BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2030—2034 (1967)

Studies of the Solvent Effects on the Chemical Shifts in NMR Spectroscopy. III. The Benzene Solutions of Cyclic Ketones and Lactones*1,*2,*3

Yukihiko ICHIKAWA[4]* and Taku MATSUO[5]*

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka

(Received February 10, 1967)

The high-field shifts of the proton signals of cyclic ketones and lactones in the benzene solutions have been investigated. The solvent effects on the chemical shifts for the β-methylene protons of these compounds are always larger than those for the α-methylene protons. The data may be explained by the use of a model in which benzene molecules are assumed to cluster around the carbonyl group of the solute. The affinity between the solute and the solvent molecules has been mainly ascribed to the fact that both the permanent electric dipole moment and the instantaneous dipole moment of the carbonyl (or carboxyl) group induce electric dipole moments in the near-by benzene molecules. The configuration and the number of the solvent molecules clustering around the solute have been suggested to be determined by the geometrical restriction around the carbonyl group.

The proton signals of various carbonyl compounds in benzene solutions have been known to appear at higher field than those in non-aromatic solvents.[1-4] It has been pointed out by Bhacca and Williams, and also by Connolly and McCrindle, that both the direction and the magnitude of the solvent effects on the chemical shifts strongly depend on the location of the proton with respect to the carbonyl group.[1,5] In order to systematize the observed solvent effects, they have defined a reference plane (P) which is drawn through the carbonyl carbon and perpendicular to the carbon-oxygen bond. If a proton is at the same side as the oxygen of the carbonyl group with respect to the P plane, the resonance signal shifts to low field as the solvent is changed from deuterochloroform to benzene. On the other hand, the high-field shifts are observed for the protons at the other side of the P plane. The benzene-induced high-field shift increases at first and then decreases again as the distance between the proton and the reference plane increases. The benzene-induced high-field shifts were originally suggested to be due to a formation of collision complex between the benzene molecules and the carbonyl-carbon which bears partially positive charge.[6] The appreciable solvent effects have been observed, however, even in the cases where the association between benzene and carbonyl group is sterically unfavourable.[1] The mechanisms of the benzene-induced solvent effects therefore have been still open to speculations. An insight into the mechanism of the benzene-induced shifts may be obtained by studying the relationship between the solvent effects and the electronic characteristics of carbonyl groups. In this connection, one of the present authors has investigated the behaviors of succinic, and maleic anhydrides and the *N*-substituted imides in the benzene solutions.[7] In the present report, the benzene-induced shifts for the protons of cyclic ketones will be compared with those for lactones.

Results and Discussion

As to the cyclic compounds investigated here, the resonance signals of the protons at β-, γ- and δ-positions with respect to the carbonyl group are

*1 Presented in parts at the 19th and the 20th Annual Meetings of the Chemical Society of Japan, Yokohama and Tokyo, April, 1966 and 1967, respectively.

*2 Previous paper of this series: Ref. 7.

*3 Contribution No. 118 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

*4 Present address: Mizonokuchi Institute of Mitsubishi Yuka Co., Ltd., Kawasaki.

*5 The person to whom any correspondence should be addressed.

1) J. D. Connolly and R. McCrindle, *Chem. & Ind.*, **1965**, 379.

2) J. D. Connolly and R. McCrindle, *ibid.*, **1965**, 2066.

3) J. H. Bowie, D. W. Cameron, P. E. Schutz, D. H. Williams and N. S. Bhacca, *Tetrahedron*, **22**, 1771 (1966), and the preceeding papers of the series.

4) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **44**, 37 (1966).

5) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

6) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco (1964), Chapter 7 and the references cited therein.

7) T. Matsuo, *Can. J. Chem.*, in press "Studies of the Solvent Effects on the Chemical Shifts in NMR Spectroscopy. II. Solutions of Succinic Anhydride, Maleic Anhydride, and the *N*-Substituted Imides."

