Conformational Equilibrium and Barrier to Internal Rotation in β-Ethylaminoacraldehyde

By Paul-Marie Vay

(*Laboratoire de Chimie Organique, Faculté des Sciences de Grenoble, Cedex-53, 38-Grenoble-Gare, France*)

Summary The u.v. spectra of β-ethylaminoacraldehyde in various solvents indicates the existence of a conformational equilibrium *trans-s-cis* ⇌ *trans-s-trans*.

RECENTLY Dabrowski[1] has studied the conformation and configuration of some β-alkylaminoacraldehydes by means of i.r. and Raman spectra. I report preliminary results concerning similar studies by means of u.v. spectra. I have studied the conformational equilibrium of *N*-ethyl-aminoacraldehyde,† the u.v. spectrum of which presents some important features.

Solvent effect. The u.v. spectra in various solvents for this compound give the following results; in heptane: λ_{max} 304 nm., ϵ 14,400; chloroform: λ_{max} 276, 312 nm. ϵ 15,700, 9200; ethanol: λ_{max} 279 nm., ϵ 33,000. The modifications of the spectrum show the displacement, due to the solvent, of a (probably) conformational equilibrium. The long-wavelength band disappears as the solvent becomes more and more polar. By comparison with the u.v. spectrum of 3-diethylaminocyclohex-2-en-1-one (λ_{max} 300 nm., ϵ 33,600 in EtOH), the short-wavelength band can be ascribed to the *trans-s-trans* form.

Temperature dependance. The effect of the temperature has been studied on spectra in heptane, dioxan, and ethanol. In the case of dioxan as solvent no effect has been observed. In the other cases, a diminution of the intensity of the more intense band and an isosbestic point have been observed. The thermodynamic quantities ΔH° and ΔS° have been measured. In heptane, the form corresponding to the long-wavelength band (probably *trans-s-cis*) is the

most stable. ($\Delta H^\circ = -0.6$ kcal./mole, $\Delta S^\circ = -3.8$ e.u.). In ethanol, the *trans-s-trans* form, corresponding to the short-wavelength band is the most stable ($\Delta H^\circ = +0.9$ kcal./mole, $\Delta S^\circ = +4.4$ e.u.). These results show that polar solvents stabilise the form having the greater dipole moment (namely the *trans-s-trans* form). ΔH° is probably nearly zero in dioxan.

Rate of equilibration. If a solution in dioxan is prepared from another solution in heptane, the new equilibrium is reached slowly. The rate of equilibration obeys first-order kinetics. Since ΔH° is negligible in dioxan, the activation energies corresponding to direct and reverse order are equal. We can write:

$$\log_e (k_1 + k_2) = - E/RT + \log_e (A_1 + A_2)$$

The activation energy E is determined from the slope of the straight-line plot of $\log_e (k_1 + k_2)$ against $1/T$. In the case of internal rotation, E is a good measure of the height of the barrier. The experimental value ($E = 7.7$ kcal./mole) clearly indicates that internal rotation takes place around the C–C single bond. This experimental value is of the same order as that obtained by de Groot and Lamb[2] for acraldehyde using ultrasonic measurements. The activation energies for *cis-trans* isomerisations are usually larger.[3] The conformational equilibrium studied seems to be the following:

trans-s-trans ⇌ *trans-s-cis*
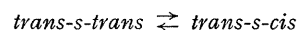
† This compound was obtained by addition of ethylamine to propynal.

[1] J. Dabrowski, *J. Mol. Structure*, 1969, 3, 227.
[2] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.*, 1957, A, 242, 36.
[3] R. B. Cundall, *Progr. Reaction Kinetics*, 1964, 2, 172.