methylacetaldehyde by the same procedure used in the case of trimethylacetaldehyde-1-d. On removal of the ether, the crude oil containing the neopentyl alcohol-1-d, as well as the normal addition product, was treated with phthalic anhydride in the usual manner.[7] The crude crystals were recrystallized to give 700 mg. (25% yield based on the (−)- 1-chloro-2-methylbutane-2-d), m.p. 68.5–70.0°. After a second and third recrystallization the m.p. was constant at 68.5–69.5°. Because of the small amount of material it was difficult to obtain accurate rotations, but within experi- mental error they were unchanged at α^{25}D −0.07 ± 0.02° (l 1, c 40; acetone). After the fourth recrystallization a precise value of α^{27}D −0.072 ± 0.010° (l 1, c 39.9; acetone), $[\alpha]^{27}$D −0.180 ± 0.010° was obtained in a Rudolph recording spectropolarimeter. A deuterium analysis[18] revealed 0.56 atom per molecule. The infrared spectrum of this com- pound was identical with that obtained from the enzymatic reduction of trimethylacetaldehyde-1-d^7 with the exception of the differences due to the relative amounts of hydrogen and deuterium in the two samples.

The Effect of Solvent on Spectra. V. The Low Intensity (n → π*) Electronic Transition of Cyclic Ketones

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RECEIVED SEPTEMBER 6, 1960

A series of cycloalkanones with ring size (n = 4–10, 15) has been examined in the near ultraviolet region in a series of solvents covering a broad polarity range. The transition energies (E_T) were plotted against the solvent polarity standard, Z (ref. 4). Cyclobutanone was found to have a n → π*-transition with rather low sensitivity to solvent, and brief examina- tion of two other cyclobutanones suggested that such low sensitivity may be characteristic of these rings. The transitions for the ketones with n = 5 through 10 correlate rather well with Z, and the correlation for cyclohexanone is so good that it can be used as a secondary standard of solvent polarity. It was found that the slope of the correlation for cyclopentadec- anone, n = 15, was unexpectedly low. Low solvent sensitivity for the n → π*-transition of the C_{15}-ketone was rationalized by postulating that the molecule tended toward "folded" conformations in polar solvents, but was "open" or "extended" in non-polar solvents. The C_{15}-ketone absorption band obeyed Beer's law in all solvents.

Not only are all measures of solvent polarity empirical, but the application of a particular meas- ure to a chemical or physical problem depends upon the congruency of the physical process from which the measure was derived to that under study. The dielectric constant, which averages both the molecular and polymolecular inhomogeneities of a liquid solvent, is not very satisfactory as a measure of solvent polarity on the molecular level. The dielectric constant of the first layer of water mole- cules around an ion, for example, must be ap- preciably different from that of the measured (macroscopic) dielectric constant.[2] For most chemical processes,[3] and for spectroscopic transi- tions, the detailed properties of the solvent group (cybotactic region)[4] immediately around the spe- cies of concern control the course of events. For the consideration of the effect of solvent polarity on the microscopic level, it is more desirable to choose model processes which are in their turn subjected to a detailed and searching analysis. For kinetic processes, the rate of solvolysis of t- butyl chloride covers a reasonable range of solvent polarity[3,5]; the parameter based on these rates is called a Y value. A more general parameter be- came available with the discovery that the charge- transfer absorption band of 1-ethyl-4-carbometh- oxypyridinium iodide was extremely sensitive to the solvent[4]; the transition energy corresponding to the absorption band was defined as the Z-value for the solvent in which it was measured.

Solvent polarity values defined on the basis of molecular processes can serve a number of useful purposes. Correlation of rates or of spectroscopic maxima can lead to the estimation of rates or maxima in solvents for which the rate or maximum has not been or can not be measured. Response to solvent change, which is an important criterion of chemical mechanism or for establishing the nature of an electronic transition, can be placed upon a semi-quantitative basis. Last, anomalous behavior with respect to an expected correlation can call attention to chemically interesting situations.

