E- and *Z*-Aldimines

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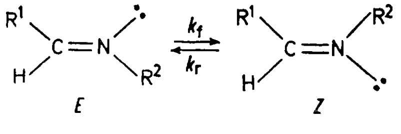
Summary The detection of *Z*-aldimines in equilibrium with the *E*-isomers in some *N*-(9-anthrylidene)alkylamines is ascribed to a lone pair repulsion effect; the barriers to interconversion of the diastereomers of *N*-(9-anthrylidene)methylamine have been estimated by direct thermal stereomutation and by dymamic n.m.r.

WHILE reported observations of *E*- and *Z*-isomers of ketimines have become numerous within the last ten years, virtually no examples of diastereomeric aldimines can be found.[1] The inability to detect the *Z*-isomer may be attributed to a low concentration at equilibrium resulting mainly from adverse non-bonded interactions between the substituents R^1 and R^2.[2]

Contrary to expectations (based on steric hindrance effects), the n.m.r. spectrum of *N*-(9-anthrylidene)methylamine (R^1 = 9-anthryl, R^2 = Me) in deuteriochloroform solution showed the presence of a minor component (10%) which we have now identified as the *Z*-isomer. Since this would appear to be the first example of stable *E*- and *Z*-aldimines (observable as an equilibrium mixture in common solvents at room temperature),[3] it was important to establish that the minor component was the *Z*-isomer and not an impurity. The major component showed, in addition to the aromatic protons, signals at τ 6·24 (d, *J* 1·6 Hz, NMe) and 0·68 (q, *J* 1·6 Hz, =CH), and the minor component exhibited a similar spectrum with signals at τ 6·96 (d, *J* 2·2 Hz, NMe) and 0·84 (q, *J* 2·2 Hz, =CH). Decoupling experiments (irradiating either the vinyl proton or the methyl group) verified the allylic coupling in both components, and the benzene solvent shift [$\Delta(CCl_4, C_6D_6)$] was much larger (0·20 p.p.m.) for the vinyl proton of the major component (*E*) than for the *Z*-isomer (*ca.* 0 p.p.m.). When previously recrystallised aldimine was dissolved in deuteriobenzene and analysed immediately by n.m.r., signals due to the *E*-isomer only were observed. Over a period of minutes a progressive increase in the intensity of the minor component was observed until equilibrium was established (7% *Z*-isomer). The half-life for the equilibration was found to be *ca.* 4 min at 42° in deuteriobenzene solution corresponding to k_f *ca.* $2{\cdot}0 \times 10^{-4}\ s^{-1}$, k_r *ca.* $2{\cdot}7 \times 10^{-3}\ s^{-1}$, $\Delta G^{\ddagger}_f$ 23·8 kcal mol^{-1}, and $\Delta G^{\ddagger}_r$ 22·2 kcal mol^{-1}. On heating a sample of the imine in diphenyl solution, the *N*-methyl doublet of the *Z*-isomer broadened reversibly near 200° (the upper limit of the spectrometer) corresponding to the onset of rapid degenerate stereomutation on the n.m.r. time scale. Computer analysis[4] of the exchange-broadened doublet gave k_r *ca.* 3·6 s^{-1}, corresponding to $\Delta G^{\ddagger}_r$ 26·9 kcal mol^{-1} at 200°; and as $K = 0{\cdot}13$ at 200°, $\Delta G^{\ddagger}_f$ 28·8 kcal mol^{-1}. The difference in the $\Delta G^{\ddagger}$ values determined at 42° and 200° may indicate a solvent effect or an unusually large (negative) entropy of activation.



The observation of *Z*-aldimines has been extended to other members of the 9-anthrylaldimine series† and the proportion of the *Z*-isomer in deuteriochloroform solution appears to diminish with increase in size of the R^2 substituent; R^2 (% *Z*) = Me (10), Et (9), $PhCH_2$ (8), neopentyl (7), Pr^i (6), and Bu^t (< 1). The significant proportion of the *Z*-isomer, despite the strong opposing steric interactions, may be attributed to an unfavourable repulsion between the nitrogen lone pair electrons and the π-electrons of the anthryl ring in the *E*-configuration.

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† Satisfactory analytical data have been obtained for the crystalline imines.

[1] C. G. McCarty in "The Chemistry of the Carbon-Nitrogen Double Bond", ed. S. Patai, Interscience, London, 1969, p. 363.

[2] J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 5085; J. Hine and C. Y. Yeh, *ibid.*, 1967, **89**, 2669; K. A. W. Parry, P. J. Robinson, P. J. Sainsbury, and M. J. Waller, *J. Chem. Soc.* (*B*), 1970, 700.

[3] Signals ascribed to *Z*-aldimines have been observed in liquid SO_2 solution where complex formation is probable; G. A. Olah and P. Kreienbuhl, *J. Amer. Chem. Soc.*, 1967, **89**, 4756; and the transient existence of *Z*-anils has been detected following irradiation of the more stable *E*-isomer: E. Fischer and Y. Frei, *J. Chem. Phys.*, 1957, **27**, 808; G. Wettermark aad E. Wallstrom, *Acta Chem. Scand.*, 1968, **22**, 675.

[4] W. B. Jennings, *Chem. Comm.*, 1971, 867; the components of the doublets were treated as separate sites and the AX coupling constants for both isomers were assumed to have the same sign.