

All fractions contained sulfur dioxide which could be removed by molecular sieve 4A but not without introducing small amounts of other light-absorbing impurities. Fractions C, D, E were combined and refluxed with 5.6 g. of potassium hydroxide for 4 hours. (A and B were saved for combination with the next run.) The TFP was rapidly distilled and then fractionated. The following fractions were obtained.

| Fraction | B.p., °C. | Vol., cc. | $n_D^{25}$ | $n_D^{25}$ | 1 cm. cell<br>O.D. = 1<br>at |
|----------|-----------|-----------|------------|------------|------------------------------|
| A        | 104       | 50        | 1.3204     |            | <sup>a</sup>                 |
| B        | 104-106   | 50        | 1.3191     | 1990 Å.    |                              |
| C        | 106-106.5 | 60        | 1.3188     | 1970 Å.    |                              |
| D        | 106.5     | 90        | 1.3188     | 1950 Å.    |                              |

<sup>a</sup> Contains some water.

Fractions C and D are eminently satisfactory as solvents for spectroscopic purposes and have been used in thin cells as low as the Cary 14 limit of 1865 Å. with success.

**Spectra.**—Absorption curves were taken with a Cary automatic recording spectrophotometer, either model 11 or model 14. The maxima were in general measured by running over the maximal absorption at the slowest speed three to four times and then averaging the maxima thus obtained. The maxima could normally be duplicated to at least  $\pm 6$  Å. for the model 11 and to  $\pm 3$  Å. for the model 14. The solutions were made up immediately before use and a 1-cm. cell was used for all the measurements, except for some of the data listed in Table V.

The data for the constancy of the spectroscopic properties of cyclopentadecanone are given in Table V.

**Air Oxidation.**—Water was used as the solvent for all of the cycloalkanones except cyclopentadecanone, for which isoöctane was used. Air was bubbled through the ketone solutions in the dark and the solutions were periodically examined spectroscopically, usually at intervals of 8 to 10 hours. (The air used was presaturated with water.) In no case was any sign of oxidation products found, the criterion

TABLE V  
CYCLOPENTADECANONE DATA ( $n \rightarrow \pi^*$ -TRANSITION)

| Solvent                          | Concn., M | $\lambda_{max}$ , Å. | $\epsilon_{max}$ |
|----------------------------------|-----------|----------------------|------------------|
| Isoöctane                        | 0.0439    | 2850                 | 23               |
|                                  | .00732    | 2860                 | 23               |
|                                  | .00366    | 2860                 | 21               |
| Methanol                         | .0413     | 2830                 | 27               |
|                                  | .00413    | 2830                 | 26               |
|                                  | .000413   | 2813 $\pm 30^a$      | 28               |
| 2,2,3,3-Tetrafluoro-<br>propanol | .0351     | 2786                 | 33               |
|                                  | .00351    | 2790                 | 31               |

<sup>a</sup> The observed optical density (10-cm. cell) was only 0.07, and it is not possible to determine accurately maxima under such circumstances without a different slide wire.

being the amount of ultraviolet absorption between 2200 and 2600 Å.

In separate experiments, solutions of certain ketones were exposed to sunlight in the absence of air for about 2 months. Aside from some apparent photoisomerization (a well-known reaction for such compounds), no "oxidation" was noted.

Although these studies should not be regarded as definitive, they do suggest that *both air and light* are responsible for the formation of light-absorbing materials during some of the purification procedures.

**Acknowledgment.**—The authors would like to thank Dr. A. C. Haven, Jr., Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. for making the fluorinated alcohol available, and Mrs. P-K. C. Huang for supplying the procedure for the purification of the fluorinated alcohol as well as small samples of the pure solvent.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

## Effect of Solvent on Spectra. VI. Detection of the Solvent Effect on Molecular Conformation or Shape through Z-Values

BY EDWARD M. KOSOWER,<sup>1a</sup> GUEY-SHUANG WU AND THEODORE S. SORENSEN

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The effect of solvent on the position of the  $n \rightarrow \pi^*$ -transitions of 2-fluoro-, *cis*-2-fluoro-4-*t*-butyl-, *trans*-2-fluoro-4-*t*-butyl- and 2-chlorocyclohexanones has been examined. Although 2-fluorocyclohexanone correlates very well with Z, the solvent polarity standard based on the charge-transfer band of 1-ethyl-4-carbomethoxy-pyridinium iodide, the data for the conformationally fixed 4-*t*-butyl derivatives indicate that a change in the position of a conformational equilibrium is occurring with a change in solvent. The same conclusion is reached for 2-chlorocyclohexanone, for which it is also shown that the equatorial isomer predominates in acetonitrile, probably because of the special mode of solvation. A qualitative theory for rationalizing the spectroscopic and thermodynamic behavior of the 2-halocyclohexanones is put forward, its chief features being the (a) inclusion of electrostatic repulsion (in the equatorial conformers) between the carbon-oxygen and carbon-halogen dipoles, (b) charge-transfer stabilization of the equatorial conformers by the interaction of the oxygen non-bonding electrons with the empty *upper* orbitals of the halogen, (c) stabilization of the axial conformers by a charge-transfer interaction between the  $\pi$ -electrons of the carbon-oxygen bond and the empty *upper* orbitals of the halogen, (d) inclusion of the preference of a halogen for the equatorial position as a "steric repulsion" and (e) explanation of the axial shift in the ultraviolet spectra as due to a charge-transfer interaction of the  $\pi^*$ -anti-bonding electron of the  $n \rightarrow \pi^*$ -excited state with the *upper* orbitals on the halogens. Further data confirming the rather good correlation between Z and electronic transitions of rigid cyclic ketones are shown for cyclohexenone, isophorone and 2,2-dimethyl-3,4-dihydro[4H]4-pyrone; in contrast, correlation is not observed for 3-acetyl-3-azabicyclo[4.4.0]dec-5-en-4-one (II, H = NCOCH<sub>3</sub>) leading to the conclusion that the compound is "folded" in non-polar solvents. The unusual spectroscopic results found for 5-methyl-2,3,4-hexatrienal in a number of solvents suggest an equilibrium between *s-cis* and *s-trans* forms. These cases represent applications of the solvent polarity values, Z, to problems of molecular shape and conformation.

In the previous article,<sup>1</sup> we have shown that the relationship between the transition energies for the low-intensity ( $n \rightarrow \pi^*$ -transition) carbonyl absorption band of certain cycloalkanones and Z-

(1a) Department of Chemistry, State University of New York, Long Island Center, Oyster Bay, N. Y.

