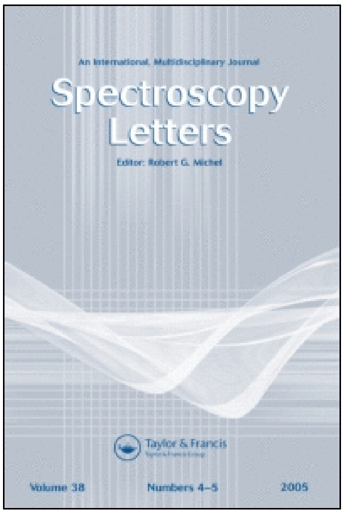

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Effects of Benzene on the ^{1}HNMR of α-Oxoketene Dithioacetals

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EFFECTS OF BENZENE ON THE ^{1}HNMR OF α-OXOKETENE DITHIOACETALS

Key words: ASIS effect, linear correlation, solvation, continuous field.

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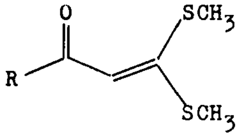
ABSTRACT ^{1}HNMR spectra of the title compounds have been measured as the function of the mole fraction of benzene in the mixture solvent of benzene and CCl_4. As the mole fraction of benzene increases, the chemical shifts (δ) of two methyl groups in a molecule and of benzene gradually move upfield. The upfield shifts of different methyl groups in a molecule are not equal to one another. The $\Delta\delta$ of β-CH_3 is larger than that of α-CH_3. Thus, the two lines appear to coalesce at a certain concentration and to cross over with the increment of the proportion of benzene. All of the chemical shifts can be related with a linear equation (δ=A+BX). Where, X is the

mole fraction of benzene in the mixture solvent. The correlation coefficients R are approximately equal to 1.

INTRODUCTION

The preparations and synthetical applications of α-oxo ketene dithioacetals (I) have been widely studied (1-6). We have recently investigated the solvent effects on their ^{1}HNMR spectra. It was shown that the resonance absorptions of methyl groups in these compounds exhibited a significant upfield shifts in benzene, compared with that observed in carbon tetrachloride.



I

Interesting properties have been shown: the resonance absorptions of two methyl groups in a molecule first coalesced and then separated further as the ratio of benzene to the solute was increased, also the absorption line of benzene was always a single sharp line. In earlier works, to account the coalesce of CH_3 groups, the ASIS of DMF was explained by complex formation (Fig. 1) (7-11). The ring current of the benzene ring produced an anti-magnetic field, and increased the shielding effect on the methyl protons

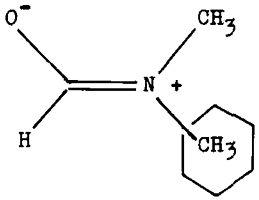
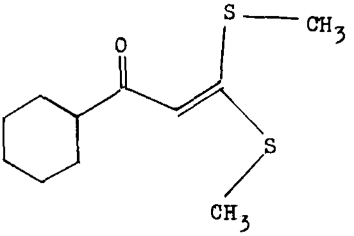


Fig. 1

located near to the center of the benzene ring. It is not unreasonable to derive the postutated structure above, since the electron-rich benzene ring would not likely close to the negatively charged oxygen.

However, in those papers, no attention was paid to the resonance absorptions of the solvents. If 1:1 complexes are present in the dilution, the absorption lines of benzene would display a split, at least show a broad peak, the exchange between complexed solvent molecules and uncomplexed ones is possible though.

In the present work, there is no reason to impose complex selectivity to the different methyl groups in the molecule, since both of them are separated from carbonyl group (Fig 2) (12). Morever, even in a very dilute solution, the absorption of benzene is always a sharp line. That is, all of C_6H_6 molecules are in the same electronic state. A solvation model derived from the polar interaction is proposed.

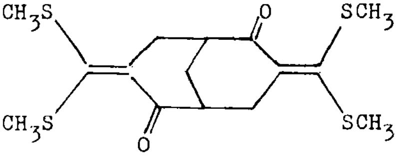


II

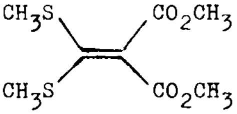
Fig. 2

EXPERIMENTAL

The species (13) used in the present work was 2,2-di(methylthio)vinyl phenyl ketone (II) (see Fig 2), 3,7-bis-(methylthiomethylene)bicyclo[3,3,1]nona-2,6-dione (III), and dimethyl dimethylthiomethylenemalonate (IV). The chemical shifts were measured as the function of the proportion of benzene in the mixture solvent of benzene and carbon tetrachloride, using a JEOL FX-90Q nmr instrument at 26±0.5 °C, tetramethyl silicane served as an external reference.



