Dielectric Polarization Measurements of Some β-Diketones & β-Ketoesters in Solutions: Part III—Dipole Moments of Benzoylacetone in Non-polar & Polar Solvents

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The dipole moments of benzoylacetone at infinite dilution in four non-polar, and three polar solvents have been determined at 30-50°C. In some solvents, linear relation has been observed between the square of the dipole moment and the corresponding keto or enol mol fraction. The equation obtained for this linear relation is made use of to calculate the dipole moments of the keto and enol forms, and consequently, to infer the most probable configurations of these molecules.

In earlier papers of this series[1,2], dipole moments of ethyl acetoacetate and acetylacetone were determined in solvents of different polarities in order to have insight into keto-enol equilibria of these ketones. These investigations have been extended to benzoylacetone.

Benzoylacetone (BDH) was crystallized twice from dilute ethanol. The solvents, viz. cyclohexane, carbon tetrachloride, benzene and dioxane (all non-polar) and chloroform, triethylamine and acetone (all polar) were purified by standard methods and their properties checked by comparing the measured densities and refractive indices with those reported in literature (agreement in the values was within ± 0.0001).

Experimental procedures and calculation of the solution moments of benzoylacetone at infinite dilution in non-polar solvents were the same as described before[1]. Solution moments of benzoylacetone in the polar solvents were determined using the modified[3] form of the Onsager[4] equation. The apparent molar volumes and refractive indices of the solid benzoylacetone were determined by the method of intercepts by plotting the specific volumes and specific refractions of solutions against solute weight fractions, W_2. The apparent specific quantity was first obtained, and multiplied with the molecular weight of solute to furnish the data in terms of molar values.

The values of the dipole moment of benzoylacetone in various solvents are listed in Table 1. Also included in Table 1 are the enol mol fractions determined at 30°C by analysis of its UV absorption spectra[5] in different solvents, as described in the literature[6,7].

If we accept that at equilibrium benzoylacetone is composed of only two forms of unknown moments, μ_{keto} and μ_{enol}, then a plot of squares of the observed moments (μ_2^2) against the enol mol fraction (N_{enol}) should be linear as is required by the simple mixture law. This expectation is borne out experimentally as is evident from Fig. 1. The equation thus obtained for this linear plot is:

$$\mu_2^2 = 12.22 - 3.52\, N_{enol} \qquad \ldots (1)$$

Hence, $\mu_{keto} = 3.49$ D and $\mu_{enol} = 2.95$ D. The value 3.52 D^2 obtained from Eq. (1) for the difference $\mu_{keto}^2 - \mu_{enol}^2$, is evidently in satisfactory agreement with the value 3.50 D^2, which could be deduced from thermal data of Powling and Bernstein[6] using an equation based on Onsager[3]-Kirkwood[8] model (An estimated value of the order 127300

Table 1—Dipole Moments and Enol Mol Fractions of Benzoylacetone in Various Solvents

Solvent	μ_2			N_{enol}(30°C)	Method	Ref
	30°	40°	50°C			
Cyclohexane	2.98	3.02	3.06	0.950	UV	Present work
CCl$_4$	2.96	3.00	3.02	0.980	UV	Present work (ref 7)
Benzene	3.14	3.16	3.17	0.667		Present work
Dioxane	3.23	3.26	3.29	0.506	UV	
Chloroform	3.00	3.01	3.02	0.921	UV	(ref 6)
Triethyl amine	3.91	3.88	3.85	1.000		
Acetone	3.68	—	—	0.907		(ref 6)

