

tracted with ether and these extracts were dried and concentrated to yield an oily liquid which was chromatographed on an alumina column. The liquid was put on the column with benzene and eluted with benzene. Bromobenzene and biphenyl were removed and finally 1.2 g. (32%) of acetophenone, m.p. of 2,4-dinitrophenylhydrazone, 243–245° (lit.²⁴ m.p. 250°), was eluted.

Anal. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.00; N, 18.67. Found: C, 55.94; H, 3.68; N, 18.33.

Further elution with benzene and then methylene chloride removed nothing from the column. Elution with ethyl acetate produced 1.7 g. (28%) of *o*-hydroxybenzophenone, m.p. of 2,4-dinitrophenylhydrazone, 250–252° (lit.²⁵ m.p. 253°).

Anal. Calcd. for $C_{13}H_{14}N_4O_6$: C, 60.32; H, 3.70; N, 14.81. Found: C, 60.59; H, 3.84; N, 14.60.

Reduction of 4-Hydroxycoumarin with Lithium Aluminum Hydride.—To a slurry of 19.0 g. (0.5 mole) of lithium aluminum hydride in 200 ml. of dry ether was added a slurry of 16.2 g. (0.1 mole) of 4-hydroxycoumarin in 200 ml. of dry benzene. The resulting mixture was heated under reflux for 6 hr., then allowed to stand at room temperature overnight. The excess hydride was destroyed with ethanol and the mixture was poured onto ice and hydrochloric acid. (In one work-up Rochelle salts were used to decompose the mixture and the same product mixture was obtained.) The organic layer was separated, dried and concentrated to yield a viscous brown oil which was distilled. The distillate proved to be *o*-hydroxypropiofenone, m.p. of 2,4-dinitrophenylhydrazone, 189–190° (lit.²⁶ m.p. 189°), yield 5.7 g. (38%).

(24) R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 263.

(25) G. D. Johnson, *THIS JOURNAL*, **73**, 5888 (1951).

(26) C. Torres and J. Amargos, *Anales soc. espana fis. quim.*, **21**, 37 (1933); *C. A.*, **27**, 1624 (1933).

Anal. Calcd. for $C_{16}H_{14}N_4O_6$: C, 54.54; H, 4.24; N, 16.97. Found: C, 54.65; H, 4.16; N, 16.86.

The residue from the distillation was chromatographically purified on alumina to yield a pale yellow solid, m.p. 106–109°, yield 6.9 g. (35%). This solid was converted to a dibenzoate, m.p. 91–93°. *o*-Hydroxycinnamyl alcohol is reported²⁷ to melt at 110° and to form a dibenzoate, m.p. 92.5–93.5°.

Reaction of *o*-Hydroxydibenzoylmethane with Phenylmagnesium Bromide.—To 40 ml. of a 3 *M* ethereal solution of phenylmagnesium bromide in 200 ml. of dry benzene was added 4.8 g. (0.02 mole) of *o*-hydroxydibenzoylmethane²⁸ in 150 ml. of dry benzene. During the addition the mixture took on a green color which darkened rapidly after heating was begun. The mixture was heated under reflux for 3 hr. and then decomposed with ammonium chloride solution. The organic extracts were concentrated and steam distilled to yield an orange residue which crystallized from warm ethanol, yield 5.3 g. (74%). Recrystallization from ethanolic yielded white plates, m.p. 131–132°. This material did not depress the melting point of the 2,2,4-triphenylbenzopyran obtained from the 4-hydroxycoumarin reaction.

Reaction of Flavone with Phenylmagnesium Bromide.—To 80 ml. of a 3 *M* solution of phenylmagnesium bromide²² in 200 ml. of dry benzene was added a solution of 11.1 g. of flavone²⁸ in 150 ml. of benzene. The resultant mixture was heated under reflux for 3 hr. and then decomposed with ammonium chloride. The organic extracts were steam distilled and the orange residue was crystallized from ethanol, yield 9.0 g. (50%). Recrystallization from ethanol produced white plates of 2,2,4-triphenylbenzopyran, m.p. 130–132°.

(27) F. A. Hochstein, *THIS JOURNAL*, **71**, 395 (1949); P. Karrer and P. Banerjee, *Helv. Chim. Acta*, **32**, 1692 (1949).

(28) T. S. Wheeler, *Org. Syntheses*, **32**, 72 (1952).

