The Conformations and ¹H Nuclear Magnetic Resonance Parameters of Dibenzylideneacetone

By **Hisao Tanaka, Koh-ichi Yamada,** and **Hiroshi Kawazura,** * Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02, Japan

Dibenzylideneacetone, $(C_6H_5CH=CH)_2CO$, with two degrees of rotational freedom imparted by the two single bonds between the olefin and the carbonyl group was studied to determine its stable conformers by ¹H n.m.r. spectroscopy and by an INDO molecular orbital method. A solvent effect induced by benzene on the *trans*-olefinic protons and a least squares analysis of the temperature dependence of the internal chemical shift (δ_{AB}) between the olefinic protons have revealed support of the theoretical calculations of δ_{AB} that the major conformation is s-*cis,cis* and the minor one is s-*cis,trans*. An INDO calculation of the conformers concerned confirmed this deduction together with the absence of the s-*trans,trans* form. δ_{AB} is a characteristic parameter of the conformation with the values 0.5 and 1.5 p.p.m. for the s-*cis* and s-*trans* forms, respectively, in the olefinic portions of dibenzylideneacetone.

DIBENZYLIDENEACETONE (DBA) has recently aroused much interest as a unique ligand which provides a novel series of zerovalent transition metal complexes.[1-3] The variety of the zerovalent complex formation reflects the number of conformations of DBA which ligate the metals. The precise elucidation of the conformations of the metal complexes, especially in solution, may lead to a better understanding of zerovalent metal complexes with potential utility in various chemical reactions. With this idea, the conformations of the complexes in solution have been studied by a ¹H n.m.r. technique.

These results will be reported elsewhere.[4] In the course of the studies, ¹H n.m.r. parameters of several conformers of DBA were needed to assess the conformations of the complexes. The determination of these parameters was possible through a study of the conformational equilibrium of DBA in solution.

We report here the results of the conformational analysis of DBA. Conformations of αβ-unsaturated carbonyl compounds have been investigated by various methods, and the stability of their rotational isomers about the bond between the olefin and the carbonyl

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[3] K. Moseley and P. M. Maitlis, *Chem. Comm.*, 1971, 1604; *J.C.S. Dalton*, 1974, 169.
[4] H. Kawazura and H. Tanaka, submitted for publication.

group has been fully discussed.[5-8] In divinyl ketone derivatives, to which DBA belongs, the existence of two degrees of rotational freedom imparted by the two single bonds between the olefin and the carbonyl group has left the conformational features unclear.

We show that the internal chemical shift δ_{AB}, which varies with temperature, can be used for conformational analysis of DBA, and the aromatic solvent effect on the chemical shifts of the olefinic protons can establish the validity of the analysis. A theoretical basis for using δ_{AB} to discriminate among the conformers of DBA molecule is given, We also report an INDO calculation of the total energies of some conformers, which supports the conformer preference determined by the n.m.r. experiments.

RESULTS AND DISCUSSION

[1]H N.m.r. Studies on the Conformations of DBA.—To clarify the conformational features of DBA, we needed to know the precise resonance pattern of the trans-olefinic protons H_A and H_B. This was achieved by examining the [1]H n.m.r. spectra of the deuteriated DBAs $(C_6D_5-CH=CH)_2CO$, $(C_6D_5CD=CH)_2CO$, and $(C_6D_5CH=CD)_2CO$. The olefinic AB quartet pattern, which is partially obscured by the phenyl proton signals, appeared clearly in the spectrum of $(C_6D_5CH=CH)_2CO$. The spectra of $(C_6D_5CD=CH)_2CO$ and $(C_6D_5CH=CD)_2CO$ confirmed that the high and low field parts of the AB quartet derive from the proton on the carbonyl side (H_A) and on the phenyl side (H_B), respectively.