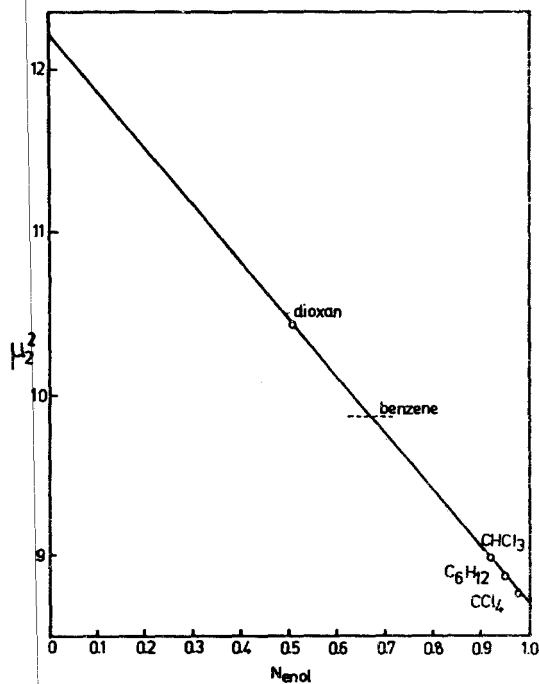Fig. 1—Relation between square of the measured dipole moment of benzoylacetone and the corresponding enol mol fraction

cal cm^3 mol^{-1} for the slope leads to a value of 3.50 D^2 for the difference $\mu_{keto}^2 - \mu_{enol}^2$).

For determining the most probable structures of the keto and enol tautomers, μ_{keto} = 3.49 D and μ_{enol} = 2.95 D have been used. For this purpose, four keto and one enol configurations are assumed (see Fig. 2). The dipole moment values of these suggested configurations (Fig. 2) were tentatively calculated applying the usual vector summation method of bond moments[9].

In view of the calculated μ_{keto} = 3.49 D and μ_{enol} = 2.95 D, the most probable configurations are structures (I) and (V), respectively.
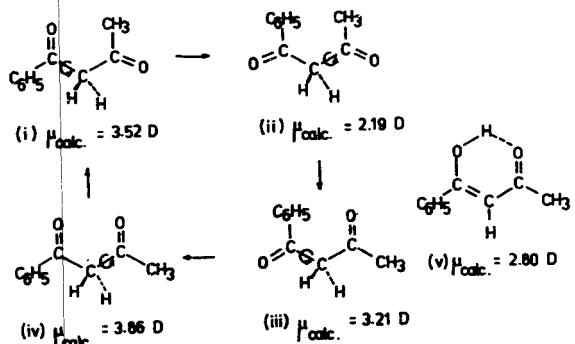

Fig. 2—Suggested keto and enol configurations of benzoylacetone and then calculated dipole moment values

The linear relation (1) is, in particular, significant in non-polar solvents. This signifies that the interaction of the types keto-keto, enol-enol, or keto-enol, is insignificant in benzoylacetone, and that the slight shift in the keto-enol equilibrium upon change of solvent, is caused by the slight difference in the solvent dielectric constant. As in case of acetylacetone[2], the enol mol fraction of benzoylacetone in benzene is calculated using Eq. (1) to be 0.667.

Dissolution of benzoylacetone in triethylamine results in a preferential development of the enol form, as a result of the interaction of the type $(C_2H_5)_3N \ldots H—O—C(C_6H_5)=CHCOCH_3$, which would assist enolization. Hence, the difference between the measured dipole moment of benzoylacetone in triethylamine (3.91 D) and that inferred for the enol form (2.95 D) is attributed to such an interaction.

The observed difference in the measured dipole moment of benzoylacetone (3.68 D) at 30°C in acetone, and that (3.00 D) calculated from Eq. (1), considering enol mol fraction as 0.907 (ref. 7), suggests a solute-solvent interaction.

In case of chloroform, the dipole moment value (2.99 D), when correlated with the enol mol fraction of 0.921, evidently lies closer to the linear plot (Fig. 1). This signifies that in chloroform, unlike in triethylamine and acetone, no specific interactions exist. Thus chloroform acts as a non-polar solvent for the solute benzoylacetone.

Finally, it is noted that increase in temperature increases the solution moment of benzoylacetone in the non-interacting solvents. This is not unexpected, since increase in temperature increases the proportion of keto tautomer, which has higher dipole moment. On the other hand, in interacting solvents, it is expected that increase in temperature would be associated with the dissociation of the interacting molecules and their observed moments would be low.

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