(1) E. M. Kosower and G.-S. Wu, *J. Am. Chem. Soc.*, **83**, 3142 (1961).

values (the solvent polarity measure derived from the position of the charge-transfer band of 1-ethyl-4-carbomethoxy-pyridinium iodide)<sup>2</sup> is linear. Against the background of linear correlations for the ketones, C<sub>5</sub> through C<sub>10</sub>, it could be discerned that the C<sub>15</sub>-cycloalkanone was anomalous. Its

(2) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

TABLE I  
 ABSORPTION MAXIMA FOR  $n \rightarrow \pi^*$ -TRANSITIONS OF 2-FLUORO- AND 2-CHLOROCYCLOHEXANONES

| Solvent (Z) <sup>2</sup>                              | 2-Fluorocyclohexanone <sup>13</sup> |                   | <i>cis</i> -2-Fluoro-4- <i>t</i> -butylcyclohexanone (equatorial) |                   | <i>trans</i> -2-Fluoro-4- <i>t</i> -butylcyclohexanone (axial) |                   | 2-Chlorocyclohexanone |                   |
|---|-------------------------------------|-------------------|---|-------------------|--|-------------------|-----------------------|-------------------|
|   | $\lambda_{\max}$                    | $\epsilon_{\max}$ | $\lambda_{\max}$  | $\epsilon_{\max}$ | $\lambda_{\max}$   | $\epsilon_{\max}$ | $\lambda_{\max}$      | $\epsilon_{\max}$ |
| Water (94.6)  | 2739                                | 6.6 <sup>a</sup>  | ..  | ..                | ..   | ..                | 2796                  | 13 <sup>b</sup>   |
| TFP <sup>c</sup> (96.3) <sup>d</sup>                  | ..                                  | ..                | 2775  | 20                | 2885   | 21                | 2854                  | 24                |
| 60% methanol <sup>e</sup> (88.4) <sup>f</sup>         | ..                                  | ..                | ..  | ..                | ..   | ..                | 2850                  | 13 <sup>b</sup>   |
| 80% methanol <sup>e</sup> (85.2) <sup>f</sup>         | ..                                  | ..                | ..  | ..                | ..   | ..                | 2891                  | 13 <sup>b</sup>   |
| Methanol (83.6)                                       | 2805                                | 5.0 <sup>a</sup>  | 2825  | 8 <sup>a</sup>    | 2945   | 7 <sup>a</sup>    | 2925                  | 16 <sup>b</sup>   |
| Ethanol (79.6)  | 2830 <sup>g</sup>                   | 18 <sup>g</sup>   | ..  | ..                | ..   | ..                | 2948 <sup>h</sup>     | 24                |
| 2-Propanol (76.2) <sup>i</sup><br>(75.9) <sup>i</sup> | ..                                  | ..                | ..  | ..                | 2978   | 19                | 2963                  | 26                |
| <i>t</i> -Butyl alcohol (71.3)                        | ..                                  | ..                | ..  | ..                | ..   | ..                | 2988                  | 30                |
| Acetonitrile (71.3)                                   | 2883                                | 16                | 2851  | 16                | 2981   | 17                | 2907                  | 21                |
| Dimethyl sulfoxide (70.4) <sup>d</sup>                | ..                                  | ..                | ..  | ..                | ..   | ..                | 2893                  | 22                |
| Cyclohexane (60.1)                                    | 2940 <sup>g</sup>                   | 18 <sup>g</sup>   | ..  | ..                | ..   | ..                | ..                    | ..                |
| Isooctane (60.1)                                      | 2965                                | 18                | 2897  | 15                | 3020   | 19                | 3042                  | 36                |

<sup>a</sup> Probably low due to 1,1-diol formation (water) or hemiacetal (methanol). The absorption intensity of 2-fluorocyclohexanone in methanol is given for the observed optical density 5 minutes after mixing; at 20 minutes after mixing, it had decreased to 4.3. The observed maxima for the other fluoroketones are somewhat inaccurate because hemiacetal formation was just fast enough to distort the curves. <sup>b</sup> It is likely that these low  $\epsilon$ -values result from addition of hydroxylic solvent to the carbonyl group, although it is not certain that solution was complete in water. <sup>c</sup> 2,2,3,3-Tetrafluoropropanol. <sup>d</sup> Derived from the correlation of  $n \rightarrow \pi^*$ -transitions of cyclohexanone with Z as described in ref. 1. <sup>e</sup> Prepared by mixing six (or eight) volumes of methanol with four (or two) volumes of water. <sup>f</sup> Derived as in note *d*. The linear relationship between Z and Y<sup>2</sup> gives somewhat different values (89.8 and 87.1, respectively) for 60% and 80% methanol but these lead to the same qualitative conclusions. The discrepancy indicates that some care must be exercised in deriving quantitative conclusions from the correlations shown in this paper. <sup>g</sup> Measured by Kende.<sup>19</sup> <sup>h</sup> Mentioned by C. W. Bird, R. C. Cookson and S. H. Dandegaonker, *J. Chem. Soc.*, 3675 (1956). <sup>i</sup> Measured in the usual manner<sup>2</sup> for the sample of solvent actually used in the spectroscopic determination.

behavior was rationalized as due to a tendency to assume "folded" conformers in polar solvents.

We now report studies of fluoro- and chlorocyclohexanones, axial and equatorial 2-fluoro-4-*t*-butylcyclohexanones, several cyclohexenones, and a novel cumulene aldehyde, 5-methyl-2,3,4-hexatrienal. The results indicate that comparison of spectroscopic maxima in several solvents with Z-values can provide useful and interesting information.<sup>3</sup>

### Results and Discussion

**2-Halocyclohexanones.**—Although it has been recognized for some years that the configuration of acyclic  $\alpha$ -haloketones was medium-dependent<sup>4-6</sup> only recently have Allinger and Allinger<sup>7</sup> investigated the variation in the conformational equilibrium of 2-bromocyclohexanone with solvent. Kozima and Yamanouchi<sup>8</sup> have reported that the conformation of 2-chlorocyclohexanone varies from the solid through solution to the gaseous state. Additional studies of the same phenomenon have been carried out on 2-chloro- and 2-bromo-5-methylcyclohexanone<sup>9-11</sup> and *trans*-2-bromo-5-*t*-

butylcyclohexanone.<sup>12</sup> The results obtained for the conformationally mobile ketones have been supported in an elegant manner by the preparation of the axial and equatorial isomers of 2-fluoro-,<sup>13</sup> 2-chloro-<sup>14</sup> and 2-bromo-4-*t*-butylcyclohexanones.<sup>15,16</sup>

The methods used to determine the ratio of equatorial and axial isomers have included infrared absorption (examination of the carbonyl region in most cases), ultraviolet absorption ( $n \rightarrow \pi^*$ -transition of the carbonyl group), dipole moment measurements, and optical rotatory dispersion. We add in this paper the additional technique of examination of the  $n \rightarrow \pi^*$ -transition in a range of solvents with different polarity as measured by Z-values. With care, one can arrive at qualitative conclusions concerning the change in the conformational equilibrium with solvent. In addition, certain anomalies in the plots of transition energies *versus* Z can be interpreted in terms of specific new solvation effects.

We have examined the  $n \rightarrow \pi^*$ -transition of the carbonyl band of 2-chlorocyclohexanone in eleven solvents, and that of equatorial and axial 2-fluoro-4-*t*-butylcyclohexanone<sup>17</sup> in four and five solvents, respectively. These are listed in Table I along with a number of values for 2-fluorocyclohexanone.<sup>18,19</sup>

(12) C. Djerassi, E. J. Warawa, R. E. Wolf and E. J. Eisenbraun, *ibid.*, **25**, 917 (1960).

(13) N. L. Allinger and H. M. Blatter, *J. Am. Chem. Soc.*, **83**, in press (1961).

(14) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja and N. A. LeBel, *ibid.*, **82**, 5876 (1960).

(15) N. L. Allinger and J. Allinger, *ibid.*, **80**, 5476 (1958).

(16) N. L. Allinger, J. Allinger and N. A. LeBel, *ibid.*, **82**, 2926 (1960).