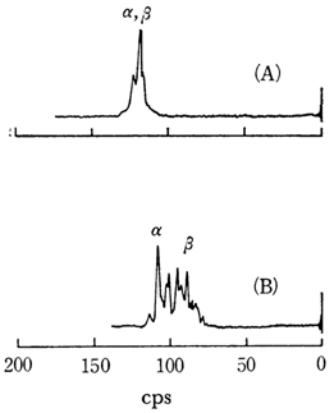

Fig. 1. Proton magnetic resonance spectra of cyclopentanone in carbon tetrachloride (A) and in benzene (B).

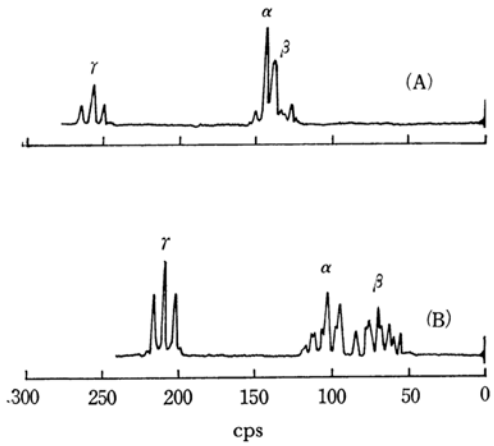

Fig. 2. Proton magnetic resonance spectra of γ-butyrolactone in carbon tetrachloride (A) and in benzene (B).

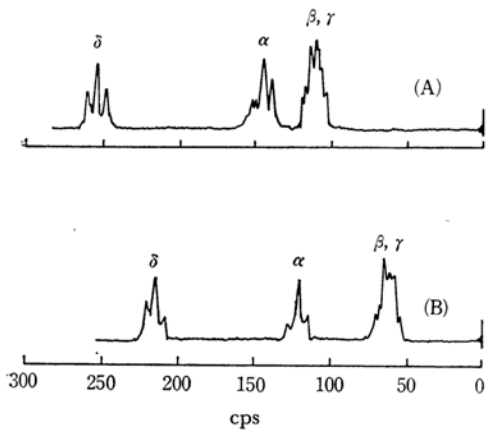

Fig. 3. Proton magnetic resonance spectra of δ-valerolactone in carbon tetrachloride (A) and in benzene (B).

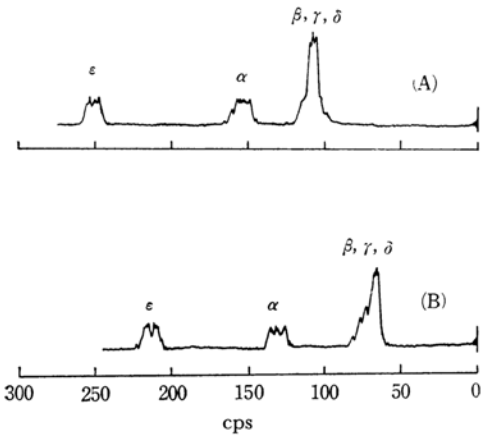

Fig. 4. Proton magnetic resonance spectra of ε-caprolactone in carbon tetrachloride (A) and in benzene (B).

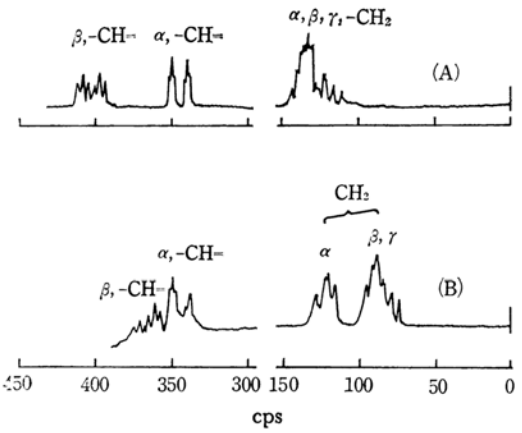

Fig. 5. Proton magnetic resonance spectra of 3-cyclohexenone in carbon tetrachloride (A) and in benzene (B).

