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THE CONFORMATIONS OF 1-ACYL-2-ALKYLCYCLOHEXENES

J. K. GROVES and N. JONES
Chemistry and Metallurgy Department,
Lanchester College of Technology, Coventry, England

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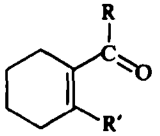
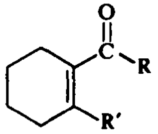
Abstract—A series of 1-acyl-2-alkylcyclohexenes are assigned s-*cis* conformations on the basis of their IR spectra. UV absorption data show that non-planarity within the chromophore parallels the steric requirements of the acyl and alkyl substituents.

THE compound 1-acetyl-2-methylcyclohexene has, at various times, been assigned both an s-*cis*[1, 2] and an s-*trans*[3, 4] conformation.



s-*cis*



s-*trans*

In a recent paper Cottee *et al.*[5] employ the following criteria in assigning conformations to αβ-unsaturated ketones: (a) the ratio of the integrated band intensities of the carbonyl/alkenyl stretching vibrations (r^i) is above 5·2 for s-*trans* conformers and between 0·6 and 3·5 for s-*cis* conformers; (b) the difference between the carbonyl and alkenyl stretching frequencies ($\Delta\nu$) is less than 60 cm^{-1} for s-*trans* and greater than 70 cm^{-1} for s-*cis* conformers. The assignment of an s-*cis* conformation to 1-acetyl-2-methylcyclohexene by these workers prompts us to publish our own observations upon a series of 1-acyl-2-alkylcyclohexenes obtained by base catalysed isomerization of the corresponding 6-acyl-1-alkylcyclohexenes.[6] For comparison 1-acetyl-cyclohexene, known to exist in the planar s-*trans* form[7] is also included in Table 1.

The r^i values confirm that the alkyl substituted ketones have an s-*cis* conformation. The $\Delta\nu$ values are in good agreement with this assignment with the exception of 1-isobutyryl-2-methylcyclohexene. This compound also exhibits an unusually broad and asymmetric band for the alkenyl stretching vibration.

One reason for the small r^i values observed with s-*cis* ketones is the strong coupling of the C═O and C═C stretching vibrations in this conformation.[8] It has been stated[5] that deviation from planarity within an s-*cis* conformation will tend to reduce this coupling and consequently increase the r^i value. On this basis the change in our r^i values may be attributed to non-planarity. In the case of 1-acetyl-2-methylcyclohexene such non-planarity has been demonstrated by ^{13}C NMR investigation.[7]

TABLE 1. THE SPECTRAL PROPERTIES OF 1-ACYL-2-ALKYLCYCLOHEXENES

CO·R	R′	$\nu_{C=O}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})	r^i	$\Delta\nu$ (cm^{-1})	λ_{max} (mμ)	ε_{max}	f	Θ
CO·Me	H	1665	1641	7·7	24	232	12,500	0·332	0°
CO·Me	Me	1688	1618	1·3	70	248	6500	0·165	31
CO·Me	Et	1687	1614	1·7	73	248	5800	0·147	36
CO·Me	Pr^n	1687	1614	1·9	73	248	5150	0·127	41
CO·Me	Bu^n	1688	1614	2·2	74	248	4050	0·103	48
CO·Me	Pent^n	1687	1614	2·3	73	248	3850	0·098	49
CO·Et	Me	1687	1620	2·8	67	247	5000	0·127	41
CO·Pr^i	Me	1688	1638	2·4	50	247	4000	0·093	50
CO·Bu^t	Me	1684*	—	—	—	249*	1300*	—	ca. 68

* Values reported by Braude *et al.*[4]

The considerable variation of the UV extinction coefficients (ε) and oscillator strengths (f) reported in Table 1 are also consistent with varying degrees of non-planarity within the chromophore.[9] Braude and Sondheimer[10] have proposed the semi-empirical[11] Eq (1) relating oscillator strengths to the angle of twist (Θ).

$$\cos^2 \Theta = f/f_0 \qquad (1)$$

For the present systems it has been estimated[1] that f_0, the oscillator strength of the corresponding fully planar chromophore, would be 0·68 times that value observed for 1-acetyl-cyclohexene. This value has been combined with our own data to calculate the angles of twist tabulated. The extent of non-planarity is seen to parallel the increasing size[12] of the acyl and alkyl substituents.

EXPERIMENTAL

IR measurements. All IR spectra were determined on a Unicam SP200 spectrometer. Spectrophotometric grade CCl_4 was used as solvent and concentrations were adjusted to give absorbance values between 0·6 and 0·7 using cells with a path length of 0·1 mm. The frequency was checked against polystyrene for each spectrum. The r^i values have been calculated from the Eq (2),

$$r^i = A^c\Delta\nu^c_{\frac{1}{2}}/A^a\Delta\nu^a_{\frac{1}{2}} \qquad (2)$$

where A^c and A^a are absorbance values and $\Delta\nu^c_{\frac{1}{2}}$ and $\Delta\nu^a_{\frac{1}{2}}$ the apparent half band widths of the carbonyl and alkenyl bands respectively.

UV measurements. UV absorptions were determined from MeOH soln using a Unicam SP 500 spectrometer. Oscillator strengths have been obtained from the general expression (3), with K = unity.

$$f = 4{\cdot}315 \times 10^{-9}\,\mathrm{K}\,\Delta\nu_{\frac{1}{2}}\varepsilon \qquad (3)$$

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