(17) Professor N. L. Allinger, Dept. of Chemistry, Wayne State University, generously provided us with samples of both of these ketones. Their preparation and properties are described by Professor Allinger elsewhere.<sup>13</sup>

(3) The authors are grateful to the Air Force Office of Scientific Research for support through Contract AF 49(638)-282, to the National Institute of Allergy and Infectious Diseases for Grant E-1608, and to the Wisconsin Alumni Research Foundation for funds granted through the Research Committee of the Graduate School.

(4) A preliminary account of this work was presented at the Symposium on Molecular Structure and Spectroscopy, June 13, 1960, Columbus, Ohio.

(5) I. Nagakawa, *et al.*, *J. Chem. Phys.*, **20**, 1720 (1952).

(6) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957).

(7) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958).

(8) K. Kozima and Y. Yamanouchi, *J. Am. Chem. Soc.*, **81**, 4159 (1959).

(9) C. Djerassi and L. E. Geller, *Tetrahedron*, **3**, 319 (1958).

(10) C. Djerassi, L. E. Geller and E. J. Eisenbraun, *J. Org. Chem.*, **25**, 1 (1960).

(11) N. L. Allinger, J. Allinger, L. E. Geller and C. Djerassi, *ibid.*, **25**, 6 (1960).

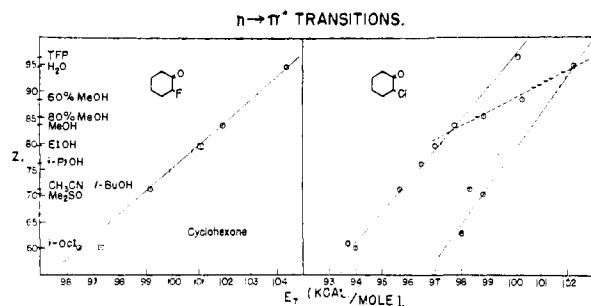


Fig. 1.— $E_T$  (transition energies) versus  $Z$  (solvent polarity values) for 2-fluorocyclohexanone and 2-chlorocyclohexanone. The points for the fluoro ketone marked with  $\square$  are based on data of Kende (ref. 19); the others are derived from the work of Johnson and Bauer (ref. 18). The dashed line in the 2-chloro ketone section indicates the anomalously high slope for the solvent range, methanol to water, a clue to the behavior described in the text. It should be noted that the two points on the line marked e for the chloroketone at low  $Z$  are those for acetonitrile and dimethyl sulfoxide.

The results for 2-chloro- and 2-fluorocyclohexanone are plotted against  $Z$  in Fig. 1, while those for the two fluoro-*t*-butylcyclohexanones are plotted in Fig. 2. Although it is obvious that the data for 2-fluorocyclohexanone yield an excellent correlation with  $Z$ , the slope (*i.e.*, the solvent sensitivity of the transition) is greater than that for cyclohexanone in contrast to previous data on the solvent sensitivity of the conformationally stable 2-bromo-4-*t*-butylcyclohexanones suggesting a considerably lower solvent sensitivity for 2-halocyclohexanones.<sup>16</sup> In fact, examination of the conformational isomers of 2-fluoro-4-*t*-butylcyclohexanone in a series of solvents shows a variation in maximum with solvent corresponding to a solvent sensitivity *lower* than that for cyclohexanone.<sup>1</sup> It is somewhat surprising that the isomers differ so little in slope against  $Z$ , since they do possess rather different dipole moments.<sup>13</sup> Thus, linearity of the transition energies for 2-fluorocyclohexanone against  $Z$  is misleading in that it suggests that a single species is responsible for light absorption in all solvents, but an accurate assessment can be made by considering the slope. These data support the conclusion of Allinger and co-workers<sup>13</sup> that 2-fluorocyclohexanone is partially in the equatorial form in the least polar solvent, and changes in the direction of greater equatorial conformer content as the solvent becomes more polar. A puzzling circumstance is the implication that 2-fluorocyclohexanone absorbs at shorter wave lengths (see Fig. 2) than the *cis*-(equatorial)-2-fluoro-4-*t*-butylcyclohexanone in the most polar media, although this conclusion depends upon the use of the high  $Z$ -value for tetrafluoropropanol.<sup>20</sup> A qualitative theory which rationalizes the trend in equatorial/axial ratio as the halogen is changed

(18) We are grateful to Professor W. S. Johnson and Dr. V. J. Bauer of this Department for providing us with the spectroscopic data for 2-fluorocyclohexanone, which they synthesized independently of A. S. Kende.<sup>19</sup> The properties of the compound were in agreement with those reported.<sup>19</sup>

(19) A. S. Kende, *Tetrahedron Letters*, No. 14, 13 (1959).

(20) Insufficient material was available for a more extensive series of measurements.

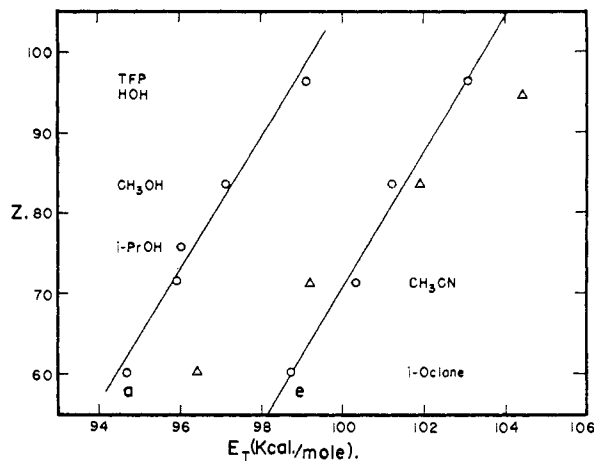


Fig. 2.— $E_T$  versus  $Z$  for *cis*- and *trans*-2-fluoro-4-*t*-butylcyclohexanone (the points for 2-fluoro cyclohexanone are indicated by a  $\Delta$ ):  $E_T(\text{cis}) = 0.11526Z + 91.830$ ;  $E_T(\text{trans}) = 0.12083Z + 87.195$ .

in 2-halocyclohexanones from fluorine to bromine is presented at the end of this section.

A linear relationship for the  $n \rightarrow \pi^*$ -transition energies of 2-chlorocyclohexanone with  $Z$  is observed (Fig. 1) only from isoöctane to methanol, after which the slope becomes far too great for an  $n \rightarrow \pi^*$ -transition.<sup>1,21</sup> Such a change indicates the incursion of significant amounts of another species which absorbs at appreciably shorter wave lengths. In agreement with a previous qualitative conclusion based on the inversion of a Cotton effect curve for an optically active chloro ketone,<sup>10</sup> the new species is supposed to be the equatorial isomer of 2-chlorocyclohexanone. The linear relationship from methanol to isoöctane suggests that the chief species present in these solvents is the axial isomer of 2-chlorocyclohexanone. It is likely that the most important isomer present in water is the equatorial isomer. Thus, comparison of the transition energies (carbonyl band positions) with  $Z$  very quickly allows a qualitative conclusion as to the range of solvents in which the axial isomer will predominate, the range in which there is a mixture present in solution, and those solvents which are likely to contain mostly equatorial isomer. In this connection, one may now point to the positions of the maximum in the solvents acetonitrile and dimethyl sulfoxide.