hardly separated each other as shown in Figs. 1—5. In the cases of cyclopentanone, 3-cyclohexenone, and γ-butyrolactone, even the α-proton signals overlap with those of the β-protons. Therefore, complete analyses of the spectra cannot be made without tremendous calculations. In the present experiment, however, the main effort is devoted to the study of the solvent effects on the signal positions rather than to the complete analyses of the spectra. Then, a conventional method is adopted to treat the data as follows: The center of a group of signals is taken as the position for the chemical shift, if the spectrum is close to a typical multiplet as expected from the first order analysis. When a group of signals corresponding to a certain proton (or protons) has a structure far from simple multiplet, the chemical shift is assumed to be given by the location of the area-weighted center of the concerning signals. The assignment of the signals is facilitated by comparing

Table 1. Chemical shifts of cyclic ketones in carbon tetrachloride and benzene*

Compound	Proton	Solvent: Carbon tetrachloride	Solvent: Benzene	$\Delta\delta$
Dipropyl ketone	α-CH_2	137	116	21
	β-CH_2	93	89	4
Cyclopentanone	α-CH_2	120	103	17
	β-CH_2	120	79	41
Cyclohexanone	α-CH_2	134	121	13
	β- and γ-CH_2	108	79	29
Cycloheptanone	α-CH_2	144	132	12
	β- and γ-CH_2	100	76	24
3-Cyclopentenone	α-CH_2	134	112	22
	β-CH_2	159	112	47
	α-CH	366	353	13
	β-CH	455	409	46
3-Cyclohexenone	α-CH	353	353	0
	β-CH	411	375	36

* Chemical shifts are in cps from internal TMS signal.

Table 2. Chemical shifts of lactones in carbon tetrachloride and benzene*

Compound	Proton	Solvent: Carbon tetrachloride	Solvent: Benzene	$\Delta\delta$
Ethyl butyrate	α-CH_2	132	124	8
	β-CH_2	97	93	4
	OCH_2	243	243	5
γ-Butyrolactone	α-CH_2	141	104	37
	β-CH_2	137	70	67
	γ-CH_2	255	209	46
δ-Valerolactone	α-CH_2	146	122	24
	β- and γ-CH_2	113	62	51
	δ-CH_2	255	217	38
ε-Caprolactone	α-CH_2	152	129	23
	β-γ- and δ-CH_2	107	68	39
	ε-CH_2	248	212	36
Isocrotonolactone	α-CH	362	330	32
	β-CH	452	375	77
	γ-CH_2	290	230	60

* Chemical shifts are in cps from internal TMS signal.

the spectra in carbon tetrachloride with those in benzene. The chemical shifts thus obtained are summarized in Tables 1 and 2. The shifts are expressed in cps units as measured from TMS signal. Carbon tetrachloride is chosen as the reference solvent because of its closeness to benzene both in their inertness and in their dielectric constants. The benzene-induced high-field shifts ($\Delta\delta$) are given in the last column of each table.

The variations of $\Delta\delta$ as the function of ring size are summarized in Fig. 6. The values for acyclic compounds also are shown in the same figure. The $\Delta\delta$-values for the protons of the cyclic compounds, except for the methylene protons of the cyclic ketones, are considerably larger than those for the acyclic compounds. As the member of the ring decreases, the $\Delta\delta$ becomes larger. As to a cyclic compound, the β-proton signals show larger high-field shifts than the α-proton signals. These characteristics of the cyclic carbonyl compounds may be correlated to the fact that the protons under investigation are confined to the opposite side of the carbonyl oxygen with respect to the P plane as described in the introduction.

On the above observation, the presence of intermolecular interactions between benzene and carbonyl compounds is strongly suggested. Several anthors have suggested that benzene solvent molecules can interact with polar solute molecules *via* a dipole-induced dipole interactions.[8,9] In this connection, it is interesting that the dipole moment of γ-butyrolactone, which gives the largest

8) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).
9) T. L. Brown and K. Stark, *ibid.*, **69**, 2679 (1965).