Effect of aromatic solvent induced shift (ASIS effect). As is well documented,[9-11] various carbonyl compounds give rise to a substantial shift of their proton signals through interaction with an aromatic solvent, and this

TABLE 1

Benzene solvent effects on H_A and H_B of DBA at 25 °C

Solvent	δ_A	δ_B	$\Delta\delta_A$	$\Delta\delta_B$
C_6D_6	6.863	7.770		
CCl_4	6.961	7.612	-0.098	0.158
Cyclohexane	6.995	7.679	-0.132	0.091
$CDCl_3$	7.058	7.714	-0.195	0.056
CD_2Cl_2	7.072	7.682	-0.209	0.088

Tetramethylsilane as standard, $\Delta\delta_A = \delta_A$(benzene) $- \delta_A$ (solvent), $\Delta\delta_B = \delta_B$(benzene) $- \delta_B$(solvent)

induced shift $\Delta\delta$, defined as δ(aromatic solvent) $- \delta$(magnetically inactive solvent), is a good index for the location of the proton concerned, i.e., if $\Delta\delta$ is positive the proton is on the oxygen side with respect to the plane perpendicular to the C=O bond axis at the carbonyl carbon, whereas if $\Delta\delta$ is negative the proton is on the reverse side.

Knowing roughly the conformational features of

DBA, the ASIS effect of the olefinic protons H_A and H_B of $(C_6D_5CH=CH)_2CO$ was examined. Table 1 shows some $\Delta\delta_A$ and $\Delta\delta_B$ parameters where the values are the benzene induced shifts for some magnetically inactive solvents. The negative signs of the $\Delta\delta_A$ values and the positive signs of the $\Delta\delta_B$ values explicitly indicate that in DBA H_B is mainly on the oxygen side, while H_A is mainly on the reverse side. This clearly shows that the s-cis form is predominant in the olefinic parts of DBA, as can be easily seen from Figure 1.
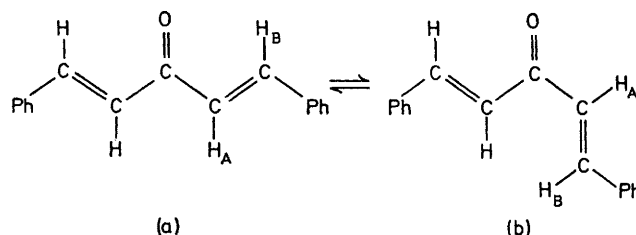

FIGURE 1 Possible conformations of DBA and the equilibrium: (a); s-cis,cis, (b); s-cis,trans

Temperature dependence of internal shift δ_{AB}. The AB quartet of $(C_6D_5CH=CH)_2CO$ did not show any further splitting or broadening even at -95 °C in CD_2Cl_2, implying a low barrier between conformers with appreciable populations. The coupling constant J_{AB}
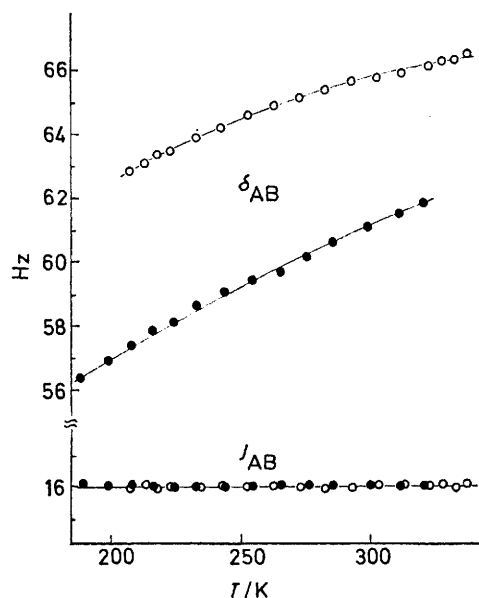

FIGURE 2 Temperature dependence of the internal shift δ_{AB} and the coupling constant J_{AB} of the trans-olefinic protons of DBA: ○, in $CDCl_3$; ●, in CD_2Cl_2

stayed * at 16.0 Hz, the typical value for olefinic protons in the trans-configuration, over the whole range of

* Temperature-invariant J_{AB} has also been observed for acrolein.[12]

[5] R. L. Lipnick, Tetrahedron Letters, 1973, 93.

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[9] J. D. Connolly and R. McCrindle, Chem. and Ind., 1965, 479.

[10] D. H. Williams and N. S. Bhacca, Tetrahedron, 1965, 21, 2021.

