

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*

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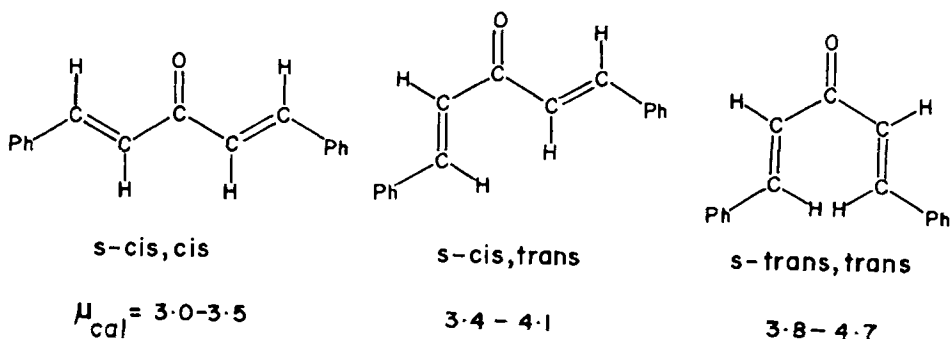


Figure 1. The three possible conformations of dibenzylideneacetone.

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.

Table 1. Stretching frequencies (cm^{-1}) and the relative intensities (A) of the carbonyl bands of dibenzylideneacetone in different solvents.

$$A = \epsilon_{\text{C=O}}(x) / (\epsilon_{\text{C=O}}(\text{I}) + \epsilon_{\text{C=O}}(\text{II}) + \epsilon_{\text{C=O}}(\text{III}))$$

	CCl_4	CHCl_3	CH_2Cl_2
C=O (I)	1676 (0.2107)	1671 (0.1750)	1674 (0.1644)
C=O (II)	1655 (0.4676)	1653 (0.4270)	1654 (0.3920)
C=O (III)	1650 (0.3216)	1648 (0.3970)	1649 (0.4430)

3. Results and discussions

The IR spectrum of DBA in CCl_4 exhibited three C=O bands at 1676, 1655 and 1650 cm^{-1} . The first two bands were reported earlier and the frequencies of the two agreed with the values reported. They are distinct and well-defined; the third, however, appeared as an inflexion on the second band. The relative intensities of the three bands were found to vary with the change in the polarity of the solvent showing that the three C=O bands correspond to the three different conformers in equilibrium. The *s-cis*, *cis* conformer may be considered as similar to the *s-cis*, form of benzylideneacetophenone with an additional *s-cis* ethylenic double bond in cross conjugation. The carbonyl frequency of this conformer is expected to be higher than that of the *s-cis* form of benzylideneacetophenone as the C=O frequency is enhanced by the interaction through space, of the C=O and C=C π electrons (Erskine and Waight 1960). This becomes evident when the frequencies of benzophenone (1664 cm^{-1}) and *s-cis* benzylideneacetophenone (1670 cm^{-1}) are compared. So the band at 1676 cm^{-1} is assigned to the *s-cis*, *cis* conformation.

The *s-cis*, *trans* conformer may be treated as the *s-cis* form of benzylideneacetophenone with an additional conjugation of an *s-trans* C=C bond. The frequency of this is expected to be lower than that of the *s-cis* form of benzylideneacetophenone as *trans* conjugation often produces a lowering of C=O frequency. This is evident from the frequencies of benzophenone (1664 cm^{-1}) and *s-trans* benzylideneacetophenone (1648 cm^{-1}). The *s-trans* conjugation thus causes a lowering of C=O frequency by 16 cm^{-1} . If the same effect prevails in the *s-cis*, *trans* conformer, the C=O frequency of this compound should be around 1654 cm^{-1} ($1670 \text{ cm}^{-1} - 16 \text{ cm}^{-1}$). The *s-cis*, *trans* conformer may also be considered the *s-trans* form of benzylideneacetophenone with an additional conjugation of the *s-cis* double bond which raises the frequency by 6 cm^{-1} . Then it may have a frequency closer to that of the *s-trans* form of benzylideneacetophenone (1648 cm^{-1}) with an upward shift of 6 cm^{-1} . Either way, the carbonyl frequency of this conformer is nearly 1654 cm^{-1} . The band observed at 1655 cm^{-1} in the spectrum of DBA is therefore assigned to this conformation.

