and 48), showed in each case that the maxima were not displaced by changing the solvent. Slight variations in the value of ϵ were observed.

The spectrum of all azlactones showed an intense absorption band, with a maximum at about 361–430 mμ, varying with substitution. In some cases a second less intense band, with a maximum at 256–310 mμ was found. This same band was definitely absent, in azlactones where a nitro group is placed in ortho or meta position, in one or both phenyls R_1 and R_2.

The authors' experimental data for 12 of the above mentioned 71 azlactones does not agree with that of Schueler and Wang.[4] In each case the maximum is always displaced toward the longer wave lengths and are located in the same region as reported by Carter and Hinman[2] and by Bennett and Niemann.[3]

In the case of the particular azlactone studied by Carter and Hinman[2] the authors were able to check their data (see Table I, Part B, No. 13).

For most of the azlactones studied by Schueler and Wang[4] and the authors, the latter found a positive difference of about 74–77 mμ between their data and that reported by Schueler and Wang[4] for the maximum present at longer wave lengths, and

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[1] T. Asahina, *Bull. Chem. Soc. Japan*, **4**, 202 (1929); **5**, 354 (1930).

[2] H. M. Carter and J. W. Hinman, *J. Biol. Chem.*, **178**, 403 (1949).

[3] E. L. Bennett and C. Niemann, THIS JOURNAL, **72**, 1803 (1950).

[4] F. W. Schueler and S. C. Wang, *ibid.*, **72**, 2220 (1950); Schueler and C. Hanna, *ibid.*, **73**, 3528 (1951).