The purpose of the present paper is to examine the effect of solvent on the low intensity (n→π*) electronic transition of cycloalkanones. It will be seen that Z-values are useful in the analysis of the results.[6]

Results

The ketones used in this investigation were all carefully purified. Our experience indicated that a number of the cyclic ketones were sensitive to photochemically-induced oxidation. One impor- tant criterion of purity was therefore the lack of a maximum or shoulder in the ultraviolet absorption curve between 2200 and 2600 Å., where α,β- unsaturated ketones and other impurities would absorb. The other more usual criteria of purity (melting point, boiling point, refractive index, derivatives, etc.) were also utilized. In the case of cyclobutanone, it proved impractical to remove 2 or 3% of two volatile impurities (detected by vapor phase chromatography), but the identical results given by two different samples afford con- fidence in the supposition that the contaminants are non-light-absorbing in the region of the maxi- mum of cyclobutanone.[7]

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(2) J. A. Schellman, J. Chem. Phys., 26, 1225 (1957).

(3) A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2770 (1956).

(4) E. M. Kosower, ibid., 80, 3253 (1958).

(5) E. Grunwald and S. Winstein, ibid., 70, 846 (1948).

(6) Cf. also E. M. Kosower, ibid., 80, 3261 (1958).

(7) The observation concerning the fact that impurities more volatile than cyclobutanone are present even in purified ketone was also
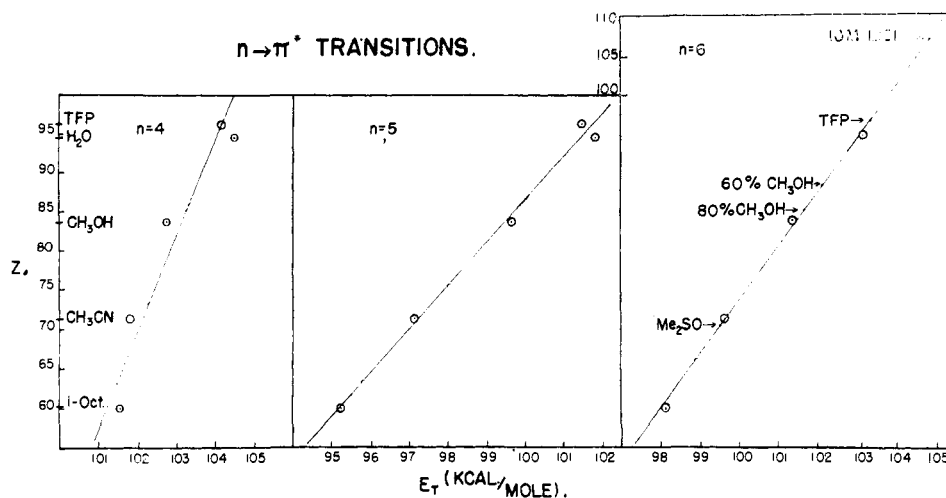
Fig. 1.—E_T (transition energies) *versus* Z (solvent polarity values) for cycloalkanones, $n = 4$, $E_T = 0.081987Z + 96.290$; $n = 5$, $E_T = 0.18246Z + 84.252$; $n = 6$, $E_T = 0.14650Z + 89.234$. The arrows on the cyclohexanone ($n = 6$) line indicate the Z-values derived for these solvents from their experimental E_T values (TFP = 2,2,3,3-tetrafluoropropanol). For $n = 7$, $E_T = 0.14038Z + 89.371$; $n = 8$, $E_T = 0.13768Z + 89.890$; $n = 9$, $E_T = 0.15112Z + 88.404$.
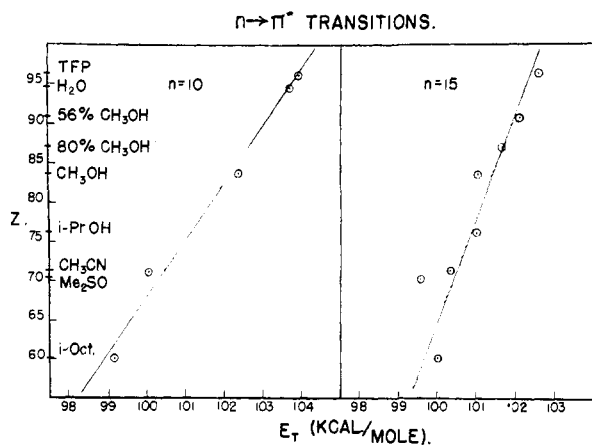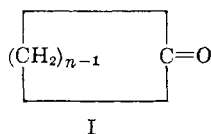