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[CONTRIBUTION FROM THE SCHOOL OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA AND THE UNIVERSITY OF SAN FRANCISCO]

Dipole Moments, Spectra and Structure of α -Halocyclohexanones, α -Halocyclopentanones and Related Compounds

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The dipole moments of α -bromo- and α -chlorocyclohexanones are not consistent with the halogens occupying axial positions in these compounds as has been concluded by others from infrared data. Contributions from forms with a separation of charge are not able to account for the observations. Some contribution from flexible forms appears to be a way of adequately explaining the observed facts. The α -halocyclohexanones show a larger variation in dipole moment in different solvents than do the α -halocyclopentanones. The $n \rightarrow \pi^*$ blue shift shows a greater variation with different cyclohexanones than with different cyclopentanones. The 5.6 kcal. usually assigned as the difference between the boat and chair form of cyclohexane is more nearly the difference in energy between the stretched conformation of the flexible form and the chair form. Cyclohexane derivatives likely to have appreciable contributions from flexible forms are (1) those with an atom in the ring with other than sp^3 binding and a strong dipole on an adjacent atom, (2) those with two or more atoms in the ring with other than sp^3 binding such as heteroatoms or carbonyl carbons. *N,N'*-Dinitropiperazine probably exists to an appreciable extent in the flexible form. The ultraviolet spectrum of cyclopentanone in heptane has much fine structure while that of cyclohexanone has virtually none.

Corey¹ has reported that β -bromocyclohexanone and α -chlorocyclohexanone have the halogen atoms in the axial position. This conclusion was based on the observation that the introduction of an α -bromine atom caused a small shift in the frequency of the carbonyl band coupled with the hypothesis of Jones, *et al.*,² "that large positive shifts of the C=O stretching frequency on α -bromination in the cyclohexanone ring system in the chair configuration occur only when the bromine atom occupies an equatorial position." The

(1) E. J. Corey, *THIS JOURNAL*, **75**, 2301 (1953).

(2) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *ibid.*, **74**, 2828 (1952).

latter hypothesis was derived from measurements on steroids where the attachment of other rings would cause the cyclohexane ring to be held in a rigid conformation. One cannot be certain, however, that the same hypothesis would apply to an unattached cyclohexane ring such as is present in the compounds under consideration.

The dipole moments of these compounds should, on the other hand, give a direct, unequivocal answer as to whether the halogens are axial since the theoretical dipole moments are 2.30 *D* axial and 4.22 *D* equatorial.

The recent papers by Hassel³ and by Kwestroo,

(3) O. Hassel, *Quart. Rev.*, **7**, 22 (1953).

Meijer and Havinga⁴ have pointed out that while most cyclohexane compounds have the chair form, with certain types of cyclohexane derivatives there is considerable evidence that the compounds exist in a flexible form. The fact that 1,4-cyclohexanedione has a moment of 1.3 *D*⁵ and partial enolization appears to be ruled out as an explanation suggests that the compound does not exist in a chair form. A calculation by Oesterhoff⁶ shows that a flexible form is probably the stable one for 1,4-cyclohexanedione and the theoretical dipole moment of this form is in agreement with the experimental dipole moment. Dallinga⁷ found electron diffraction patterns of 1,2-*trans*-dichlorocyclohexane and 1,1,2-trichlorocyclohexane in the vapor state to be best interpreted by assuming the molecule to be in the so-called stretched conformation of the flexible form.

Beckett, Pitzer and Spitzer⁸ concluded that while cyclohexane is predominantly in the chair form at room temperature larger and larger contributions from the boat form are necessary to account for the heat capacity as the temperature increases.

It has been stated⁴ that the flexible form is often misleadingly represented by the boat, bed or tub form which is the form least likely to occur. The reason for this is the near approach of hydrogens on the 1 and 4 carbon atoms. The extra energy of 5.6 kcal. that Beckett, Pitzer and Spitzer⁸ have calculated for the boat conformation takes into account only the two opposed CH₂ pairs and does not include any term for the interaction between hydrogens across the ring. Since the other flexible conformations, including the so-called stretched conformation, have essentially the same potential energy as far as interaction between consecutive CH₂ groups is concerned^{6,8} and do not have hydrogens on 1 and 4 carbon atoms close enough to add appreciable additional energy, it follows that the 5.6 kcal. represents more correctly the excess energy of the other flexible forms including the stretched conformation rather than that of the extreme boat conformation.