III



IV

Tab 1. Proton Chemical shifts of compound (II) in the mixture solvent of carbon tetrachloride and benzene.[a]

Mole fraction of benzene	Chemical shifts (in ppm)					
	$CH_3(\alpha)$	$\Delta\delta_1$ [b]	$CH_3(\beta)$	$\Delta\delta_2$ [b]	$\Delta\delta_2-\Delta\delta_1$	Ar-H
0	2.46		2.54			
0.05	2.39	0.07	2.43	0.11	0.04	7.24
0.10	2.35	0.11	2.37	0.17	0.06	7.21
0.15	2.29	0.17	2.29	0.25	0.08	7.17
0.20	2,24	0.22	2.20	0.34	0.12	7.14
0.30	2.14	0.32	2.04	0.50	0.18	7.06
0.40	2.04	0.42	1.90	0.64	0.22	6.99
0.50	1.94	0.52	1.76	0.78	0.26	6.92
0.55	1.88	0.58	1.67	0.87	0.29	6.88
0.60	1.84	0.62	1.60	0.94	0.32	6.84
0.70	1.74	0.72	1.47	1.07	0.35	6.76
0.80	1.65	0.81	1.34	1.20	0.39	6.69
0.90	1.55	0.91	1.20	1.34	0.43	6.60
0.95	1.50	0.96	1.13	1.41	0.46	6.56
1.00	1.45	1.01	1.07	1.47	0.46	6.52

a) The mole fraction of solute is 1.25×10^{-2}; b) variations from that observed in pure CCl_4.

RESULTS AND DISCUSSION

In compounds (II) and (III), there were two types of methyl groups distinguished by cis or trans to the carbonyl group. It is probable that the methyl group attached to the S atom which is cis to the carbonyl group will be of an upperfield absorption than that of one trans to the carbonyl group, due to the nonbonding polarization of cis S-CH_3 bond by the negatively charged carbonyl oxygen. We tentatively assign the upperfield CH_3 as α and other one as β. The results are summarized in tables 1-3.

Several relationships can clearly be seen from the tables: a) all the resonance lines of SCH_3 groups are gradually moved to upfield as the mole fraction of benzene in solvent increases; b) the extents of upfield shifts of different SCH_3 groups in a molecule of (II) or (III) were not equal to each other, the $\Delta\delta$ of β-SCH_3 (trans to the carbonyl groups) were larger than that of α-SCH_3 which are cis to the carbonyl groups, thus the two lines appear to coalesce at a certain concentration and to cross over then, and separate further with the increasing of the proportion of benzene; c) the resonance absorption of OCH_3 in the compound (IV) was also gradually subjected to an upfield shifts as the mole fraction of benzene increased.

Tab 2. Proton chemical shifts of com pound (III) in the mixture solvent of carbon tetrachloride and benzene.[a]

Mole fraction of benzene	Chemical shifts (in ppm)					
	$CH_3(\alpha)$	$\Delta\delta_1$[b]	$CH_3(\beta)$	$\Delta\delta_2$[b]	$\Delta\delta_2-\Delta\delta_1$	Ar-H
0	2.31		2.33			
0.05	2.26	0.05	2.26	0.07	0.02	7.25
0.10	2.21	0.10	2.21	0.12	0.02	7.22
0.15	2.16	0.15	2.13	0.20	0.05	7.18
0.20	2.12	0.19	2.08	0.25	0.06	7.16
0.30	2.01	0.30	1.94	0.39	0.09	7.07
0.40	1.92	0.39	1.82	0.51	0.12	7.00
0.50	1.84	0.47	1.73	0.60	0.13	6.93
0.55	1.79	0.52	1.66	0.67	0.15	6.89
0.60	1.73	0.58	1.59	0.74	0.16	6.84
0.70	1.65	0.66	1.49	0.84	0.18	6.77
0.80	1.56	0.75	1.38	0.95	0.20	6.68
0.90	1.48	0.83	1.27	1.06	0.23	6.60
0.95	1.43	0.88	1.21	1.12	0.24	6.56
1.00	1.38	0.93	1.16	1.17	0.24	6.52

a) The mole fraction of solute is 1.25×10^{-3}; b) variations from that observed in pure CCl_4.