[11] D. H. Williams and D. A. Wilson, J. Chem. Soc. (B) 1966, 144.

[12] J. E. D. Davies, J. Mol. Spectroscopy, 1969, 29, 499.

temperature observed, both in $CDCl_3$ and CD_2Cl_2. On the other hand, the internal chemical shift δ_{AB} ($= \delta_B - \delta_A$) decreased substantially with lowering the temperature in both solvents as shown in Figure 2, indicating sensitivity * towards a conformational change in DBA. By taking into account these facts, we could assume that a change in δ_{AB} reflects a change in the equilibrium between the s-cis,cis and the s-cis,trans conformers as shown in Figure 1. Indeed, among the three conformers with planar conjugated structures, s-cis,cis, s-cis,trans, and s-trans,trans, the presence of the former two and the absence of the last in the equilibrium mixture may be expected in view of the sterically hindered structure of the s-trans,trans where two B protons are contiguous to each other (see later).

Thus thermodynamic treatment of the equilibrium gives the relationship (1) [14] in which δ^{ct}_{AB} and δ^{cc}_{AB} mean

$$\ln(\delta^{obs}_{AB} - \delta^{ct}_{AB})/(\delta^{cc}_{AB} - \delta^{obs}_{AB}) = -\Delta H/RT + \Delta S/R \quad (1)$$

δ_{AB} of the s-cis,trans and the s-cis,cis conformer, respectively. ΔH and ΔS represent the enthalpy and entropy differences between the conformers. ΔS, interpreted usually as the entropy of mixing of the conformers, may be set to zero.† By denoting the mole fraction of the corresponding conformers as c^{ct} and c^{cc} where $c^{ct} + c^{cc} = 1$, the observed internal shift δ^{obs}_{AB} is related as in equation (2). δ^{cc}_{AB} and δ^{ct}_{AB} can be substituted by

$$\delta^{obs}_{AB} = c^{cc}\delta^{cc}_{AB} + c^{ct}\delta^{ct}_{AB} \quad (2)$$

δ^c_{AB} and δ^t_{AB}, the intrinsic shifts for the s-cis and the s-trans forms of the olefinic portion of DBA by the formulae (3) and (4). This replacement is only valid when δ^c_{AB} and

$$\delta^{cc}_{AB} = \delta^c_{AB} \quad (3)$$

$$\delta^{ct}_{AB} = (\delta^c_{AB} + \delta^t_{AB})/2 \quad (4)$$

δ^t_{AB} are differentiated by the positional locations of H_A and H_B with respect to the carbonyl group in both conformers,

The least squares calculations using equation (1) with ΔS 0 were repeated for successive values of ΔH in the range 0—30 kcal mol^{-1} at intervals of 0.05 kcal mol^{-1} to search for minima in the standard deviation. This procedure for both solvents gave only one minimum for the range examined. Thus ΔH and δ^c_{AB} and δ^t_{AB} were determined from the minimum as shown in Table 2 which also contains the c^{cc} and c^{ct} values at 25 °C, calculated by equation (2). The ΔH values found for DBA are small as expected and are in the same order as those for

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* An intramolecular chemical shift such as δ_{AB}, but not an intermolecular chemical shift, may be a reliable parameter for detecting conformational change. A similar treatment using an intramolecular shift in buta-1,3-diene has been reported.[13]

† It becomes zero where the same number of conformers exists in both extremes of an equilibrium. For applications of mixing entropy in similar cases, see refs. 5 and 13.

‡ More precisely, for long range shielding, contributions from the magnetic anisotropies of the phenyl group and the contiguous olefin which has no proton involved must be considered. However, these were negligibly small and produced shifts of only a few Hz because of the long distance from the protons concerned.