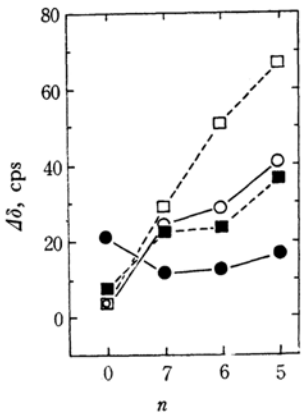

Fig. 6. Variation of $\Delta\delta$ as the function of ring size. The number, n, on the abscissa indicates the members of the ring. Acyclic compound is designated as a zero-membered ring compound.
●: The α-methylene protons of ketones
○: The β-methylene protons of ketones
■: The α-methylene protons of lactones
□: The β-methylene protons of lactones

$\Delta\delta$ in Fig. 6, is as high as 4.13 D,[10] whereas all of the cyclic ketones have dipole moments close to 3.0 D.[11] As it is seen in Fig. 6, however, the $\Delta\delta$-values for lactones are approximately two times larger than those for cyclic ketones of the same ring size. Therefore, the dipole-induced dipole interaction cannot be the sole reason for the solute-solvent interactions in question. If the dipole-induced dipole interaction (or induction force) is of any importance, the other weak interactions of similar types, *i. e.*, van der Waals forces, should be also taken into consideration. Since an accurate calculation of van der Waals force is formidable in the present cases, the interactions are estimated qualitatively by the use of both formula given by Debye (for induction force) and that by London (for dispersion force).

$$\text{Induction Force:} \quad E_f = -\alpha_1\mu_2^2/R^6 \tag{1}$$

Dispersion Force:

$$E_d = -2I_1I_2\alpha_1\alpha_2/3(I_1+I_2)R^6 \tag{2}$$

In the above equations, the subscripts 1 and 2 denote benzene and carbonyl group, respectively. Considering the cases of actual molecules, one can assumes the dipole moment, the polarizabilities and the ionization potentials as shown below: $\mu_2=3.0$ D,[11] $\alpha_1=1.1\times10^{-23}$ cm^3,[12] $\alpha_2=0.2\times10^{-23}$ cm^3,[13] and $I_1=I_2=10$ eV.[14] If it is assumed further that the distance R is 5 Å, E_f and E_d become 0.09 and 0.11 kcal/mol, respectively. This simple calculation clearly indicates that the dispersion force is as important as the dipole-induced dipole interaction. In addition, the charge-transfer force[7] and the dipole-quadrupole interaction[15] also may contribute to the intermolecular attractions as the supplementary forces.

On the basis of variable-temperature studies, the energies of interactions between polar molecules of various types and solvent benzene have been estimated to be of the order of 1 kcal/mol.[7,16-18] The values are very reasonable ones if the interactions are due to van der Waals forces and the others of similar types as proposed above. Then the interaction had better be defined as a general solvation rather than as a specific complexing. In the present cases, the benzene solvent molecules around the carbonyl group take such orientations that maximum attractions between the solute and the solvent molecules are obtained. On the time average, the situation may be represented by a model where several benzene molecules are assumed to cluster around the carbonyl group. On the basis of the clustering model here proposed, the present authors speculate the nature of the solvent effect under investigation as described in the following paragraph.

In the close neighborhood of a solute molecule, the contour of electron clouds as given by the van der Waals radii of the concerning atoms will severely restrict the possible orientations of the approaching solvent molecules. Consequently, the number and the configuration of the clustering benzene molecules will be determined by the geometrical conditions in the vicinity of the carbonyl group. In the case where a benzene molecule is at the back of the P plane (*i. e.* the opposite side to the carbonyl oxygen) of a cyclic carbonyl compound, the most probable mode of solvation may be the one where the molecular plane of the benzene is parallel to the ring of the solute. Then, high-field shifts will be obtained for the methylene protons of the ring system. The number of the solvating benzene molecules will decrease with the distance from the carbonyl group. Then, the high-field shift must be small for a proton located away from the P plane. At the other side of the P plane, however, benzene molecules are able to