Tab 3. Proton Chemical shifts of compound (IV) in the mixture solvent of carbon tetrachloride and benzene[a].

Mole fraction of benzene	Chemical shifts (in ppm)					
	SCH_3	$\Delta\delta_1$ [b]	OCH_3	$\Delta\delta_2$ [b]	$\Delta\delta_1-\Delta\delta_2$	Ar-H
0	2.45		3.76			
0.05	2.39	0.06	3.72	0.04	0.02	7.26
0.10	2.33	0.12	3.67	0.09	0.03	7.23
0.15	2.27	0.18	3.63	0.13	0.05	7.20
0.20	2.21	0.24	3.58	0.18	0.06	7.16
0.30	2.10	0.35	3.49	0.27	0.08	7.09
0.40	1.98	0.47	3.40	0.36	0.11	7.02
0.50	1.89	0.56	3.32	0.44	0.12	6.96
0.55	1.82	0.63	3.27	0.49	0.14	6.92
0.60	1.75	0.70	3.22	0.54	0.16	6.88
0.70	1.65	0.80	3.14	0.62	0.18	6.81
0.80	1.54	0.91	3.05	0.71	0.20	6.73
0.90	1.43	1.02	2.95	0.81	0.21	6.65
0.95	1.38	1.07	2.91	0.85	0.22	6.62
1.00	1.32	1.13	2.86	0.90	0.23	6.57

a) The mole fraction of solute is 5×10^{-2}; b) variations from that observed in pure CCl_4.

Tab 4.- Linear correlation of the chemical shifts of protons

	Compound (II)	
(β)CH_3	(α)CH_3	Benzene
A=2.5005	A=2.4431	A=7.2939
B=-1.4580	B=-0.9980	B=-0.7630
R=-0.9992	R=-0.9998	R=-0.9937
	Compound (III)	
(β)CH_3	(α)CH_3	Benzene
A=2.3104	A=2.2991	A=7.3115
B=-1.1661	B=-0.9205	B=-0.7766
R=-0.9994	R=-0.9996	R=-0.9937
	Compound (IV)	
SCH_3	OCH_3	Benzene
A=2.4404	A=3.7620	A=7.3098
B=-1.1249	B=-0.8972	B=-0.7260
R=-0.9998	R=-0.9999	R=-0.9995

All of the chemical shifts in the tables can be related by a straight line (δ=A+BX). Where, A is the gradiant which is obtained from extrapolation, B-- slope, and X -- the mole fraction of benzene in the mixture solvent. The correlation coefficients are approximately equal to 1 (Table 4).

It has been suggested that the chemical shifts induced in components of the mixture of benzene and chloroform are due to the solvation of $CHCl_3$ by benzene (14). In the present work, we tentatively assume that the solvation between substrates used and benzene would be responsitive to the upfield shifts for either component. There may be a continuous

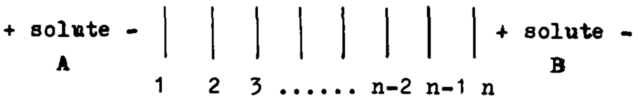


Fig. 3

" charge deviation " in the solvation shell (Fig 3).

The " Charge deviation " is caused by the polarization of benzene by the substrate. The " charge deviation " between solute molecule B and solvent molecule n ($Cd_{n\rightarrow B}$) is larger than that between solvent molecules n-1 and n ($Cd_{n-1\rightarrow n}$) by a value ΔE,

$$Cd_{n\rightarrow B} - Cd_{n-1\rightarrow n} = \Delta E$$

in the same way,

$$Cd_{n-2\rightarrow n-1} - Cd_{n-1\rightarrow n} = \Delta E$$

and so on. Therefore, all solvent molecules are in the same electronic state (normal state of $C_6H_6 - \Delta E$). So they display a sharp single absorption line. However, motion and exchange between them was possible.

The upfield shifts of benzene is attributed to the weakening of the ring current, which arises from the transfer of negative charge. For the solutes, the solvation by C_6H_6 is directional. It would be parallel to the dipolar direction. The different extents of upfield shifts for methyl groups in a molecule canbbe explained that the trans CH_3 is closer to the positive pole of the molecule, so that it obtaines some more negative charge from the solvation. that is, the increment of negative charge of trans CH_3 will be larger than that of cis CH_3.

The present of carbon tetrachloride undoubtedly inteferes with the solvation of solute with benzene. Accordingly, the less the mole fraction of CCl_4, the greater are upfield shifts of protons (both in the solutes and benzene).

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