When heteroatoms or carbonyl groups replace CH₂ groups in the cyclohexane ring, the energies of the flexible forms are going to be less due to fewer interactions between consecutive CH₂ groups and to more favorable angles in the rings. Replacing a CH₂ with a carbonyl reduces from 6 to 4 the adjacent CH₂ groups and replaces an atom having sp³ binding and bond angles of 109° 28' with an atom having sp² binding and bond angles of 120°. The change in angles would tend to make the ring less puckered and more flexible.

In view of the fact that additional accurate data are needed to elucidate the structures of these compounds,⁴ we have measured the dipole moments of α -halocyclohexanones and α -halocyclopentanones in three different solvents and have also

(4) W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. trav. chim. Pays-Bas*, **73**, 717 (1954).

(5) C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.*, 1696 (1935).

(6) L. J. Oesterhoff, Thesis, Leiden, 1949; P. Hazebroek and L. J. Oesterhoff, *Disc. Faraday Soc.*, **10**, 82 (1951).

(7) G. Dallinga, Thesis, Leiden, 1951.

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

investigated their ultraviolet and infrared spectra.

Experimental

The compounds were fractionally distilled through a Todd precise fractionation assembly with a 90-cm. column.

α -Chlorocyclopentanone was prepared by the method of Kotz, *et al.*⁹; b.p. 62° (5 mm.), *n*_D¹⁸ 1.4778.

α -Chlorocyclohexanone was made by the method given in Organic Syntheses,¹⁰ b.p. 90° (15 mm.), *n*_D²⁰ 1.4830.

α -Bromocyclohexanone was prepared by the method of Schmid and Karrer¹¹; b.p. 78.5° (5 mm.), *n*_D²⁵ 1.5095.

trans-1,2-Dichlorocyclopentane was prepared by the method of Mousseron, *et al.*¹²; b.p. 48° (19 mm.), *n*_D²⁰ 1.4798.

α -Bromocyclopentanone.—A mixture of 21 g. of cyclopentanone, 30 ml. of water, 50 ml. of carbon tetrachloride and 14 g. of calcium carbonate was heated to 55°. The mixture was stirred vigorously while 40 g. of bromine was introduced with a stream of nitrogen at such a rate that the heat of the reaction maintained the temperature between 55 and 58° and that the bromine was decolorized as soon as it entered the mixture with a total time of addition of about 40 minutes. The carbon tetrachloride layer was separated and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* under nitrogen and the product fractionated under nitrogen, giving a colorless liquid, b.p. 80° (8 mm.), *n*_D¹⁸ 1.502 (lit.¹¹ b.p. 68° (2 mm.) and *n*_D¹⁸ 1.5105). The product is unstable when exposed to air and light at room temperature, but can be kept for some time when stored under nitrogen below zero degrees and protected from light.

α -Bromocyclopentanone was also prepared by the reaction of cyclopentanone with N-bromosuccinimide, but distillation of the product so obtained often resulted in a vigorous decomposition of the product with evolution of HBr. No such difficulty was encountered with the product obtained by the method described above.

Dipole Moments.—The dipole moments were calculated using the equation and method of Halverstadt and Kumler.¹³ The plots of ϵ_{12} versus ω_2 and ν_{12} versus ω_2 were straight lines within the limits of experimental error and the values of ϵ_1 and ν_1 were obtained by extrapolating the ϵ_{12} and ν_{12} values to zero weight fraction. The solute molar electronic polarization P_{E2} are the molar refractions as calculated from the electron group refractions.

Results and Discussion

The theoretical dipole moments in Table I and also the angles in Table II were calculated using a value of 1.91 *D* for the C-Cl and C-Br moment.¹⁴ This was calculated from *cis*-1,2-dichlorocyclohexane and *cis*-1,2-dibromocyclohexane, which were assumed to have the chair configuration. The moment is lower than that found for cyclohexyl chloride 2.24 because of the cancellation of inductive effects and lowering of the C-X moments when these are close together.¹⁵ The C=O moment will also be lowered somewhat by its proximity to the C-X moment. The value of the C=O moment of 2.83 *D* was calculated from the observed moment of α -chlorocyclopentanone, using 1.91 for the C-Cl moment and assuming a flat five-membered ring with an angle of 79° 31' between the two dipoles. This value is smaller than the values for cyclohexanone due to the lowering

(9) A. Kotz, K. Blendermann, E. Karpoti and R. Rosenbush, *Ann.*, **400**, 47 (1913).

(10) *Org. Syntheses*, **25**, 22 (1945).

(11) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(12) M. Mousseron, R. Granger and J. Valette, *Bull. soc. chim.*, 244 (1946).