Fig. 2.—E_T (transition energies) *versus* Z (solvent polarity values) for cycloalkanones, $n = 10$, $E_T = 0.13727Z + 90.680$; $n = 15$, $E_T = 0.073445Z + 95.276$.

Fig. 3.—E_T (transition energies) *versus* n, ring size for cycloalkanones in two solvents, water and isoöctane. Note point for $n = 15$ at far right.

The solvents for the ultraviolet measurements were chosen so as to provide the full range of solvent polarity from isoöctane (Z 60.1) to 2,2,3,3-tetrafluoropropanol (TFP) (Z 96.3). The Z-value for the fluorinated alcohol differs from that previously reported,[4] and is derived from the linear relationship of transition energies for the n→π*-transition of cyclohexanone with Z. All solvents were Spectrograde or of equivalent quality. The maxima were measured carefully in the usual way.[4]

The maxima for the n→π*-electronic transition of the cyclic ketones I, where $n = 4,5,6,7,8,9,$

$$(CH_2)_{n-1} \quad C=O$$

I

10 and 15, are presented in Table I. In order to

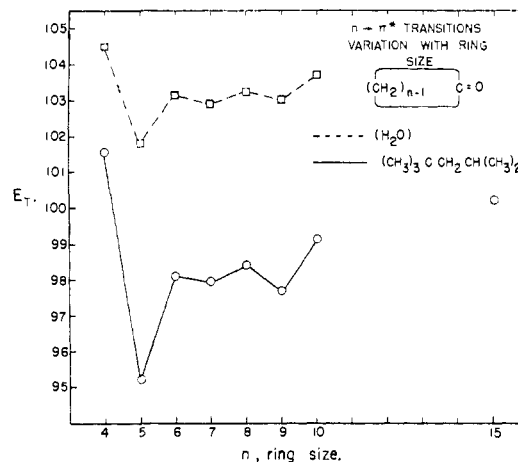made by R. Arndt, Hs. H. Günthard and T. Gäumann, *Helv. Chim. Acta*, **41**, 2213 (1958).

make the comparisons, the maxima were converted to transition energies in kcal./mole by the relation E_T (kcal./mole) $= 2.859 \times 10^5 \times 1/\lambda_{max}$ (in Å.). The transition energies were then plotted against Z; Fig. 1 (I, $n = 4,5,6$) and Fig. 2 (I, $n = 10,15$).

Certain quantities can be directly derived from the experimental data. These are the slopes of the least-squares line drawn to relate the points in the figures, and the difference in transition energies for the solvents isoöctane and water. Both quantities are related to the degree to which the position of the n→π*-transition responds to the polarity of the solvent, the slope averaging out the changes over a range of solvent polarities. The "solvent sensitivities" derived by difference, E_T (HOH) $- E_T$ (isoöctane), are listed in Table II, while the slopes and the solvent sensitivities corresponding to these slopes (obtained by multiplying by the Z-value difference between the solvents, ΔZ) are listed in Table III.