$\alpha\beta$-unsaturated carbonyl compounds.[6] The population of the olefinic portions in the s-cis form at 25 °C were estimated by using equations (2)—(4) and are 0.81 in $CDCl_3$ and 0.90 in CD_2Cl_2, indicating an agreement with the ASIS results. Relying on the compatability of the

TABLE 2

Enthalpies ΔH (kcal mol^{-1}), populations c^{cc} and c^{ct} (25 °C) in the equilibrium between s-cis,cis and s-cis, trans forms of DBA, and internal shifts δ^c_{AB} and δ^t_{AB} in the s-cis and s-trans forms

Solvent	ΔH	c^{cc}	c^{ct}	δ^c_{AB}	δ^t_{AB}
$CDCl_3$	0.30	0.627	0.373	0.442	1.588
CD_2Cl_2	0.80	0.792	0.208	0.518	1.415

ASIS results and the thermodynamic treatment, the following deductions may be valid: the s-cis,cis conformer is the most stable followed by the s-cis,trans. The internal shift of the s-cis form (δ^c_{AB}) is ca. 0.5 p.p.m., while that of the s-trans form (δ^t_{AB}) covers ca. 1.5 p.p.m.; the difference between the shifts is ca. 1 p.p.m.

Theoretical Calculations of Internal Shift δ_{AB}.—The presence of the minor s-trans form in the olefinic part of DBA, though plausible, remains hypothetical. The question arises whether the s-trans form could really spread the internal shift over ca. 1.5 p.p.m. or is some other conformer responsible. To eliminate this uncertainty, calculations of the internal shifts for three forms, s-trans, s-cis, and s-skew(90°), were carried out by evaluating ‡ the long range shielding effects of the carbonyl group towards the olefinic protons H_A and H_B.

The proton chemical shift induced by the long range shielding (σ^{LR}) can be delineated as in equation (5),[15,16] using a point dipole approximation for the carbonyl group. χ_{xx}, χ_{yy}, and χ_{zz} are principal values of the

$$\sigma^{LR} = [(1 - 3\cos^2\theta_x)(\chi_{xx} - \chi_{zz}) + (1 - 3\cos^2\theta_y)(\chi_{yy} - \chi_{zz})]/3R^3 - k\mu\cos\alpha/R^3 \quad (5)$$

diamagnetic susceptibility tensor of the carbonyl group in cartesian co-ordinates where the x-axis is along the C=O bond and the z-axis is perpendicular to the sp^2 plane of the carbonyl carbon. R is the distance of the proton from the point dipole located in the centre of the carbonyl bond, and θ_x and θ_y are the angles R makes with the respective cartesian axes. The first term represents a contribution from the diamagnetic anisotropy of the carbonyl group. The second term, where k is a constant, μ the electrical dipole moment of the carbonyl group, and α the angle R makes with the C–H bond, represents a contribution from the direct electrostatic effect which does not involve a negligible second-order term in μ. The values of R, θ_x, θ_y, and α were obtained as noted in the skeletal representation of the three forms (Figure 3) by

[13] R. L. Lipnick and E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 6370.

[14] E. W. Garbisch, B. L. Hawkins, and K. D. Mackaay, ' Scope and Limitations in Conformational Analysis' in ' Conformational Analysis ', ed. E. Chiurdogue, Academic Press, New York, 1971.

[15] R. F. Zurcher, ' Nuclear Magnetic Resonance in Chemistry,' ed. B. Pesce, Academic Press, New York, 1965.

[16] J. W. ApSimon, P. V. Pecmarco, and D. W. Matherson, *Tetrahedron*, 1970, **26**, 119.

assuming [17] bond lengths C(1)=O, C(1)–C(2), C(2)=C(3), and C–H of 1.22, 1.44, 1.36, and 1.08 Å, respectively, and bond angles of the sp^2 carbon atoms of 120°. The calculated results for σ^{LR} of H_A and H_B in the three forms, using Zurcher's values [15] $\chi_{xx} - \chi_{zz} = 15.4 \times 10^{-12}$ and $\chi_{yy} - \chi_{zz} = 7.35 \times 10^{-12}$ m³ mol⁻¹ and the ApSimon's value [16] $k\mu = 4.16 \times 10^{-12}$ m³ mol⁻¹ obtained by putting the point dipole in the centre of the carbonyl bond, are