The *s-trans*, *trans* conformer should have the C=O frequency which is lower by 16 cm^{-1} than that of the *s-trans* benzylideneacetophenone which becomes 1632 cm^{-1} ($1648 \text{ cm}^{-1} - 16 \text{ cm}^{-1}$). The absence of such a band in this region revealed the nonexistence of this conformer. It may be due to the sterically-hindered structure of this form. This is evident from the framework model of DBA

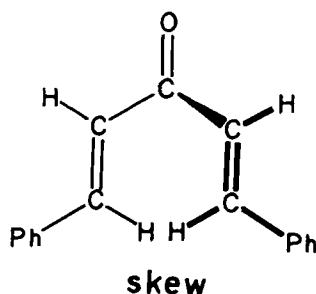


Figure 2. The skew conformation of the *s-trans*, *trans* form of DBA.

which showed significant steric interaction between the two β -H atoms and possibility of π -electron repulsion between the two C=C bonds which are sufficiently close. From these considerations it is believed to have a skew conformation so as to minimise the steric and π -electron repulsions (figure 2).

In this conformation conjugation of the second *s-trans* C=C is greatly inhibited and the frequency of this conformer is expected to be closer to that of *s-trans* benzylideneacetophenone (1648 cm^{-1}). The inflexion observed at 1650 cm^{-1} is therefore attributed to the nonplanar *s-trans*, *s-trans* (skew) conformation.

3.1 Solvent effect

The frequencies and intensities of all the C=O bands are markedly affected by the solvents. The frequencies of the bands in CH_2Cl_2 and CHCl_3 are lower as compared to those in CCl_4 . The solvent shifts are in the order $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3$. In CCl_4 the intensities of the C=O bands are in the order *s-cis*, *trans* > nonplanar *s-trans*, *trans* > *s-cis*, *cis*. The intensity changes of the bands are quite significant. With increasing polarity of the solvent, there is a progressive decrease in the intensities of the C=O (*s-cis*, *cis*) and C=O (*s-cis*, *trans*) bands while the intensity of the C=O (skew) band increases. It is of interest to note that on passing from CCl_4 to CH_2Cl_2 the intensities of the bands of *s-cis*, *trans* and skew are reversed (figure 3).

From this it is clear that the skew form is more stable in solvents of greater polarity while *s-cis*, *cis* and *s-cis*, *trans* forms are more stable in nonpolar or less polar solvents. This is consistent with the fact that more polar forms are stabilized in more polar solvents and less polar ones in lower or nonpolar solvents.

Amongst the three conformers the *s-cis*, *cis* form is the least polar as the two C=C dipoles oppose the C=O dipole. The skew form (or *s-trans*, *trans*) is the most polar form as the C=O dipole is reinforced by the two C=C dipoles. In the *s-cis*, *trans* form the dipole of one C=C reinforces the C=O dipole and the dipole of other C=C is opposed to it. The dipole moment of this is expected to be midway between the dipole moments of the above two forms. This is evident from the dipole data (Bentley *et al* 1949) of the different conformers (figure 1).

