Tetrahedron Letters Vol. 21, pp 1937 - 1940 0040-4039/80/0502-1937$02.00/0

THE $\nu_{C=Y}$ DOUBLET IN THE IR SPECTRA OF NEOPENTYL $(CH_3)_3C-CH_2-C(=Y)-Z$ COMPOUNDS. EVIDENCE FOR THE EXISTENCE OF A CONFORMATIONAL EQUILIBRIUM FOR $(CH_3)_3C-CH_2-CO-CH_3$ IN SOLUTION.

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The associative behaviour of neoPe-CO-Me and the solvent sensitivity of the neoPe-CO-R ketones provide evidence supporting the hypothesis of a conformational equilibrium accounting for the splitting of the $\nu_{C=Y}$ *band of the title compounds.*

Among the many factors that can be invoked to interpret the complexity of a $\nu_{C=Y}$ band, the existence of a conformational equilibrium could expectedly account for the splitting into two bands observed in solution for neoPe-C(=Y)-Z compounds. In this case, a small amount of proton-donor added into the solution should cause the formation of hydrogen bonds with each of the two conformations and thereby provoke a new splitting. The validity of this hypothesis is tested here with neoPe-CO-Me.

ASSOCIATIVE BEHAVIOUR OF $(CH_3)_3C-CH_2-CO-CH_3$

The binary solutions of this ketone in carbon tetrachloride and in cyclohexane (Figs. 1a,b) show two components, I and II; the addition of a proton-donor, parachlorophenol, to these solutions gives rise to two more components, I' and II' (Figs. 1c,d).[1,2]

I' and II' are associated bands corresponding to free bands I and II, respectively, since their areas increase as the intermolecular interactions with the solvent decrease[3] when passing from CCl_4 to C_6H_{12} (i.e. as the solvent becomes less active according to the G scale of Allerhand and Schleyer[4]), and since they are both favoured by an increase in donor concentration.

I' and II' correspond to associated dimers. Actually, under the same temperature, concentration and solvent conditions, comparison with tBu-CO-Me and cyclohexanone,[5] which in binary solutions exhibit only one free ν band and in ternary solutions exhibit one

Therefore, such an associative behaviour can only be due to an equilibrium between two conformations denoted by A and B, corresponding to bands I and II, respectively.

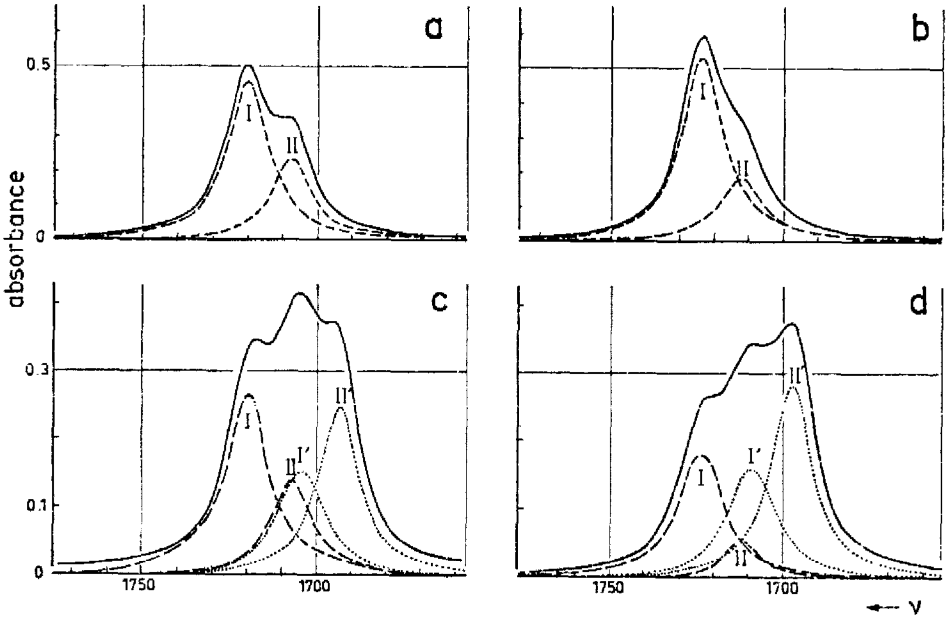

Figure 1. Splitting of the $\nu_{C=O}$ band for neoPe-CO-Me (0.02M) in binary solutions in (a) CCl_4 and (b) C_6H_{12}; in ternary solutions (0.1M) with parachlorophenol (0.1M) in (c) CCl_4 and (d) C_6H_{12}.