(13) I. F. Halverstadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

(14) P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3462 (1955).

(15) A. Tulinskie, A. DiGiacomo and C. P. Smyth, *ibid.*, **75**, 3552 (1953).

TABLE I

Compound	Solvent ^a	ϵ_1	ν_1	α	β	P_{20}	P_{E2}	Obsd.	μ	
									Theor.	
α -Chlorocyclopentanone	H	1.9189	1.48132	7.8875	-0.69714	292.40	27.97	3.63		
	B	2.2759	1.15246	11.7167	-.320	292.14	27.97	3.62		
	D	2.2109	0.977395	14.080	-.200	302.56	27.97	3.69		
α -Bromocyclopentanone	H	1.9124	1.48138	5.3125	-.8375	275.93	30.87	3.49		
	B	2.2760	1.15243	7.871	-.51857	273.45	30.87	3.47		
	D	2.20415	0.97800	9.900	-.34667	297.38	30.87	3.64		
α -Chlorocyclohexanone	H	1.9123	1.48136	6.375	-.61375	272.25	32.59	3.45	4.22	2.30
	B	2.2691	1.14768	11.400	-.2783	319.82	32.59	3.78		
	D	2.2124	0.97817	13.983	-.11167	339.67	32.59	3.91		
α -Bromocyclohexanone	H	1.9195	1.48168	4.600	-.81143	263.49	35.49	3.37	4.22	2.30
	B	2.2779	1.15196	7.3833	-.490	281.86	35.49	3.50		
	D	2.2039	0.97798	9.080	-.284	302.07	35.49	3.64		
<i>trans</i> -1,2-Dichlorocyclopentane	H	1.91165	1.48138	1.350	-.646	81.58	32.83	1.56		1.78
	B	2.2702	1.15193	1.980	-.306	87.15	32.83	1.64		
	D	2.2119	0.97804	2.400	-.128	89.19	32.83	1.67		
<i>trans</i> -1,2-Dibromocyclopentane ^b	D	2.2029	0.97380	1.270	-.417	84.20	38.63	1.51		1.78

^a H, *n*-heptane; B, benzene; and D, dioxane. ^b This compound was made by H. K. Hall, Jr., W. G. Young and S. Winstein and the details of preparation and the constants are to be published in another paper.

resulting from the proximity of the C=O and C-X dipoles. This same value of the C-X moment, 1.9 or 1.91, has been used by both Tulinskie, DiGiacomo and Smyth,¹⁵ and Bender, Flowers and Goering,¹⁴ in their calculations concerning compounds having two halogens near one another. Since the C-X moment must be reduced to some extent in such compounds for the reasons the above authors¹⁵ have given and this moment differs from that of cyclohexyl chloride by only 0.33, it is not likely that the calculated moment is off by more than about 0.1. We are justified in using the same value in the α -haloketones because here also the adjacent dipole would reduce the C-X moment below what it was in cyclohexyl chloride. In fact, since the C=O dipole is larger than the C-X dipole, one might expect the reduction to be greater here than in the dihalogen compounds. However, if we had used a smaller value for the C-X moment in the α -haloketones it would make the discrepancy even greater between the observed moments and those calculated for the axial compounds.

The assumption that the ring is flat in α -chlorocyclopentanone is probably not strictly true and therefore the angle between the C-Cl and C=O dipoles is probably somewhat different from the values we have assumed of $79^\circ 31'$. However, the fact that the calculated C=O moment comes out 2.83 which is a bit less than that of cyclopentanone 3.00 suggests that the angle we have assumed is not greatly different from the correct one. The error in the axial and equatorial positions is probably not greater than 0.2 *D*. The experimental error is probably of the order of 0.02 or 0.03 *D*.

The degree of compliance between observed and theoretical dipole moments in compounds of this type where equilibrium between the equatorial, flexible and axial forms is not expected and is not present to any appreciable extent is illustrated by the 2-(*p*-halophenyl)-cyclohexanones.¹⁶ Here the other dipole is far removed from the carbonyl so dipole interaction is not a factor in favoring a flexi-

ble form. The values for the chloro and bromo compounds for μ (observed), μ (equatorial), and μ (axial) are 4.25, 4.33, 2.40 and 4.11, 4.30 and 2.40. There is thus only 0.08 and 0.19 *D* difference between the observed moments and the calculated moments with the *p*-halophenyl groups in the equatorial position. With the experimental and calculation errors of this magnitude, the fact that the differences between the theoretical axial moments and the average observed moments as shown in Table I vary from 1.20 to 1.41 *D* with the α -halocyclohexanones is reasonably conclusive proof that the compounds do not have the halogens in the axial position. Particularly is this so when it is realized that dipole interaction would cause the angle between dipoles to spread which would reduce the moment. Therefore, the actual moments for the compounds with the halogens in axial positions would be something less than 2.30 so the discrepancy is even greater than 1.20 to 1.41 *D*.