3.2 Conformations of the DBA and their stabilities

From the intensities of the C=O bands of the three conformers of DBA in CCl_4 it is clear that the populations of these conformers are in the order *s-cis*,

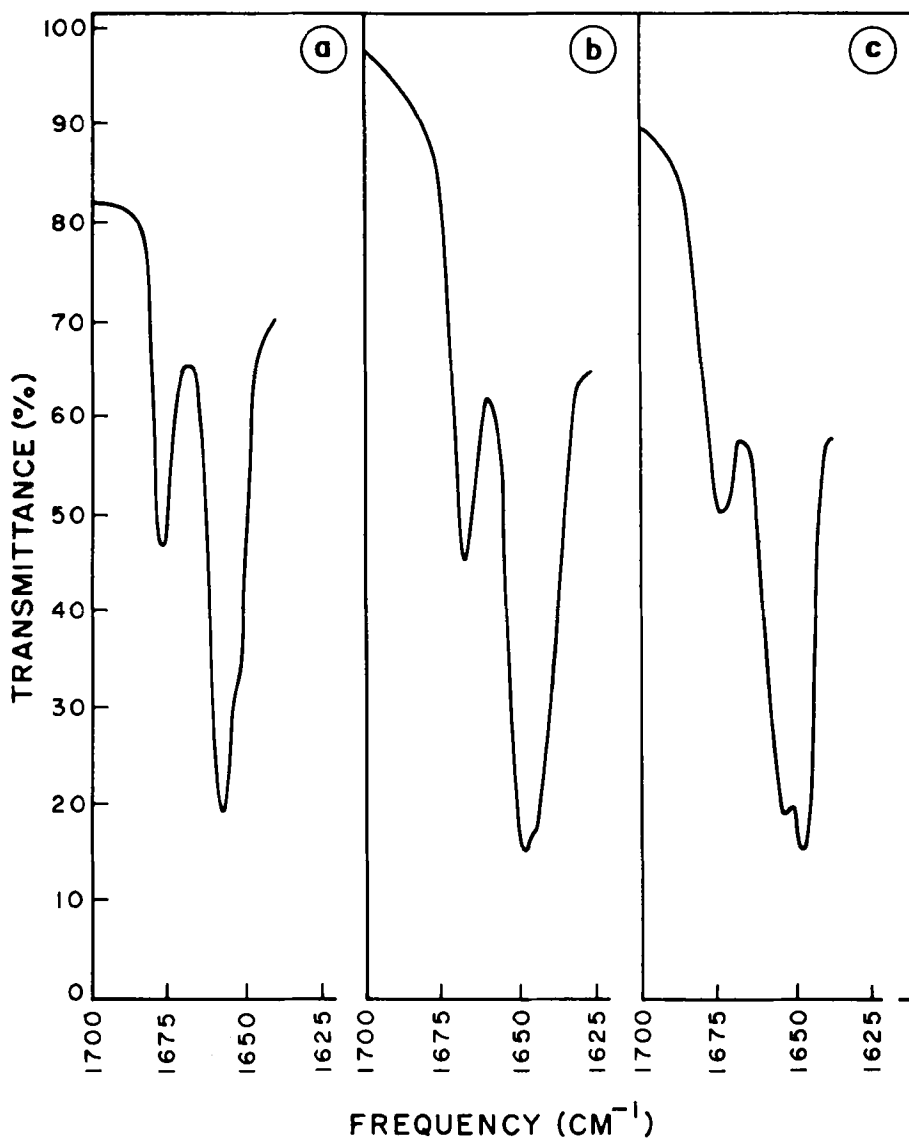


Figure 3. The C=O bands of DBA in different solvents. (a) CCl₄, (b) CHCl₃, (c) CH₂Cl₂.

trans > nonplanar *s-trans*, *trans* > *s-cis*, *cis*. The lowest proportion of the *s-cis*, *cis* form may be due to greater destabilization caused by stronger repulsion between π -electrons of the C=O and two C=C bonds. The π -electron density of the C=O in this form is higher which is evident from the high C=O frequency. Of the two forms viz. *s-cis*, *trans* and nonplanar *s-trans*, *trans* the latter is less stable than the former, probably due to decrease in the resonance stabilization energy owing to the nonplanarity of this conformation.

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