ASSIGNMENT OF THE CONFORMATIONS

From the associative behaviour of neoPe-CO-Me, it can be deduced that conformation B has a stronger proton-donor character than conformation A, since II', the associated band of B, is more favoured than I' when: i) passing from CCl_4 to the less active solvent C_6H_{12} [as attested to by the ratio II'/I': 1.27 in CCl_4, 1.50 in C_6H_{12}, Figs. 1c,d] , ii) there is an increase in donor concentration.

Another consideration lies in the different solvent sensitivities of A and B, as measured by the slope p of Allerhand and Schleyer's relation[4] expressed here as

$$\nu^{Sv} = \nu^{gas}_{G\to 0} - p\ G$$

in which G is the solvent parameter, ν^{Sv} the frequency in solvent Sv, and $\nu^{gas}_{G\to 0}$ the extrapolated value to G→0 which corresponds to the gas phase.[8] Conformation A (p = 0.18 ± 0.009) is less sensitive to solvents than B (p = 0.215 ± 0.005).[9]

Such a behaviour towards solvents is also observed with other R-CO-neoPe ketones exhibiting a $\nu_{C=O}$ doublet (Fig. 2). Comparison of the p values of A and B with their $\nu^{gas}_{G\to O}$ values considered as a measure of structure effect[10] shows that conformations B follow the general behaviour of a great number of ketones presenting a single $\nu_{C=O}$ band in the media studied,[8] whereas conformations A markedly deviate from this behaviour. It can be inferred therefrom that there is a strong inhibiting effect in conformations A with respect to both solvation and association.

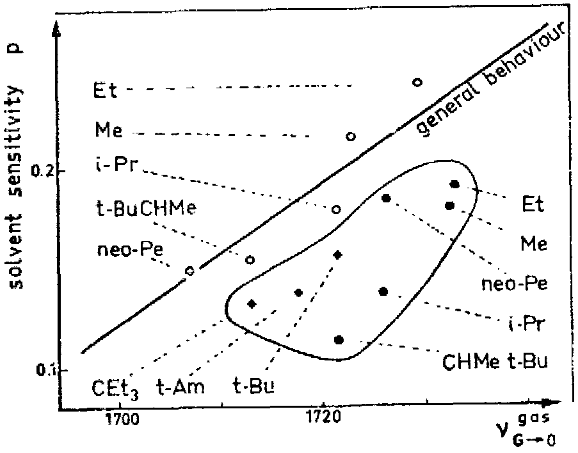

Figure 2. Solvent sensitivity (p) vs. structure effect ($\nu^{gas}_{G\to O}$) for conformations B (components II: o) and A (components I: •) of R-CO-neoPe ketones compared with the general behaviour of single-banded ketones.[7] All components I and the singlets of tertiary neopentyl ketones (♦) deviate from the line.

The behaviour of R-CO-neoPe ketones with a tertiary group is noteworthy because they exhibit a single $\nu_{C=O}$ band, but behave like conformations A. This is consistent with the very weak associating power of the tBu-CO-neoPe ketone[5] in which, according to strong evidence, there is a steric hindrance of the n orbitals of the oxygen atom.[11]

The conclusion that can be directly drawn is that the carbonyl group is eclipsed by the alkyl group in conformations A, whereas it remains accessible to intermolecular interactions in conformations B. In fact, an a priori vibrational calculation[9] shows that, for neoPe-CO-Me, the experimental difference of 12.4 cm^{-1} between the two components of its $\nu_{C=O}$ doublet is compatible with the existence of an equilibrium between a syn-periplanar form (A), absorbing at higher frequency, and two syn-clinal forms (B) with dihedral angles ϕ of ± 63°.

A B

GENERALIZATION TO OTHER SERIES

Similar a priori vibrational calculations indicate that the $\nu_{C=Y}$ doublet of H-CO-neoPe, Me_2N-CO-neoPe and Me-C(=CH_2)-neoPe[9,12] can also be attributed to such conformational equilibria. Therefore, the previously proposed hypothesis[13] of a conformational equilibrium between staggered and eclipsed R forms, with respect to C=Y, in aldehydes and ketones can be extended to amides and alkenes. In particular, in the case of the series H-CO-R, Me-C(=CH_2)-R, Me_2N-CO-R and Me-CO-R in CCl_4, the change-over to staggered conformations would occur, in the first two series, when the R groups are less bulky than neoPe and, in the very last series, when the R groups are more bulky than neoPe, as shown by the ratios I/II measured for R = neoPe in all four series (0.30, 0.64, 0.96 and 2.33, respectively).

References

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(Received in France 7 November 1979)