TABLE 3

Calculated chemical shifts of H_A and H_B

Form	s-cis		s-skew(90°)		s-trans	
Protons	H_A	H_B	H_A	H_B	H_A	H_B
σ^{mag}	−0.512	0.000	−0.202	0.160	−0.091	−0.381
δ^{elec}	−0.308	−0.082	−0.332	−0.089	−0.351	−0.084
σ^{LR}	−0.820	−0.082	−0.534	0.071	−0.442	−0.465
$\sigma_A^{LR} - \sigma_B^{LR}$	−0.738		−0.605		0.023	

σ^{mag} and σ^{elec} refer to the chemical shifts induced by the diamagnetic and electrostatic terms in equation (5) to give σ^{LR}.

summarized in Table 3, together with the corresponding values for the magnetic and electric contributions,

The internal shift δ_{AB} can be given by equation (6)

$$\delta_{AB} = (\sigma_A^i - \sigma_B^i) + (\sigma_A^{LR} - \sigma_B^{LR}) \qquad (6)$$

where σ_A^i and σ_B^i are intrinsic shieldings other than long range shielding and may be considered to remain constant during conformational change, as inferred from the fact that the value of the indirect coupling J_{AB} was constant throughout. Hence, the difference between δ_{AB} of the s-trans and that of the s-cis form was 0.76 p.p.m., in reasonable agreement with 1 p.p.m., the difference determined thermodynamically. If we take 1 p.p.m. for $\sigma_A^i - \sigma_B^i$, the value of the internal shift of the trans-olefinic protons in styrene,[18] we obtain δ_{AB}^c 0.26, δ_{AB}^t 1.02, and δ_{AB}^s 0.40 p.p,m. These values indicate that the s-trans form has the largest internal shift and the s-cis form the smallest, in approximate conformity with the experimental values in Table 2. Thus, only the s-trans form could spread the internal shift to the observed range, since even the s-skew(90°) form gives an internal shift close to that of the s-cis form. It is noteworthy that the sum of the σ^{LR} values for H_A and H_B is 0.90 for the s-cis and 0.91 p.p.m. for the s-trans form. This means that the centre of the AB quartet in both forms should remain unchanged. Both forms reflect their mutual conversion only in the δ_{AB} value among the n.m.r. parameters.

INDO Calculations of Total Energies of Several Conformers of DBA.—In order to confirm the n.m.r. results, INDO total energy calculations on several conformers were carried out using a library program * extended to accommodate the 86th ordered Fock matrix of DBA.

The bond lengths and angles of the molecule used for the calculation were assumed to be, for the phenyl part, standard values,[19] 1.39 C(phenyl)–C(phenyl), 1.46

* Program Y4-CB03, K. Kihara and K. Morio, Computer Center, University of Tokyo.

C(phenyl)–C(olefin), 1.08 Å (C–H), and 120° (all sp^2 carbon angles) and for the divinyl ketone part, those given in the preceding section. The results of the calculation on the three planar conformations, s-cis,cis, s-cis,trans, and s-trans,trans, are in Table 4. The order

TABLE 4

INDO total energies ΔE_t, electronic energies ΔE_e, and core repulsion energies ΔE_c of the three planar conformations of DBA (in eV)

Conformation	ΔE_e	ΔE_c	ΔE_t
s-cis,cis	0.000	0.000	0.000
s-cis,trans	−224.947	225.075	0.128
s-trans,trans	−749.426	757.436	8.010

The energies of the s-cis,cis form are taken as the base: E_e −18 445.862, E_c 14 518.070, E_t −3 927.792 eV.

of the magnitude of the total energies for the three conformers agrees well with that from the n.m.r. studies. In fact the energy difference, 3.0 kcal mol⁻¹, between s-cis,cis and s-cis,trans reflects well the low enthalpy difference estimated from the thermodynamic treatment. The calculations also show that the extremely high energy required to produce the s-trans,trans form is due to a strong core repulsive force which overcomes the largest electronic stabilization energy of the three conformers. This repulsion was confirmed to arise mainly from the repulsive interaction between the two H_B atoms on the phenyl side as shown by the values, 16.380, 2.300, and 2.258 eV for the s-trans,trans, s-cis,-trans, and s-cis,cis forms, respectively.
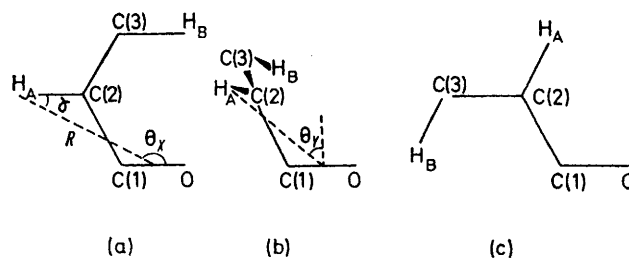