TABLE I

ABSORPTION MAXIMA OF CYCLIC KETONES

Cyclic ketone, cyclo-	Water (94.6)[a]		Methanol (83.6)[a]		Acetonitrile (71.3)[a]		Isoöctane (60.1)[a]		Tetrafluoro-propanol (96.3)[a]		Other		
	λ_{max}[b]	ϵ_{max}	λ_{max}[b]	ϵ_{max}	λ_{max}[b]	ϵ_{max}	λ_{max}[b]	ϵ_{max}	λ_{max}[b]	ϵ_{max}	λ_{max}[b]	ϵ_{max}	Solvent (Z)
Butanone	2736	20	2783	20	2808	20	2815	20	2746	19			
Pentanone	2808	21	2870	18	2943	17	3001	18	2817	22			
Hexanone	2771	21	2829	15	2870	15	2914	15	2766	20	2872	18	Me$_2$SO (70.4)[f]
											2726	24	10 M LiCl (106.8)[f,g]
Heptanone	2777	26	2838	20	2878	18	2918	17	2779	26	2857	20	i-PrOH (76.6)[d]
Octanone	2770	21	2832	17	2872	15	2905	14	2770	21	2871	17	Me$_2$SO (70.4)[f]
Nonanone	2776	25	2850	17	2882	15	2926	15	2772	25			
Decanone	2757	27	2794	18	2858	17	2883	15	2752	22			
Pentadecanone	..[c]		2830	27	2850	26	2859	23	2788	36	2831	27	i-PrOH (76.2)[d]
											? 2800	24	56% MeOH (90.9)[e]
											2813	24	80% MeOH (87.1)[e]
											2851	30	Me$_2$SO (70.4)[f]

[a] Z-value.   [b] All values are considered valid to at least ±5–6 Å.   [c] Insufficiently soluble.   [d] Determined for the sample of Spectrograde isopropyl alcohol actually used.   [e] Calculated from the linear relation between Y-values and Z-values for methanol–water mixtures.[4]   [f] Derived from the linear relation between E_T and Z for cyclohexanone.   [g] Determined by Mr. Peter L. Schwartz.

TABLE II

SOLVENT SENSITIVITIES[a] OF CYCLIC KETONES (n → π^*- TRANSITION)

Ketone, C_n=O n = ring size	ΔE_T, kcal./mole	Ketone, C_n=O n = ring size	ΔE_T, kcal./mole
4	2.94	8	4.80
5	6.58	9	5.30
6	5.07	10	4.53
7	4.97		

[a] Defined as the difference between water and isoöctane transition energies.

TABLE III

SOLVENT SENSITIVITIES OF CYCLIC KETONES

$$E_T = mZ + b$$

Ketone C_n=O n (ring size)	m	$m(\Delta Z)$,[a] kcal./ mole	Ketone, C_n=O n (ring size)	m	$m(\Delta Z)$,[a] kcal./ mole
4	0.082	2.83	8	0.138	4.76
5	.182	6.28	9	.151	5.21
6	.147	5.07	10	.137	4.73
7	.140	4.83	15	.073	2.52

[a] The numbers in this column should be compared with those under ΔE_T in Table II.

Two other relationships may be derived from the data in Tables I and II. If the transition energies, E_T, are plotted against ring size, n, an interesting alternation is found, which is much less apparent in polar solvents (Fig. 3). There also is a curious and possibly meaningful linear connection between the solvent sensitivities (Table II) and the transition energies in isoöctane.

Discussion

The low intensity, ultraviolet absorption of carbonyl compounds[8] has been undeservedly ignored by many organic chemists, even though its use in the analysis of the stereochemistry of halo-ketones[9] should have encouraged measurement of other substances. The only complete experimental study of simple carbonyl compounds is that

(8) The history and theory of the n → π*-transition in carbonyl and other compounds have been reviewed by J. W. Sidman, Chem. Revs., 58, 689 (1958).