10) K. Sukigara, Y. Hata, Y. Kurita and M. Kubo, *Tetrahedron*, **4**, 337 (1958).
11) Hs. H. Gunthard and T. Gaumann, *Helv. Chim. Acta*, **34**, 39 (1951).
12) C. G. Le Fèvre and R. J. W. Le Fevre, *J. Chem. Soc.*, **1953**, 4041.
13) C. G. Le Fevre, R. J. W. Le Fevre and B. P. Rao, *ibid.*, **1959**, 2340.
14) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Arnold (Publishers) Ltd., London (1966), pp. 151—190.
15) N. Nakagawa, Private communications to T. Matsuo.
16) H. M. Hutton and H. Schaefer, *Can. J. Chem.*, **41**, 1857 (1963).
17) H. Bowie, J. Ronayne and D. H. Williams, *J. Chem. Soc. (B)*, **1966**, 785.
18) Y. Nakayama and T. Matsuo, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1925 (1966).

approach the whole cylindrical region around the C=O bond axis with equal probability. The average effect of the clustering benzenes in this region will cause deshielding of the protons close to the carbonyl group. As the result of these two modes of solvations, the benzene-induced high-field shifts for α-methylene protons are expected to be less than those for β-methylene protons. The clustering model here proposed is, of course, one of the possible explanations given to the benzene-induced shifts. The present authors believe, however, that their model is closer to the truth than the stereo-specific one-to-one complexes as suggested before.[6,8]

Several features of the solvent effects on the chemical shifts in Tables 1 and 2 have been left to be discussed here. The decrease in $\Delta\delta$ as observed for the cases of the large-membered ring compounds may be due to the increase in the steric hindrance to the approaching benzene molecules. In the cases of dipropyl ketone and ethyl butyrate, the β-methylene signals are affected by benzene to lesser extents than the α-methylene signals. Due to the rotations around the C–C bond connecting the α-methylene group to the carbonyl group, the α-methylene protons in the acyclic systems are expected to have high probability of taking trans positions with respect to the carbonyl group. On the other hand, similar rotations bring the β-methylene protons closer to the P plane as compared with the cases of cyclic compounds where the rotations are forbidden. Then it is quite reasonable that the α-proton signals show large $\Delta\delta$ than the β-proton signals. If a C=C bond is conjugated to a carbonyl group, the $\Delta\delta$-values are very large. The examples are found in the cases of α- and β-methylene protons of 3-cyclopentenone (as compared with cyclopentanone), and also in the cases of γ-methylene protons of isocrotonolactone (as compared with γ-butyrolactone). The reason may be ascribed to the fact that both the dipole moment and polarizability of a α, β-unsaturated carbonyl compound are larger than those of the corresponding compound without the conjugating double bond.*6 It is peculiar, however, that the $\Delta\delta$-values for the methine protons on the double bond are rather smaller than those expected. This unexpected result and the solvent effects on the chemical shifts of methylene protons next to the ethereal oxygen of lactones are to be explained in future.

Experimental

Chemicals. Cyclohexanone, benzene, and carbon tetrachloride were purchased from the Wako Pure Chemicals Industries Ltd., and were purified by the standard chemical procedures followed by the repeated distillations. Other chemicals were synthesized as follows from the starting materials given in the parentheses, respectively: dipropyl ketone (butyric acid), cyclopentanone (adipic acid), cycloheptanone (cyclohexanone), 3-cyclopentenone (cyclopentanone), 3-cyclohexenone (cyclohexanone), ethyl butyrate (butyric acid and ethanol), γ-butyrolactone (ethyl malonate and ethylene oxide), δ-valerolactone (cyclopentanone), ε-caprolactone (cyclohexanone), and isocrotonolactone (glycerol). Repeated purifications were applied to the products until the purity exceeded 98% as observed on the gas chromatogram.

Measurement of NMR Spectra. The spectra were measured by the use of a Varian A-60 analytical NMR spectrometer. The concentration of the sample was kept at 3 mol%, and a small amount of TMS was dissolved in the solution as the internal reference.

The authors are grateful to Dr. Naoya Nakagawa of the University of Electro-communications for helpful discussions.

*6 The dipole moment of isocrotonolactone is 4.62 D in comparison with 4.13 D for γ-butyrolactone.[10]