FIGURE 3 Skeltal arrangements of the three forms of the olefinic portion of DBA; (a) s-cis; (b) s-skew(90)°; (c) s-trans

	(a)	(b)	(c)
R_A(Å)	2.71	2.52	2.33
R_B(Å)	2.47	2.89	3.24
θ_{x_A}(°)	152.5	118.9 (θ_{y_A} 61.7°)	110.0
θ_{x_B}(°)	79.7	129.2 (θ_{y_B} 47.2°)	174.5
α_A(°)	27.5	39.3	50.0
α_B(°)	79.7	72.1	65.5

A three dimensional diagram of the total energies as a function of rotating angles around the two single bonds should demonstrate that the s-cis,cis and s-cis,trans forms are settled in a well with a substantial potential barrier. We have found that when one of the olefinic

[17] J. Ukaji, *Bull. Chem. Soc. Japan*, 1959, **32**, 1266, 1270.
[18] R. W. Fessenden and J. S. Waugh, Abstracts, Amer. Chem. Soc. Meeting, New York, 1957.
[19] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970, p. 110.

portions is s-*cis* or s-*trans* and the other rotates clockwise or anti-clockwise towards the s-*skew* form, a double minimum potential curve appears in both cases. This result coincides with that of an energy calculation for $\alpha\beta$-unsaturated carbonyl compounds [6] in which two symmetrical rotamers slightly skewed from the planar s-*cis* or s-*trans* form are often settled at the bottom of a potential well. The present INDO calculations allow a potential well to be drawn around the s-*cis,cis* and s-*cis,trans* forms, though a potential map based on more reliable parameters for DBA would be desirable.

EXPERIMENTAL

Materials.—The decadeuteriated dibenzylideneacetone, $(C_6D_5CH=CH)_2CO$, was prepared by condensation [20] of acetone and pentadeuteriobenzaldehyde, C_6D_5CHO. The derivatives $(C_6D_5CD=CH)_2CO$, m.p. 104—107°, $\delta(CCl_4)$ 6.96(s), and $(C_6D_5CH=CD)_2CO$, m.p. 111—112°, $\delta(CCl_4)$ 7.61(s), were prepared by the same method from the corresponding aldehyde and acetone. Both gave yellow crystals in 90 and 92% yield, respectively.

^1H *N.m.r. Measurements.*—The samples used for temperature variation measurements were prepared as a solution containing *ca.* 1 wt.% DBA with tetramethylsilane as internal standard. The spectra were recorded in the Fourier transform mode on a JEOL PFT-100 spectrometer operating at 100 MHz with an internal deuterium lock. Typically, 16 384 data points were taken with one pulse over a 1 kHz spectral width at a tilt angle of 90°. Resonance positions were reduced by an EC-100 computer. A VT-3C variable temperature unit was also attached to the spectrometer and calibrated by placing a copper–constantan thermocouple in a sample tube inside the probe. The temperature was read from a Okhura AM-1001 microvoltmeter and was constant to within ± 1 °C. ASIS Experiments were performed in the continuous wave mode on a JEOL PS-100 spectrometer operating at 100 MHz.

INDO Calculations.—INDO calculations were run on a HITAC 8800 machine at the Computer Center, University of Tokyo. The computing time per one conformation of DBA was *ca.* 3 min with 10—20 iterations to reach sufficient convergence.

Least Squares Analysis.—Least squares calculations of the temperature dependence of the internal shift δ_{AB} were performed with a program written by one of us and using an IBM 1130 machine at Josai University.

[20] C. R. Conard and M. A. Dolliver, *Org. Synth.*, 1943, Coll. Vol. 2, p. 167.