(9) Cf. article VI in this series, E. M. Kosower, G. S. Wu and T. S. Sorensen, J. Am. Chem. Soc., 83, 3147 (1961).

of Maroni,[10] who measured the ultraviolet maxima of thirty-two alkyl ketones in three solvents, hexane, ethanol and water. Ignorance of the appreciable solvent effect on many electronic transitions has often led to the failure to mention the solvent used in an ultraviolet measurement.[11] Even when the identity of the solvent is stated, the choice is not always the most satisfactory from the point of view of interpretation. Many years ago, Scheibe[12] warned that non-polar solvents should be used to study the ultraviolet spectra of many compounds, including carbonyl compounds, so as to minimize the effects of solvent–solute interaction. In the case of cyclic ketones, the differences between compounds with different n are minimized by the use of the polar solvent water (Fig. 3), and the use of ethanol caused Leonard and Owens[13] to conclude that ring size has no significant effect upon the position of the maxima for the n→π*-transition. In point of fact, considerable caution should even be exercised in the measurement of carbonyl bands in the infrared region, for these maxima are solvent-sensitive[14] and the variation can be correlated with those in the ultraviolet.[15] Cookson[16] recommended the use of hexane for n→π*-transitions on the grounds that observation of the maxima was easier. At the beginning of our investigation, it was clear that an appreciable solvent effect could be expected. The point to be settled was whether or not the utilization of Z as the solvent polarity parameter could provide further insight into the solvent effect. Inspection of Figs. 1 and 2 for the plots of the ke-

(10) P. Maroni, Ann. chim., [13] 2, 757 (1957); cf. also P. Maroni and J. E. Du Bois, J. chim. Phys., 51, 402 (1954).

(11) Cf. discussion of this and other non-uniformities in presentation of data by J. D. Cawley and H. E. Ungnade, Anal. Chem., 31, 42A (1959).

(12) G. S. Scheibe, Ber., 58, 592 (1925).

(13) N. J. Leonard and F. H. Owens, J. Am. Chem. Soc., 80, 6039 (1958).

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

(15) M. Ito, K. Inuzuka and S. Imanishi, J. Chem. Phys., 31, 1694 (1959).

(16) R. C. Cookson and S. H. Dandegaonker, J. Chem. Soc., 1651 (1955).

tones I, $n = 4, 5, 6$ and 10, reveals a moderately good linear relationship between the band position (as transition energy) and the Z-value of the solvent. In two cases, that of cyclopentanone and cyclohexanone, *the linearity is strikingly good.* It may be concluded that a linear correlation between n→π*-transition energies and Z may be the rule for relatively rigid cyclic carbonyl compounds.[9,17] Furthermore, the linear relation may be taken as support for the electrical parallelism between the n→π*-transition and the charge-transfer transition which defines the Z-values; it had previously been suggested that the excited state of the n→π*-transition can be regarded as electrically neutral.[6]

The less perfect correlation of the transition energies of cycloheptanone, cyclooctanone and cyclononanone with Z may be ascribed to the conformational mobility of these ketones,[18] with a solvent effect upon the proportions of conformers present in the solutions.

The small variation in the over-all solvent sensitivities (as defined previously in Table III) for the ketones, $n = 6, 7, 8, 9$, and 10 ($m = 0.14$ to 0.15), provides a means for choosing a *"normal"* slope. Marked deviations from "normal" slope or from linearity of E_T against Z may be regarded as anomalies which require rationalization. Thus, three anomalies are to be found in Table III, *i.e.*, cyclopentanone, cyclobutanone and cyclopentadecanone.

The solvent sensitivity of cyclopentanone is appreciably greater than that of the other cyclic ketones. As pointed out by Cook[19a] and Diner,[19b] the non-bonding electrons on the oxygen of the carbonyl group are probably in sp^2 hybrid orbitals.[20,21] The structure of the acetone–bromine complex is consistent with such an orbital arrangement, and not with one dependent upon pure p-orbitals for the oxygen non-bonding electrons.[22] In cyclopentanone, the non-bonding oxygen electrons are non-eclipsed by the α-hydrogens, a situation which should permit a somewhat more highly organized cybotactic region than in cyclohexanone, and thus a greater solvent sensitivity as measured by the technique used in this paper. It should be noted that hydrogen-bonding ability *vis-à-vis* a single hydrogen bond as measured by the shifts in OD stretching frequency of methanol-d decreases in the order $7 > 6 > 5 > 4$.[23]