Surprisingly, the maxima for 2-chlorocyclohexanone in dimethyl sulfoxide and acetonitrile were, with respect to their positions in the  $E_T$  versus  $Z$  plot, far from their expected places. Their location suggested that the major component in these solvents might be the *equatorial isomer*. In acetonitrile, a comparison of the infrared carbonyl maximum for the 2-chloro ketone with that of cyclohexanone was in complete accord with this conclusion, whereas a similar infrared comparison in isoöctane confirmed the axial character of the 2-chlorocyclohexanone present in that non-polar solvent (Table II).<sup>22</sup>

(21) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).

(22) It is clear that the macroscopic parameter, the dielectric constant, does not reflect the polarity of a solvent in the *cybotactic*

TABLE II  
INFRARED MAXIMA FOR CYCLOHEXANONE AND 2-CHLORO-  
CYCLOHEXANONE

| Solvent      | $\nu_{\text{C}} = \text{O}, \text{cm.}^{-1}$ |                       |
|--------------|--|-----------------------|
|              | Cyclohexanone                                | 2-Chlorocyclohexanone |
| Isooctane    | 1724-1727 <sup>a</sup>                       | 1727                  |
| Acetonitrile | 1712 <sup>a</sup>                            | 1727                  |

<sup>a</sup> The carbonyl maximum in hexane is listed by Bellamy and Williams<sup>24</sup> from work of Josien and Lascombe<sup>25</sup> as 1726  $\text{cm.}^{-1}$ , while that measured<sup>24</sup> in acetonitrile is reported as 1709  $\text{cm.}^{-1}$ .

The most likely explanation for the preference for equatorial conformation in acetonitrile may be in the stereochemistry of solvation. In contrast to the hydrogen bonding solvents, which are primarily acceptors through the positively charged hydrogen, acetonitrile may act as a donor. (It forms strong complexes with metal ions, for example.) Examination of models shows that only the equatorial conformation is readily solvated at the carbonyl carbon by the non-bonding pair of the nitrogen in acetonitrile. A similar explanation may hold for dimethyl sulfoxide.

The maximum found for 2-chlorocyclohexanone in 2,2,3,3-tetrafluoropropanol was unexpected, since the fluoro-alcohol is highly polar.<sup>1</sup> The infrared data obtained for cyclohexanone and 2-chlorocyclohexanone in this solvent were unfortunately too complicated in the carbonyl region to be easily interpreted, but indicated, if anything, an equatorial conformation for the chloroketone in this solvent. This result illustrates the difficulty in applying empirical solvent polarity values to the analysis of spectroscopic data. Nevertheless, as long as one is aware of the limitations and bears in mind what the  $Z$ -values actually represent in terms of the interaction of a solute with the solvent,<sup>2</sup> comparisons of  $E_T$  with  $Z$  can provide information on the behavior of molecules in solution.

The discovery that 2-fluorocyclohexanone contains more of the equatorial conformer in non-polar solvents than either the 2-chloro- or 2-bromocyclohexanones<sup>13,19</sup> emphasizes the need for a detailed consideration of the behavior, both equilibrium and spectroscopic, of these haloketones. The proximity of the carbon-fluorine and carbon-oxygen dipoles *must* lead to a repulsion in the

region<sup>2</sup> and is thus unsuitable for correlation of kinetic and spectroscopic data. Although the confirmation of the equatorial character of 2-chlorocyclohexanone in acetonitrile was not extended to dimethyl sulfoxide, there is no reason to doubt that the position of the  $n \rightarrow \pi^*$ -transition in dimethyl sulfoxide reflects the presence of equatorial conformer. In this connection, it is of interest to refer to the report of Allinger and Allinger<sup>23</sup> on ultraviolet data for the  $n \rightarrow \pi^*$ -transition of 2-bromocyclooctanone. A plot of the data against  $Z$  reveals that the "slope" determined by the data in heptane and 95% ethanol is *ca.* 0.09, not very different from that derived from the data for either *cis*- or *trans*-2-bromo-4-*t*-butylcyclohexanone<sup>15</sup> plotted against  $Z$ ; *i.e.*, *ca.* 0.08. The point for 2-bromocyclooctanone in dimethyl sulfoxide then suggests a marked change in conformer composition to one in which the major component is "equatorial," *i.e.*, absorbs at considerably shorter wave lengths in the ultraviolet than the axial isomer (or mixture of conformers<sup>23</sup>) present in heptane. The maximum for cyclooctanone itself in dimethyl sulfoxide reported in ref. 23 is in error, the value for a carefully purified sample of cyclooctanone in pure dimethyl sulfoxide being  $\lambda_{\text{max}}$  2871 Å.,  $\epsilon_{\text{max}}$  17.

(23) J. Allinger and N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5736 (1959).

(24) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

(25) M. L. Josien and J. Lascombe, *J. Chem. Phys.*, **52**, 162 (1955).

equatorial 2-fluorocyclohexanone. Although calculation is not of great value in such cases because the effective dielectric constant is not known and the assumption of point dipoles is really not valid, we shall adopt here the estimate of 2.0 kcal./mole<sup>19</sup> for the repulsion. Now, this repulsion should appear spectroscopically in the form of a reduced transition energy for the  $n \rightarrow \pi^*$ -transition of the carbonyl group. However, the equatorial 2-fluorocyclohexanone absorbs at shorter wave lengths than cyclohexanone. There must then be present a factor which prevents the electron from being excited, and that factor would also stabilize the equatorial conformer. We propose that this factor is a charge-transfer interaction between the oxygen non-bonding electrons ( $sp^3$ )<sup>1</sup> and the empty 3s and/or 3p orbitals of fluorine. If this factor is the only one which affects the position of the  $n \rightarrow \pi^*$ -transition, it must be evaluated as *ca.* 2.6 kcal./mole. Further, if such a charge-transfer interaction is present in the equatorial conformer, it must also be present in the axial conformer, with its contribution diminished by the higher ionization potential of the  $\pi$ -electrons. We can arbitrarily assign this interaction as 33% of the  $O_{sp^3}-F_{p,s}$  interaction, *i.e.*, 0.9 kcal./mole. The parallel interaction for the chloro- and bromoketones is taken as 66% (probable increased orbital overlap) of the interaction energy estimated for the equatorial compound. The electrostatic repulsion in the chloro- and bromoketones is also taken as 2.0 kcal./mole since the bond moments are quite close to that of carbon-fluorine.<sup>25</sup>

To summarize our approach, we believe that the electrostatic repulsion in the equatorial conformers between the carbon-oxygen and carbon-halogen dipoles should lead to a reduced  $n \rightarrow \pi^*$ -transition energy. The discrepancy between this expectation and the experimental value (Table III) for the equatorial conformers is best interpreted as a

TABLE III  
2-HALOCYCLOHEXANONES IN NON-POLAR MEDIA

| 2-X     | $\lambda_{\text{max}}, \text{Å.}$ | $E_T, \text{kcal./mole}$ | $\Delta$ | Ref.    |
|---------|-----------------------------------|--------------------------|----------|---------|
| ...     | 2914                              | 98.11                    |          |         |
| 2-F(e)  | 2897                              | 98.69                    | 0.58     | Table I |
| 2-F(a)  | 3020                              | 94.67                    | -3.44    | Table I |
| 2-Cl(e) | 2860                              | 100.0                    | 1.89     | 14      |
| 2-Cl(a) | 3060                              | 93.4                     | -4.7     | 14      |
| 2-Br(e) | 2910                              | 98.3                     | 0.2      | 15      |
| 2-Br(a) | 3150                              | 90.7                     | -7.4     | 15      |

charge-transfer interaction between the oxygen non-bonding electrons and the upper orbitals of the halogen. A lesser interaction between the  $\pi$ -electrons and the halogen in the axial case must also be present. These interactions, which, added to the "steric repulsion" of axial halogen, constitute the factors that determine the relative thermodynamic stability of the halocyclohexanones, are larger than the "induced dipole interaction" or the "van der Waals repulsion" estimated by Allinger, *et al.*,<sup>14</sup> and are listed in Table IV. No simple relationship between the halogen electron affinity and the extent of interaction can be ex-

(25a) R. J. W. Le Fevre, "Dipole Moments," Methuen & Co., Ltd., London, 1953, p. 133.

