Conformations of dibenzylideneacetone: An IR spectroscopic study

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Abstract. The conformational analysis of dibenzylideneacetone has been carried out using IR spectroscopy. Appearance of a triplet C=O band is attributed to the coexistence of three conformers viz. s-cis, cis, s-cis, trans and nonplanar s-trans, trans in contrast to the earlier findings which showed the existence of only two conformers. The relative proportions of the conformers are in the order s-cis, trans > nonplanar s-trans, trans > s-cis, cis in less polar solvents and nonplanar s-trans, trans > s-cis, trans > s-cis, cis in more polar solvents.

Keywords. Dibenzylideneacetone; triplet C=O band; skew conformation; polarity of the conformers; stability of conformers.

1. Introduction

Conformational analysis of dibenzylideneacetone (DBA) assumed greater importance in view of its ability to form a novel series of zerovalent transition metal complexes because of its existence in several isomeric forms (Takahashi et al 1970; Moseley and Maitlis 1971; Ukai et al 1974). By virtue of the existence of two degrees of rotational freedom imparted by two single bonds between the olefin and carbonyl group, three conformations viz s-cis, cis, s-cis, trans and s-trans, trans are possible for DBA (figure 1).

A number of attempts have been made earlier to study the conformations of DBA, using different methods viz. molar polarizabilities and Kerr constants (Bramley and Le Fevre 1962), dipole moments (Bentley et al 1949; Tsukerman et al 1968), NMR (Tanaka et al 1978) and UV spectroscopy (Hoshi et al 1986).

From Kerr constants and dipole moments study DBA was shown to exist in only one form (s-cis, cis). Subsequent study of dipole moments by Tsukerman et al (1968) indicated the existence of more than one conformation which was supported by the two C=O bands observed in the IR spectrum. By a study of NMR spectra and INDO molecular orbital calculations Tanaka et al (1978) came to the conclusion that DBA contains a large proportion of the s-cis, cis with a small proportion of s-cis, trans form. Hoshi et al (1986) who studied the UV absorption spectra of DBA at room temperature and at 101 K, concluded that the s-cis, cis...
conformer is nonplanar at room temperature and attains planarity at low temperatures.

When the IR spectrum of DBA was recorded in our laboratory in connection with a study of its metal complexes three carbonyl bands were observed in contrast to the earlier report (Tsukerman et al. 1968). This prompted a detailed study of the conformations of this compound. To distinguish between the different conformers, the IR spectra were recorded in solvents of different dielectric constants. The relative proportions of the conformers were determined from the relative intensities of the bands.

2. Experimental

2.1 Materials

DBA was prepared by the aldol condensation in alkaline medium, from benzaldehyde and acetone in 2:1 molar ratio, in ethanol (Vogel 1970). The yellow solid obtained was recrystallized twice from ethyl acetate and thrice from methanol and was TLC pure, m.p. 114°C. The solvents were purified and freshly distilled before use and the middle fractions only were collected.

2.2 Measurement of the spectra

The IR spectra of equimolar solutions (M/20) of the sample in solvents of varied dielectric constants were recorded on a Shimadzu-400 grating double beam spectrophotometer at 28°C using NaCl matched cells of 1 mm path length. The wavenumber scale was expanded by a factor of four and the spectra were calibrated by using the polystyrene film. Extensive overlap of the three carbonyl bands prevented the measurements of their integrated intensities. The relative populations of the different conformers were therefore estimated by measuring the apparent optical densities of the C=O bands as was done in many investigations earlier (Erskine and Waight 1960; Hayes and Timmons 1968; Subrahmanyam et al. 1980). The positions of the C=O bands together with their relative apparent optical densities are presented in table 1.