The low solvent sensitivity of cyclobutanone is somewhat puzzling, although in agreement with decreased hydrogen-bonding ability.[23] It is furthermore disturbing that a small, relatively rigid ketone does not exhibit an E_T *versus* Z relationship of greater linearity; however, the force con-

stant for the carbonyl stretching frequency is curiously low[24] and the naive approximation we have made concerning the "neutrality" of the excited state of the n→π*-transition may not be applicable for cyclobutanone. The low solvent sensitivity of cyclobutanone n→π*-transition is

also found for the bicyclic ketones II and III[2] (Table IV).

TABLE IV

n → π*-TRANSITIONS OF CYCLOBUTANONES

Ketone	Solvent	$\lambda_{max},$ Å.	ϵ_{max}	E_T	ΔE_T
II	Isoöctane	2967	24[a]	96.36	
	Water	2921	30[a]	97.88	1.52
III	Isoöctane	2940	21[a]	97.24	
	Water	2870	..[b]	99.62	2.38
Cyclobutanone					2.94

[a] It was not possible to purify the small amounts of ketone supplied; small amounts of pentane or ether may have been present. [b] Limited solubility.

In comparison to the solvent sensitivities for the n→π*-transitions of the cycloalkanones from cyclohexanone to cyclodecanone, the solvent sensitivity of the low intensity carbonyl band of cyclopentadecanone is *anomalously low.* The behavior of the C_{15}-ketone apparently was not due to change in degree of association because a check of Beer's law revealed essentially no concentration effect either on the position of the maximum or on the absorption intensity (see Table VI, Experimental section). Examination of models suggests at least two important classes of arrangements (*i.e.*, conformers) of cyclopentadecanone which may be loosely described as the "open" or "extended" form, and the "folded" form. The low solvent sensitivity indicates that the cybotactic region[4] around the carbonyl group includes regions of lower polarity than one would expect on the basis of the Z-value for the solvent, in solvents of high polarity (high Z-value). The implication of the low solvent sensitivity is that the "folded" form is present in high polarity solvents.

The cause of the "folding" is relatively easy to understand. Large non-polar molecules disrupt the hydrogen-bonded structure of polar solvents; "folding" therefore represents the triumph of the hydrogen-bonding tendency of the solvent over the resistance of cyclopentadecanone to "folding." The "folded" form is more compact than the "extended" form and thus has less net effect upon the hydrogen bonding of the solvent.

One might expect, for suitable molecules, both chemical and photochemical consequences of the principle that molecular conformation is solvent dependent. "Medium-ring" chemistry offers many examples of the effect of having another part of the molecule in proximity to a reaction center. Provided that a "normal" standard is available, the study of the variation of an electronic transition

(17) *Cf.* the bicyclic ketones reported in E. M. Kosower and D. C. Remy, *Tetrahedron,* **5**, 281 (1959).

(18) N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959).

(19) (a) D. Cook, *ibid.*, **80**, 49 (1958); (b) S. Diner, *Bull. soc. chim. France,* 1025 (1959).

(20) The "whole-numbers" are, of course, approximations (*cf.* R. S. Mulliken, *Tetrahedron,* **6**, 68 (1959)).

(21) M. Kasha, personal communication, now prefers p and sp on the basis of some ultraviolet measurements by W. Simpson.

(22) O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, **13**, 275 (1959).

(23) M. Tamres and S. Searles, Jr., *J. Am. Chem. Soc.*, **81**, 2100 (1959).

(24) H. Frei and Hs. H. Günthard, paper presented to the Fourth European Molecular Spectroscopy Symposium, Bologna, Italy, September, 1959.