TABLE IV

CONTRIBUTIONS TO AXIAL/EQUATORIAL RATIO OF 2-HALOCYCLOHEXANONES<sup>a,b</sup>

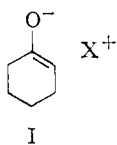
| Interaction                                      | (e)F | (a)F | (e)Cl | (a)Cl | (e)Br | a(Br) |
|--|------|------|-------|-------|-------|-------|
| Dipole-dipole                                    | -2.0 |      | -2.0  |       | -2.0  |       |
| Charge-transfer                                  | 2.6  |      | 3.9   |       | 2.2   |       |
| O <sub>sp</sub> <sup>2</sup> -X <sub>p,σ,d</sub> |      |      |       |       |       |       |
| Charge-transfer                                  |      | 0.9  |       | 2.6   |       | 1.4   |
| π-X <sub>p,σ,d</sub>                             |      |      |       |       |       |       |
| "Steric repulsion"                               |      | -0.4 |       | -0.4  |       | -0.4  |
| NET  | 0.6  | 0.5  | 1.9   | 2.2   | 0.2   | 1.0   |

<sup>a</sup> All figures are in kcal./mole. <sup>b</sup> Negative sign indicates destabilization.

pected because the orbital overlap is not the same for each halogen.

Inspection of the net interaction energies for each conformational pair shows that the proper trend in axial/equatorial ratio is given. Given the arbitrary nature of the numbers used, Table IV should be regarded as supplying a *possible* rationalization of the observed axial/equatorial ratios, which are themselves only known in an approximate way.

A more easily demonstrated point concerns the origin of the shift to longer wave lengths found for axial 2-halocyclohexanones. Although a common explanation involves supposed contributions from the resonance form<sup>14,26</sup> I, presumably as a way of favoring the excited state, the accepted theoretical picture of low intensity, n→π\*-transitions of carbonyl groups<sup>27</sup> suggests that such electron-supply would *raise* rather than decrease transition energy. A similar objection holds for the related proposal that a bromine 4p(filled) orbital may overlap with the π\*-anti-bonding orbital.<sup>23</sup> The transition involves transfer of an electron from a non-bonding orbital on oxygen into a π\*-anti-bonding orbital between the carbon and the oxygen. Any electron supply to this region of the molecule should hinder the excitation. It follows that a mechanism must



exist for removing charge, and one is led quite naturally to the idea that the electron in the π\*-orbital should have a low ionization potential and should therefore be an excellent donor to upper (unfilled) orbitals on the neighboring axial halogen. The trend from fluorine to chlorine to bromine is clearly marked in the axial cases listed in Table III, and may be attributed to the increasing electron affinity. Again, because of the variation in distances (and even in angles<sup>25</sup>), one should not expect a smooth correlation with size.

Not only is the foregoing formulation satisfactory for understanding the "axial shift" but it makes clear why the imperfectly "axial" bromo- and chlorocamphors show the shift<sup>29</sup> as well as the imperfectly axial bromoketone reported by Dje-

(26) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6041 (1958).

(27) J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).

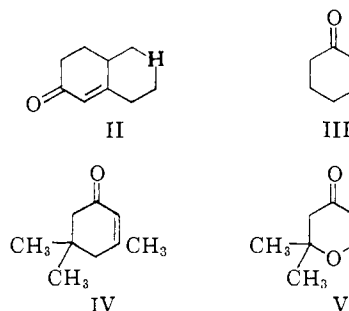
(28) V. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, **13**, 1737 (1959).

(29) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

rassi.<sup>30</sup> Furthermore, the general status of hyperconjugation (a previously used explanation<sup>26</sup>) as a mode of electron-supply is in serious question now<sup>31</sup> even if no other objection could be voiced.

There are many atoms (or groups) which can accept electrons into upper orbitals, and further interesting observations may be possible with molecules like substituted thiocyclohexanone.

**Cyclohexenones.**—Previous studies on the π→π\*- and n→π\*-transitions of bicyclic α,β-unsaturated ketones II (H = CH<sub>2</sub>, NCH<sub>3</sub>, and N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>)<sup>32</sup> have shown that a good correlation is found between transition energies and Z. The correlation permitted the calculation of excited state dipole moments and the conclusion that the shift in the π→π\*-transition from H = CH<sub>2</sub> to N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> was primarily electrostatic. In order to confirm that cyclohexenones would show solvent-sensitive light absorptions which could be correlated with Z, we have now examined cyclohexenone (III), isophorone (IV) and 5,5-dimethyl-4-oxa-2-cyclohexenone (2,2-dimethyl-3,4-dihydro-[4H]-4-pyrone) (V).<sup>33</sup>



The π→π\*-transitions for III, IV and V are given in Table V, while the low-intensity n→π\*-transitions are given in Table VI. In the case of the pyrone V, the n→π\*-transition is obscured by the π→π\*-transition in all solvents but isoctane. The data in Table V are plotted against Z in Fig. 3, and that of Table VI (treated in the same manner) summarized at the end of the Experimental section.

TABLE V  
π → π\*-TRANSITIONS OF CYCLOHEXENONES

| Solvent (Z) <sup>2</sup>       | III                     |                  | IV                      |                  | V                       |                  |
|--------------------------------|-------------------------|------------------|-------------------------|------------------|-------------------------|------------------|
|                                | λ <sub>max.</sub><br>Å. | ε <sub>max</sub> | λ <sub>max.</sub><br>Å. | ε <sub>max</sub> | λ <sub>max.</sub><br>Å. | ε <sub>max</sub> |
| TFP (96.3)                     |                         |                  | 2416                    | 14,200           |                         |                  |
| Water (94.6)                   | 2300                    | 10,000           | 2422                    | 13,100           | 2693                    | 9800             |
| Methanol (83.6)                | 2245                    | 10,200           | 2353                    | 13,200           | 2635                    | 9800             |
| Ethanol, 95% (81.2)            | 2248                    | 10,000           | ..                      | ..               | ..                      | ..               |
| 2-Propanol (76.8) <sup>a</sup> | 2235                    | 9,600            | 2338                    | 12,600           | ..                      | ..               |
| Acetonitrile (71.3)            | 2220                    | 10,600           | 2314                    | 13,600           | 2588                    | 9800             |
| Isooctane (60.1)               | 2172                    | 12,000           | 2253                    | 14,200           | 2523                    | 9600             |

<sup>a</sup> Measured for the solvent used.

The solvent sensitivities found for the transitions of III, IV, and V are in accord with those found for other ketones, collected in Table VII.