The differences between the theoretical moments with the halogens in the equatorial position and the average observed moments are considerably less, namely, 0.51 to 0.72 *D*. Furthermore, the observed moments are smaller than the theoretical moments so some of this difference could be caused by dipole interaction causing a spreading of the angles between the dipoles. If one were confined to an explanation that the molecules were either in the axial or equatorial conformations, the dipole moment evidence clearly favors the equatorial. One is not so restricted, however, and the comparatively large variation of moment of the α -halocyclohexanones with change of solvent which is not exhibited by the cyclopentanones indicates that the α -halocyclohexanones change their conformation quite readily when their environment is altered by changing the solvent. The most obvious explanation is that there is a shift in equilibrium between the axial and equatorial conformations. Since the molecule must go through the flexible conformation in going from the axial to the equatorial conformation, the flexible form will make an appreciable contribution if

(16) A. C. Huitric and W. D. Kumler, *THIS JOURNAL*, **78**, 614 (1956).

its energy is comparable to the energy of the equatorial or the axial form whichever is lower.

The observed dipole moments could be accounted for by having the molecules in the chair form with the halogens equatorial and the angle between the dipoles increased by rotation about bonds due to dipole interaction, or it could be accounted for by the molecule existing in a flexible form, or by contributions from the equatorial, flexible and axial forms.

Another interpretation of the data that must be

considered is that forms such as  may be

responsible for the observed moment being over 1.2 to 1.4 D higher than that calculated for the axial configuration. Corey and Burke¹⁷ have pointed out that contributions from such forms can account for the apparent anomaly that with 6-halo-2,2-dimethylcyclohexanone and 7-halospiro(4,5)-decane-6-one, the chloro compounds give evidence of having less of the axial isomer than do the bromine compounds. Contributions from such forms also are consistent with the ultraviolet data. The greater overlap of the $sp^3 \rightarrow p$ orbital made available by the leaving halogen, and the p orbital of the carbonyl carbon, when the halogen is axial compared with when it is equatorial, is the reason given for a greater contribution of such forms when halogen is axial. The greater ease with which bromine compared with chlorine goes into the X^+ ion is the reason for the larger contribution of this form with bromine.

An appropriate contribution from such forms could account for the observed moment. A necessary consequence of an appreciable contribution from such forms, however, is that *the compound no longer has the typical axial configuration*. If the compound were all in this form there would be no axial and equatorial positions on the 2-carbon as it would have sp^2 binding with the σ -bonds at 120° and the positively charged halogen ion is unattached. For the $sp^3 \rightarrow p$ orbital to become available and overlap the carbonyl p orbital, the halogen must *first leave* and *if it leaves it is no longer in its typical axial position*. The compound is, of course, not all in this form but insofar as the form contributes the halogen in the resonance hybrid must of necessity be proportionately displaced from its typical axial position. So if contributions from these forms are responsible for the observed dipole moment a direct consequence is that the halogen cannot occupy the normal axial position.

Fortunately, there is a way of telling from the observed dipole moments if contributions from these forms are the main reason our observed moments are higher than those calculated for the molecules having the halogen in the axial position. Clearly since this form with a separation of charge is said to contribute more when X is bromine¹⁷ than when X is chlorine, it follows that the bromo compounds should have higher dipole moments than the chloro compounds, since the dipole moment values of the normal C-Br and C-Cl moments

are the same. The values in Table I show that the opposite is true. The dipole moment of α -chlorocyclohexanone is greater than that of α -bromocyclohexanone in each of the three solvents used. Also the dipole moment of α -chlorocyclopentanone is greater than that of α -bromocyclopentanone in each of the solvents. Here the chance of overlap of the $sp^3 \rightarrow p$ orbital made available by the leaving halogen and the p orbital of the carbonyl carbon is less due to the greater angle between them. A consequence of this if these forms with a separation of charge are the main factor is that the dipole of α -bromocyclohexanone should be larger than that of α -bromocyclopentanone and this also is not the case. In heptane the dipole moment of the α -bromocyclopentanone is larger by 0.12 D , in dioxane it is identical, and in benzene it is smaller by 0.03 D which is hardly significant. It is apparent from the above that it is not only impossible to reconcile the observed dipole moments of the α -halocyclohexanones with the halogen being in the normal axial position by assuming the molecules have contributions from these forms with a separation of charge but the magnitude of dipole moment values coupled with the predicted relative contributions of these forms in the bromo and chloro compounds clearly indicate that the forms with a separation of charge do not account for the observed moments.