(25) Made available by Dr. F. Nelson.

with solvent polarity and the correlation of that electronic transition with Z offers a facile way for discovering whether or not serious changes in molecular conformation with solvent actually occur. The accompanying paper presents some additional examples of the use of Z-values for study of conformation changes in a number of molecules.[9]

It does not seem possible at this time to rationalize the positions (Fig. 3) of the n→π*-transitions of the cycloalkanones, although we doubt that "hyperconjugation" is a significant factor.[26-29]

With respect to the apparent linear relationship between ΔE_T and E_T, it can be adduced that the solvent sensitivity is implied in the same factor which determines the band position in a non-polar, non-interacting solvent. A rather similar relationship is found between band position and solvent sensitivity for alkyl ketones by Maroni,[10] although in that case it seems more a matter of increasing steric hindrance to solvation as the alkyl groups become bulky and shift the maximum to longer wave lengths.

Experimental

Materials.—**Cyclobutanone** (Aldrich Chemical Co.) was treated with dilute solution of potassium permanganate, dried with molecular sieves and then fractionated. A middle cut of b.p. 96–97°, $n^{26.5}$D 1.4172 (reported[30] b.p. 97–98°, n^{25}D 1.4179), was used. A preparation of 2,4-dinitrophenylhydrazone was carried out as quantitatively as possible and the m.p. of both the crude product and the recrystallized sample were recorded. The crude product was red needles, m.p. 147.0–148.5° (86.9%). A sample recrystallized from methanol gave a m.p. of 146.0–146.5°, red long needles (reported, 144.5°,[30] 147–147.2°[31]).

Cyclopentanone (Aldrich Chemical Co.) was shaken with potassium permanganate solution several times until there was no indication of absorption in the 2300–2400 Å. region. After drying a careful fractionation was carried out. A constant boiling fraction, b.p. 128°, n^{25}D 1.4340 (reported, b.p. 128–130°,[32] b.p. 129°, n^{20}D 1.4370[33]), was collected. A 2,4-dinitrophenylhydrazone was obtained as orange needles, m.p. 145.5–146.5° (95.8%); recrystallized sample, short orange-yellow needles, m.p. 145.0–145.5° (from methanol) (reported[34] 145.5–146.0°).

Cyclohexanone.—A commercial product was treated with with potassium permanganate and fractionated as above; constants of the fraction used: b.p. 154°, n^{23}D 1.4482 (reported, b.p. 155°, n^{20}D 1.4507[35]; b.p. 152–153°[32]). The crude 2,4-dinitrophenylhydrazone was a yellow powder, m.p. 160–161° (95.0%); recrystallized from methanol, yellow plates, m.p. 160.0–160.5° (reported, 161–162°,[34] 157°[36]).

Cycloheptanone.—A sample from Aldrich Chemical Co. was carefully purified as in the case of cyclopentanone; material used: b.p. 172.5°, n^{26}D 1.4592 (reported b. p. 105°[37] (80 mm.), n^{24}D 1.4607[38]). The yield of crude 2,4-dinitrophenylhydrazone melting at 147–148° was 90.0% (orange-yellow

powder). After recrystallizing from methanol–acetone it gave orange-yellow needles with m.p. 148.0–148.8° (reported, 148°,[38] 146–147°[39]).

Cyclooctanone.—For purification, the recrystallization was first tried using several solvents of different polarities. Difficulties were encountered either in the crystallization of the substance or in the separation of the recrystallized crystals from the mother liquor. The compound was best purified by sublimation. The resublimed material gave m.p. of 41.0–41.8° (reported[40] 42°); 2,4-dinitrophenylhydrazone: crude product, orange-yellow powder, m.p. 174.0–175.5° (90%); recrystallized from ethanol, orange-yellow plates, m.p. 174.6–175.5° (reported[37] 163°).

Anal. Found: C, 54.76; H, 5.97. Calcd. for $C_{14}H_{13}N_4O_4$: C, 54.89, H, 5.92.