(30) C. Djerassi, N. Finch and R. Mauli, *J. Am. Chem. Soc.*, **81**, 4997 (1959).

(31) Cf. the summary in E. M. Kosower and J. A. Skorz, *ibid.*, **82**, 2195 (1960).

(32) E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 281 (1959).

(33) Convenient procedures for the preparation of V and VI will be reported elsewhere; T. S. Sorensen, unpublished results.

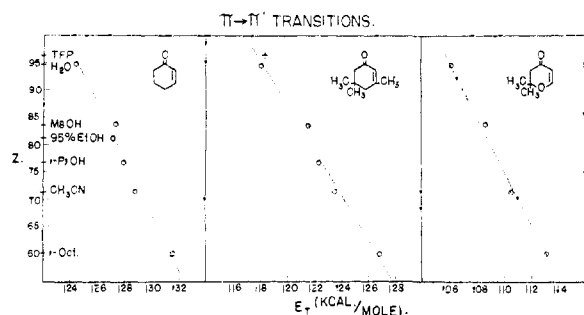


Fig. 3.— $E_T$  (transition energies) versus  $Z$  (solvent polarity values) for the high intensity band of cyclohexenone, isophorone and 2,2-dimethyl-3,4-dihydro[4H]-4-pyrone;  $E_T(\text{III}) = -0.20145Z + 143.56$ ;  $E_T(\text{IV}) = -0.24382Z + 141.28$ ;  $E_T(\text{V}) = -0.20223Z + 125.27$ .

The maxima found for the  $\pi \rightarrow \pi^*$ -transitions present no particular surprises, oxygen moving the maximum to longer wave lengths as a good electron-supplying group. It is perhaps less-well known that electron-supplying groups on  $\alpha, \beta$ -unsaturated ketones shift the  $n \rightarrow \pi^*$ -transition to shorter wave lengths. This effect is particularly marked when the groups are substituted directly on the carbonyl, as in the comparison of formaldehyde, acetaldehyde

TABLE VI  
 $\pi \rightarrow \pi^*$ -TRANSITIONS OF CYCLOHEXENONES

| Solvent (Z)                    | III                         |                         | IV                          |                         | V                           |                         |
|--------------------------------|-----------------------------|-------------------------|-----------------------------|-------------------------|-----------------------------|-------------------------|
|                                | $\lambda_{\text{max}}$ , Å. | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ , Å. | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ , Å. | $\epsilon_{\text{max}}$ |
| TFP (96.3)                     |                             |                         | 2920 <sup>a</sup>           | 91 <sup>a</sup>         | ..                          | ..                      |
| Water (94.6)                   | 3072                        | 51                      | 2959 <sup>a</sup>           | 99 <sup>a</sup>         | ..                          | ..                      |
| Methanol (83.6)                | 3192                        | 34                      | 3108                        | 47                      | ..                          | ..                      |
| Ethanol, 95% (81.2)            | 3197                        | 36                      | ..                          | ..                      | ..                          | ..                      |
| 2-Propanol (76.8) <sup>b</sup> | 3229                        | 33                      | 3154                        | 44                      | ..                          | ..                      |
| Acetonitrile (71.3)            | 3292                        | 30                      | 3241                        | 38                      | ..                          | ..                      |
| Isooctane (60.1)               | 3420                        | 27                      | 3367                        | 31                      | 3166                        | 46                      |
|                                |                             |                         |                             |                         | 3282                        | 44                      |

<sup>a</sup> Overlap with the  $\pi \rightarrow \pi^*$ -absorption band probably causes some displacement to shorter wave lengths and an increase in intensity. <sup>b</sup> Measured for the solvent actually used.

TABLE VII  
SOLVENT SENSITIVITIES OF KETONE ELECTRONIC TRANSITIONS

| Compound                  | $E_T = mZ + b$          |          | Ref.            |
|---------------------------|-------------------------|----------|-----------------|
|                           | Transition              | $m$      |                 |
| Cycloalkanones, $C_n = O$ |                         |          |                 |
| $n = 4$                   | $\pi \rightarrow \pi^*$ | 0.08     | 1               |
| $n = 5$                   | $\pi \rightarrow \pi^*$ | .20      | 1               |
| $n = 6-10$                | $\pi \rightarrow \pi^*$ | .14-0.15 | 1               |
| Mesityl oxide             | $\pi \rightarrow \pi^*$ | -.18     | 2               |
|                           | $\pi \rightarrow \pi^*$ | .20      | .. <sup>a</sup> |
| II, $H = CH_2$            | $\pi \rightarrow \pi^*$ | -.20     | 32              |
|                           | $\pi \rightarrow \pi^*$ | .36      | 32              |
| III                       | $\pi \rightarrow \pi^*$ | -.20     | .. <sup>b</sup> |
|                           | $\pi \rightarrow \pi^*$ | .27      | .. <sup>b</sup> |
| IV                        | $\pi \rightarrow \pi^*$ | -.24     | .. <sup>b</sup> |
|                           | $\pi \rightarrow \pi^*$ | .34      | .. <sup>b</sup> |
| V                         | $\pi \rightarrow \pi^*$ | -.20     | .. <sup>b</sup> |

<sup>a</sup> G. S. Wu, unpublished results on pure mesityl oxide.  
<sup>b</sup> Present work.

and acetone in which the transition energy is changed by 9.1 and 4.1 kcal./mole, respectively. Replacement of a hydrogen by a methyl group in

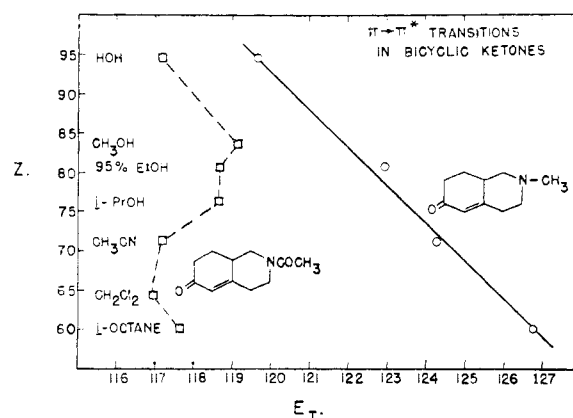


Fig. 4.— $E_T$  (transition energies) versus  $Z$  (solvent polarity values) for the high intensity band of II ( $H = NCH_3$ ) and II ( $H = NCOCH_3$ ).

the  $\beta$ -position of an  $\alpha, \beta$ -unsaturated ketone (III  $\rightarrow$  IV) raises the transition energy by a smaller amount, *ca.* 1.3 kcal./mole.<sup>34</sup> The oxygen substituent (V) is quite effective in raising (6.7 kcal./mole) transition energy, although additional double bonds lower the transition energy in comparison to cyclohexanone.<sup>35</sup>

Against this background of linear correlation with  $Z$  of the electronic transitions of  $\alpha, \beta$ -unsaturated ketones, it is clear that the data of McElvain and Remy on 3-acetyl-3-azabicyclo[4.4.0]dec-5-en-4-one (II,  $H = NCOCH_3$ )<sup>39</sup> represents a decidedly anomalous situation.<sup>32</sup> Their data are given in Table VIII, and the plot of transition energies against  $Z$  for the  $\pi \rightarrow \pi^*$ -transition is shown in Fig. 4. The absorption intensity data are also roughly linear in  $Z$ .