Recent workers^{4,15,18,19} have interpreted their results on the 1,2- and 1,4-dihalocyclohexanes on a basis of an equilibrium mixture of the chair forms. The dipole moment evidence is that the moments of the *trans*-1,2-dihalo-derivatives vary with solvent and with temperature while the moment of the *cis*-1,2-, *cis*-1,4- and *trans*-1,4-dihalo-derivatives do not so vary. Since the two chair forms of the *trans*-1,2-derivatives are the only chair forms that have different dipole moments, the above facts have been interpreted as evidence for the chair forms, assuming that all undergo conversion which involves each axial position becoming equatorial and *vice versa*.

In Table I it will be noted that the dipole moments of α -chlorocyclohexanone and α -bromocyclohexanone vary from heptane to benzene by 0.33 and 0.13 D , while *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane in going from carbon tetrachloride to benzene vary by 0.36 and 0.40 D .⁴ The variation of α -chlorocyclohexanone and α -bromocyclohexanone from heptane to dioxane was 0.46 and 0.27 D , respectively. The variation of the dipole moments of all of these six-membered ring compounds was considerably greater than that shown by the five-membered ring compounds. The following variations from heptane to dioxane were found as shown in Table I, thus α -chlorocyclopentanone 0.06 D , α -bromocyclopentanone 0.17 D and *trans*-1,2-dichlorocyclopentane 0.11 D . These smaller variations for the five-membered ring compounds are not unexpected. There would not be two different positions for the halogens to occupy analogous to the equatorial and axial positions in the six-membered ring compounds which give rise to structures with different moments whose propor-

(18) K. Kozima and T. Yoshino, *ibid.*, **75**, 166 (1953); K. Kozima, K. Sahashita and S. Maeda, *ibid.*, **76**, 1985 (1954).

(19) P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955).

(17) E. J. Corey and H. J. Burke, *THIS JOURNAL*, **77**, 5418 (1955).

tions would be expected to vary in different solvents. The dipole moments of the different flexible forms would also vary over a wide range. The fact that the variation is as great as it is with some of these five-membered ring compounds, particularly the α -bromocyclopentanone, suggests that the models which indicate a rigid ring are not a very good representation of the actual molecule. This is in agreement with experimental evidence²⁰ which indicates that one carbon is considerably out of the plane and the cyclopentane ring has some flexibility. Nevertheless, the change in dipole moment between the possible different conformations of α -halocyclopentanones would be expected to be considerably smaller than that between an axial and an equatorial α -halocyclohexanone or between the various flexible forms of an α -halocyclohexanone. The greater variation of the dipole moment on changing the solvent indicates that this is the case.

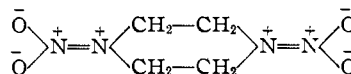
It appeared possible that the flexible form may make some contribution to the structure of α -halocyclohexanones even though it apparently does not to 1,2-dihalocyclohexanones. These compounds are intermediate between 1,4-cyclohexadione and the 1,2-dihalocyclohexanes. In the former a flexible form can be attained with all adjacent CH_2 groups staggered and the carbonyl dipoles pointing in opposite directions. This is the form which probably makes the major contribution to the structure of this molecule. The flexibility of the form would permit the molecule to spend some time with the carbonyl groups at angles of less than 180° which accounts for the observed moment. In the α -halocyclohexanones the flexible forms have one CH_2 pair opposed on the average involving an energy of about 2.8 kcal. while the 1,2-dihalocyclohexanes have two CH_2 pairs opposed. Dipole interaction between a halogen and a carbonyl might be expected to involve 2 or 3 kcal. but not twice that amount.