Cyclononanone.—Commercial product (Aldrich Chemical Co.) was first purified by distillation under reduced pressure. The physical constants of the distillate are in good agreement with the literature. A trace of unsaturated material, however, could not be entirely removed. The compound was also best purified by repeated sublimation under 0.05–0.1 mm. vacuum; 2,4-dinitrophenylhydrazone: orange needles, m.p. 141.5–142.5°, 90.0% yield; two recrystallizations from methanol, orange needles, m.p. 142.0–142.8° (reported, 146°,[41] 136°[42]).

Cyclodecanone.—An Aldrich Chemical Co. product was sublimed twice to obtain the pure sample; 2,4-dinitrophenylhydrazone: orange-yellow powder, m.p. 161.5–163.0° (99%); recrystallized from methanol, orange-yellow powder, 161.8–162.8° (reported[43] 165°).

Cyclopentadecanone.—A recrystallization from aqueous ethanol does not remove a trace of contaminated material, presumably formed by air oxidation. Although the potassium permanganate-treated ether solution of recrystallized cyclopentadecanone gave no indication of this impurity, the melting point of the material obtained from the evaporation of this ether solution did not seem to be very sharp. The purification by sublimation proved to be the best for cyclopentadecanone; m.p. of the material used, 62.0–63.0° (reported[40] 63°); 2,4-dinitrophenylhydrazone, yellow powder, m.p. 103–104° (96%); recrystallized from methanol–acetone, yellow powder, m.p. 107.8–109.0° (reported[37] 105°).

Bicyclo[3.2.0]-7-heptanone and Bicyclo[3.2.0]-3-heptene-7-one.—The crude products obtained from F. Nelson were used directly.

Solvents.—Isooctane, acetonitrile and isopropyl alcohol were Matheson, Coleman and Bell Spectroquality solvent and were used directly. The Z-value of the alcohol was checked with 1-ethyl-4-carbomethoxypyridinium iodide for each fresh bottle.[4]

Water was first distilled from potassium permanganate and then from a small amount of sodium hydroxide.

The 2,2,3,3-tetrafluoropropanol was a gift of the Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc. The first sample was fractionated, b.p. 105–106°, n^{29}D 1.3182. Although the material was suitable as a solvent for most purposes it contained a small amount of ultraviolet-absorbing impurity (benzene?) which could not be removed. A second and much larger sample was purified by a procedure developed by Pih-kwei C. Huang, as follows.

Water (90 ml.) was mixed with the 2,2,3,3-tetrafluoropropanol (450 ml.) (TFP) and 2.25 g. of sodium bisulfite. The turbid solution was vigorously shaken and allowed to stand for 24 hours, after which the mixture was fractionated as tabulated

Fraction	B.p., °C.	Vol., cc.	$n^{24.5}$D
A	92	80	1.3275
B	92–99	160	1.3255
C	99–105	80	1.3196
D	105–107	150	1.3190
E	107	50	1.3189

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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.	$n^{24.5}D$	1 cm. cell O.D. = 1 at
A	104	50	1.3204	a
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.

a 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 ±6 Å. for the model 11 and to ±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 → π*-TRANSITION)

Solvent	Concn., M	λ_{max}, Å.	ϵ_{max}
Isoöctane	0.0439	2850	23
	.00732	2860	23
	.00366	2860	21
Methanol	.0413	2830	27
	.00413	2830	26
	.000413	2813 ± 30^a	28
2,2,3,3-Tetrafluoro-	.0351	2786	33
propanol	.00351	2790	31

a 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.

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

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RECEIVED SEPTEMBER 6, 1960

The effect of solvent on the position of the n → π*-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-carbomethoxypyridinium 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 π-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 π*-anti-bonding electron in the n → π*-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 = NCOCH₃) 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,[1] we have shown that the relationship between the transition energies for the low-intensity (n→π*-transition) carbonyl absorption band of certain cycloalkanones and Z-

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(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-carbomethoxypyridinium iodide)[2] is linear. Against the background of linear correlations for the ketones, C_5 through C_{10}, it could be discerned that the C_{15}-cycloalkanone was anomalous. Its

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