TABLE VIII

| Solvent (Z)               | $\lambda_{\text{max}}$ , Å. | $\epsilon_{\text{max}}$ |
|---------------------------|-----------------------------|-------------------------|
| Water (94.6)              | 2440                        | 13600                   |
| Methanol (83.6)           | 2400                        | 12100                   |
| Ethanol, 95% (81.2)       | 2410                        | 11600                   |
| 2-Propanol (76.3)         | 2410                        | 11400                   |
| Acetonitrile (71.3)       | 2440                        | 10700                   |
| Methylene chloride (64.2) | 2445                        | 10400                   |
| Cyclohexane (60.1)        | 2430                        | 8900                    |

The anomalous pattern of  $E_T$  versus  $Z$  for the N-acetyl ketone is in marked contrast to the N-methyl derivative (II,  $H = NCH_3$ ) for which the data are also plotted in Fig. 4. The  $\pi \rightarrow \pi^*$ -transition of the acetyl derivative moves to shorter

(34) Comparison of crotonaldehyde and mesityl oxide with the appropriate *des*-methyl molecules leads to the same increment in  $n \rightarrow \pi^*$ -transition energies.

(35) *E.g.*, 6-methyl-6-dichloromethyl- $\Delta^{2,4}$ -cyclohexadienone,  $\lambda_{\text{max}}$  3575 Å. ( $\epsilon$  114),  $E_T$  80.8,  $\lambda_{\text{max}}$  3725 Å. ( $\epsilon$  114),  $E_T$  76.8<sup>36</sup>; 4-methyl-4-dichloromethyl- $\Delta^{2,5}$ -cyclohexadienone,  $\lambda_{\text{max}}$  3550 Å.,  $E_T$  80.5,<sup>36</sup> and phorone,  $\lambda_{\text{max}}$  3694 Å. ( $\epsilon$  71),  $E_T$  77.4.<sup>38</sup>

(36) A. F. Bickel, E. C. Kooyman and C. La Lau, *J. Chem. Soc.*, 3218 (1953); slightly different figures for the  $\Delta^{2,4}$ -dienone are recorded elsewhere.<sup>37</sup>

(37) J. Derkosch and W. Kaltenecker, *Monatsh.*, **88**, 778 (1957).

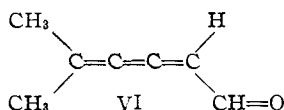
(38) G. S. Wu, unpublished results.

(39) S. M. McElvain and D. C. Remy, *J. Am. Chem. Soc.*, **82**, 3960 (1960).

wave lengths as expected when the solvent is changed from water to methanol, but the trend does not continue in less polar solvents (ethanol, etc.) and is actually reversed in the least polar solvents. The  $\pi \rightarrow \pi^*$ -transition of the acetyl ketone in cyclohexane occurs at a wave length which is only consistent with the presence of a "polar medium" in the region of the  $\alpha, \beta$ -unsaturated ketone system. The only source for polar "solvation" is the acetyl group, and one is forced to the conclusion that the molecule has folded in such a way as to allow the oxygen non-bonding electrons of the acetyl group to interact with the  $\beta$ -carbon of the  $\alpha, \beta$ -unsaturated ketone grouping. Models indicate that the juxtaposition of the oxygen electrons to the  $\beta$ -carbon of the  $\alpha, \beta$ -unsaturated ketone is only accomplished at the cost of amide resonance. According to n.m.r. studies, the energy barrier to rotation around the N—C=O bond is  $7 \pm 3$  kcal./mole (dimethylformamide) to  $12 \pm 2$  kcal./mole (dimethylacetamide).<sup>40</sup> More recent work gives  $9.6 \pm 1.5$  kcal./mole as the barrier in dimethylformamide.<sup>41</sup> From the previous calculations on this bicyclic ketone system<sup>32</sup> it can be estimated that the ground-state electrostatic interaction would be at least 75% of a decrease in transition energy. From Fig. 4, it may be estimated that the transition energy in isoöctane should have been 123.2 kcal./mole, while in fact it was only 117.7 kcal./mole. The augmented interaction leading to a decrease in the transition energy expected for such an  $\alpha, \beta$ -unsaturated ketone system is *ca.* 5.5 kcal./mole. Thus at least 4 kcal./mole are available in the ground state as a result of interaction of the oxygen electrons on the acetyl group and the positive charge present at the  $\beta$ -carbon to compensate for the loss of amide resonance. While the proposal has not been tested further, no other explanation for the anomalous spectroscopic behavior of the ketone readily comes to mind.

It may be concluded from this example that molecular shape even of moderately flexible molecules may be more sensitive to the medium than heretofore considered. While it would be difficult to predict chemical consequences for this situation (the addition of other molecules (reactants, catalysts, etc.) to a medium produces a change in solvent polarity and the cybotactic region<sup>2</sup> which is not easy to evaluate), it should be possible to control the photochemical reactions of certain molecules by manipulating the polarity of the environment in which the photolysis is carried out.

**5-Methyl-2,3,4-hexatrienal.**—The synthesis of the cumulene aldehyde, VI<sup>33</sup> made available a novel unsaturated system with a relatively rigid structure for which the solvent sensitivity of the electronic transitions could be measured. The



(40) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance." McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 366-371.

(41) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

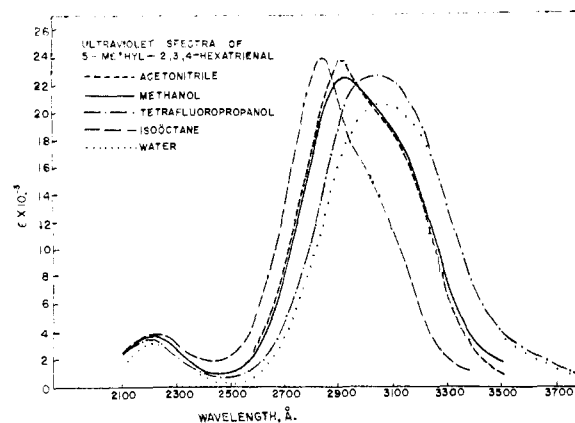


Fig. 5.—Absorption spectra for the cumulene aldehyde VI in a series of solvents.

high-intensity  $\pi \rightarrow \pi^*$ -transitions were examined in five solvents, isoöctane, acetonitrile, methanol, tetrafluoropropanol (TFP) and water. The spectra obtained are shown in Fig. 5. Inspection of the spectra reveals two peculiarities. First, it is characteristic for related conjugated unsaturated systems (*e.g.*, III, IV and V) to exhibit a single, smooth absorption band in the region of their longest wave length maximum. Second, the related systems have absorption bands which change in a fairly smooth manner with solvent, that is, there are no radical changes in the shape of the curve.<sup>42</sup> Further, the half-width of the cumulene aldehyde absorption band in all solvents is rather high, 4800  $\text{cm}^{-1}$  in isoöctane and 5200  $\text{cm}^{-1}$  in water. The corresponding figures for ketone V are 4200 and 4800  $\text{cm}^{-1}$ . We conclude from (a) the shape of the curve in isoöctane and acetonitrile, (b) the serious changes in band shape which arise with solvent change and (c) the breadth of the band that we actually have two bands which overlap. Crude resolution of the curves into two Gaussian shape curves indicates that the long wave length band has very roughly the same solvent sensitivity as the short wave length band, but has an intensity response to solvent change which is different from that of the short wavelength band (Table IX).