Another aspect of this situation which should be considered is that possibly the difference in behavior between the *trans*-1,2-dihalocyclohexanes and the α -halocyclohexanones on the one hand, whose moments vary with the solvent, and the *cis*-1,2-*cis*-1,4- and *trans*-1,4-dihalo-derivatives whose moments do not vary, may be due simply to the fact that the former are mainly in a flexible form and the latter are in a rigid chair form, and stay there. Although the models show that the *cis*-1,2-dihalocyclohexanes cannot undergo conversion without the halogens first becoming appreciably closer together and the angle between the two C-X dipoles decreasing, the height of the energy hump is probably less than 10 kcal. which would mean numerous conversions would take place per second at room temperatures. The energy hump would be even smaller in the *cis*-1,4 and *trans*-1,4 compounds so because of these factors one must abandon the explanation that conversion does not take place.

Six-membered ring compounds most likely to have flexible forms are: (1) those with two or more atoms in the ring that do not have sp^3 binding such as a bivalent atom or a carbonyl which has essen-

tially sp^2 binding; (2) those with one atom in the ring not having sp^3 binding and a strong dipole on an adjacent atom. In two preceding papers^{16,21} dealing with cyclohexane compounds having one carbonyl and a large substituent in the α -equatorial position, but not having a strong dipole adjacent, it has been found that the chair form adequately accounts for their structures.

The discovery of Professor George F. Wright²² that N,N'-dinitropiperazine has a moment of 1.18 D with the dielectric constant of the solid being normal, thus indicating that the moment is real and does not come from a high atomic polarization, is significant. Costain and Cox²³ have pointed out that dimethylnitramine has considerable double bond character between the nitrogens, so the same situation would be expected to be present in the analogous piperazine compound. This could arise from an appreciable contribution from the form which gives some sp^2 character to the nitrogens in



the ring and thus makes them somewhat analogous to carbonyl carbons. Thus this compound fits into one of the types mentioned above in which a flexible form would be expected.

TABLE II

Compound	Normal angle ^a	Angle required to give obsd. moment	Solvent	Δ angle
<i>trans</i> -1,2-Dichlorocyclopentane	125°	128°	Dioxane	3°
		132°	<i>n</i> -Heptane	7°
<i>trans</i> -1,2-Dibromocyclopentane	125°	133°	Dioxane	8°
<i>trans</i> -1,2-Dichlorocyclohexane	71°	93°	Benzene	22°
		107°	CCl_4	36°
<i>trans</i> -1,2-Dibromocyclohexane	71°	111°	Benzene	40°
		125°	CCl_4	54°
α -Chlorocyclohexanone	55°	70°	Dioxane	15°
		89°	<i>n</i> -Heptane	34°
α -Bromocyclohexanone	55°	82°	Dioxane	27°
		92°	<i>n</i> -Heptane	37°

^a Normal angle is the calculated angle for the rigid or "chair" conformation. All angles are given to the nearest degree.

In Table II are given the angles the dipoles in *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclopentane would have to be spread to give the observed moments. These are small being less than 9° and serve as a basis for what to expect with molecules that do not have the possibility of existing in different conformations. In sharp contrast are the angles of 22 to 54° which the dipoles in *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane would have to be spread from the equatorial positions to give the observed moment. Still larger are the angles of 55 to 87° the dipoles would have to be compressed from the axial positions. Dipole interaction would of course cause a spreading of the angles, not a compression.

The α -halocyclohexanones show a similar behav-

(20) J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, THIS JOURNAL, **63**, 2029 (1941); J. G. Aston, H. L. Fink and S. C. Schumann, *ibid.*, **65**, 341 (1943).

(21) A. C. Huitric and W. D. Kumler, *ibid.*, **78**, 1147 (1956).

(22) G. F. Wright, private communication.

(23) W. Costain and E. G. Cox, *Nature*, **160**, 826 (1947).

ior to the *trans*-1,2-dihalocyclohexanes that the observed dipole moments correspond to angles far removed from those corresponding either to that of the axial or the equatorial positions. With *n*-heptane as solvent the moments correspond to angles approximately half way between those for the axial and equatorial positions.

The ultraviolet spectra of these cyclic ketones show a blue shift in going from heptane to alcohol as shown in Table III.

TABLE III^a

	Heptane	95% Ethanol	$n \rightarrow \pi^*$ blue shift, cm. ⁻¹
Cyclopentanone	34,200	34,800	600
α -Bromocyclopentanone	31,450	32,150	700
α -Chlorocyclopentanone	32,360	33,110	750
Cyclohexanone	34,450	35,340	890
α -Bromocyclohexanone	32,050	32,570	520
α -Chlorocyclohexanone	32,900	34,250	1350

^a The spectra were run by M. Hrenoff.

This shift has been designated an $n \rightarrow \pi^*$ blue shift and has been attributed to²⁴ the non-bonding electrons on the oxygen, hydrogen bonding with the solvent. The magnitude of the blue shift was shown by these workers to be related to the energy of the hydrogen bond. The extent of the shift in case of the cyclopentanone compounds is small, varying from 600 cm.⁻¹ for the cyclopentanone, and 700 cm.⁻¹ for α -bromocyclopentanone to 750 cm.⁻¹ for α -chlorocyclopentanone. On the other hand, cyclohexanone has a value of 890 cm.⁻¹, α -bromocyclohexanone 520 cm.⁻¹, and α -chlorocyclohexanone 1,350 cm.⁻¹. Again as with the dipole moment values, the cyclohexane compounds show a much greater variation than the cyclopentane compounds both on changing the solvent and in going from one compound to the other. It is also to be deduced that the hydrogen bond formed between the alcohol and the non-bonding electrons on the oxygen of α -bromocyclohexanone is weaker than

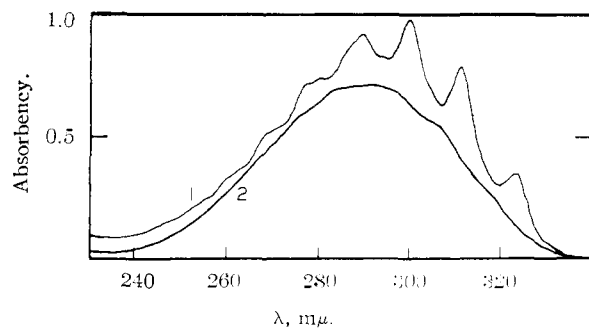


Fig. 1.—1, cyclopentanone; 2, cyclohexanone; both 500 mg. % in *n*-heptane.

(24) G. J. Brealey and M. Kasha, *THIS JOURNAL*, **77**, 4462 (1955).

that formed with cyclohexanone itself while that with the α -chlorocyclohexanone is much stronger. This obviously cannot arise from an inductive effect or from a bending of the normal bond angles because these factors are present in the cyclopentanone compounds. It must arise from a steric effect indicating a difference in configuration between the chloro and bromocyclohexanone, which again suggests these molecules have an appreciable contribution from a flexible form.

The almost complete lack of fine structure in the spectrum of cyclohexanone in heptane as compared with much fine structure in the spectrum of cyclopentanone as shown in Figure 1 is of considerable interest. Although one cannot say the lack of fine structure in cyclohexanone is due to contributions of a flexible form, since other factors could be responsible, nevertheless the lack of fine structure is consistent with the presence of a flexible form.

It appears worthwhile to try to find why the infrared evidence gave a different answer with regard to the structures of these compounds and to that end we have measured the infrared spectra and calculated the Δ values on which they were based. In Table IV it will be observed that our Δ values agree in every case with those of Corey¹ within his stated variation which rules out experimental error as the cause of the discrepancy.²⁵

TABLE IV

Compound	Frequency shift, Δ due to α -halogen, cm. ⁻¹	
	This work	Corey's
α -Bromocyclopentanone	6	8
α -Chlorocyclopentanone	10	13
α -Bromocyclohexanone	2	4
α -Chlorocyclohexanone	8	10

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(25) NOTE ADDED IN PROOF.—In a recent communication, F. W. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *THIS JOURNAL*, **78**, 1507 (1956), found the Δ values of the 1-halo-2-indanones to be 13 cm.⁻¹ for the bromo and 19 cm.⁻¹ for the chloro compounds. These compounds must have four carbon atoms in one plane and the fifth, the carbonyl group, can maintain favorable bisections with the α -substituents by also being in the plane. The fact that the Δ values for these compounds are larger than those for α -chloro and α -bromo cyclopentanone is significant and suggests the dipole moments of these should be measured. Dr. Brutcher has very kindly sent us two of the indanones, and preliminary measurements in dioxane on the 1-chloro-2-indanone indicate that its dipole moment is virtually identical with that of α -chlorocyclopentanone. This fact can be accounted for in two ways. If moments for the C—Cl as well as the C=O groups are the same in the two compounds, then the angles between the dipoles must be the same. If the C—Cl or the C=O moments are different in the two compounds then the angle between the C—Cl and C=O must by coincidence be different by just the right amount to make the moments come out the same. Of the two possibilities the former appears more probable. The dipole moments of other compounds of the general type are being investigated.