TABLE IX

RESOLUTION OF CUMULENE ALDEHYDE  $\pi \rightarrow \pi^*$ -TRANSITION

| Solvent          | Short wave length<br>$\lambda_{\text{max}}, \text{Å}$ | $E_{\tau}$ | Long wave length<br>$\lambda_{\text{max}}, \text{Å}$ | $E_{\tau}$ | Intensity<br>ratio |
|------------------|---|------------|--|------------|--------------------|
| Isoöctane        | 2840  | 102        | 3040   | 94         | 2.5:1              |
| Acetonitrile     | 2900  | 99         | 3130   | 91         | 1.5:1              |
| Methanol         | 2920  | 98         | 3160   | 91         | 1.5:1              |
| TFP <sup>b</sup> | 2960  | 97         | 3180   | 90         | 1:1                |
| Water            | 2990  | 96         | 3210   | 89         | 1:1                |

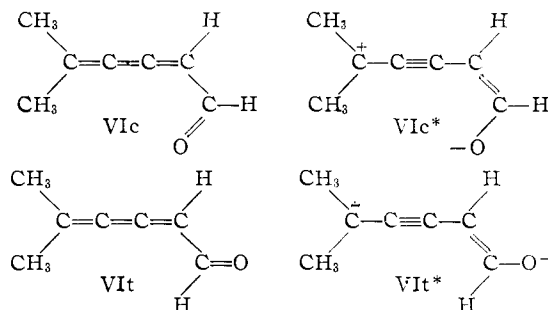
<sup>a</sup> Not better than  $\pm 30 \text{Å}$ . <sup>b</sup> 2,2,3,3-Tetrafluoropropanol.

There are at least two possible explanations for the appearance of the absorption bands of the cumulene aldehyde VI. It may be that the two

(42) In general, the change from a non-hydrogen bonding solvent to one which can hydrogen-bond leads to a considerable spreading of the absorption band without a very serious change in the *integrated absorption intensity*. Merocyanines show this change very clearly.<sup>43</sup>

(43) N. S. Bayliss and E. G. McRae, *J. Am. Chem. Soc.*, **74**, 5803 (1952).

bands arise from two vibrational levels of the excited state, but it would then be unexpected that the intensity ratios of the two bands would change so markedly with solvent. A second hypothesis is that each band is due to a separate species present in solution. We have, however, shown that the material used is one chemical entity.<sup>44</sup> The only type of isomerism which could occur is around the single bond connecting the cumulene system to the aldehyde group. Thus, it is necessary to consider both *s-cis*- and *s-trans*-5-methyl-2,3,4-hexatrienal as components of a solution. We can account for the substantial difference in the positions of the transitions for the isomers by a consideration of the excited states which arise from the electronic transition. For the *s-cis* form, the transition is shown as VIc→VIc\*, while that of the *s-trans*-



is indicated as VIIt→VIIt\*. The *s-cis*-excited state (VIc\*) should be higher in energy than the corresponding *s-trans*-excited state because the extra negative charge appearing on the oxygen in the excited state will be repelled by the negative charge cloud of the  $\pi$ -electrons of the middle double bond (the one written as a triple bond in the excited state). It is also reasonable that the apparent concentration of the *s-trans* form should increase with increasing solvent polarity since the extended conjugated system has the higher dipole moment.<sup>45</sup>

**Conclusions.**—*Z*-Values, solvent polarity as determined by the interaction of a solvent with the 1-ethyl-4-carbomethoxypyridinium iodide ion pair, offer a reasonable way of choosing solvents over a range of polarities for use in connection with spectra or kinetics. It has been shown that comparison of the spectroscopic data obtained in sol-

vents of different polarity with *Z*-values can lead to useful and interesting conclusions about (1) the conformation of cyclohexanone derivatives, (2) the shape of a bicyclic ketone and (3) the orientation of a group around a single bond. In each case, a pattern of "normal" behavior was established empirically, and conclusions were reached by a decision as to whether the case under study conformed to or deviated from the "normal" behavior.<sup>46</sup>

### Experimental

The sample of 2-chlorocyclohexanone was prepared according to the directions of Newman, *et al.*<sup>47</sup> The crude product was fractionated twice through a 2-ft. glass helices column to give material with b.p. 101° (33 mm.),  $n_D^{25}$  1.4798; reported<sup>48</sup> b.p. 90° (15 mm.),  $n_D^{25}$  1.4830.

Isophorone was obtained from a careful fractionation of commercial product (practical grade, Eastman Kodak Co.). A middle fraction, b.p. 89° (20 mm.),  $n_D^{25}$  1.4452, was used. The 2-cyclohexen-1-one was prepared by the pyrolysis of 2-acetoxycyclohexanone by the procedure of Wanzlich, Gollmer and Milz.<sup>49</sup> A fractionation of the product gave ketone b.p. 68° (15 mm.),  $n_D^{25}$  1.4809; reported<sup>50</sup> b.p. 61–62° (10 mm.),  $n_D^{25}$  1.4897. We wish to thank Dr. K. Williamson for supplying this material and 2-chlorocyclohexanone.

A sample of 2,2-dimethyl-3,4-dihydro-[4H]-pyran-4-one<sup>51</sup> (V) was redistilled under a nitrogen atmosphere through a 15 × 1.2 cm. straight tube to yield a colorless liquid. The material had b.p. 67–68° (8 mm.),  $n_D^{25}$  1.4770.

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>: C, 66.64; H, 7.99. Found: C, 66.89; H, 8.05.

The cumulene aldehyde VI was purified by repeated recrystallizations from pentane at –70° and subsequent distillation at 25° (0.1 mm.) gave pure aldehyde, a pale yellow liquid with a pungent lachrymatory vapor, m.p. –11 to –9°,  $n_D^{25}$  1.606.

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>O: C, 77.75; H, 7.46. Found: C, 77.82; H, 7.34.

Solvents were purified or used as previously described.<sup>1,2</sup>

All spectra were obtained with a Cary model 11 or 14 as described in the previous article.

The  $n \rightarrow \pi^*$ -transitions of III and IV give quite good linear correlations with *Z* (solvent polarity values) with  $E_T$  (III) = 0.26835*Z* + 67.589 and  $E_T$  (IV) = 0.33530*Z* + 64.56.

**Acknowledgments.**—The authors wish to acknowledge valuable discussion with Professor C. D. Cornwell, Chemistry Department, University of Wisconsin.

(46) At the very least, it is hoped that *le vieux jeu* of interpreting a few scattered pieces of spectroscopic data will be abandoned in favor of more searching examination of simple systems. Examples of *la nouvelle vague* are to be found in N. J. Leonard, *Chimica*, **14**, 231 (1960), and N. J. Leonard, T. W. Milligan and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960).

(47) M. S. Newman, M. D. Earbman and H. Hipsher, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 188.

(48) W. D. Kuntler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956).

(49) H. W. Wanzlich, G. Gollmer and H. Milz, *Ber.*, **88**, 69 (1955).

(50) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 607 (1954).

(44) The n.m.r. spectrum of a pure sample shows no sign of another compound and is so simple that its interpretation is only consistent with the structure given.<sup>32</sup>

(45) The response of the absorption coefficient to solvent change could have the same form (Table VIII) in special cases, but the data in Table V show that a linear dependence of absorption intensity on *Z* is not the general rule.