

CONFORMATIONAL AND ELECTRONIC EFFECTS ON IMINE STEREOCHEMISTRY

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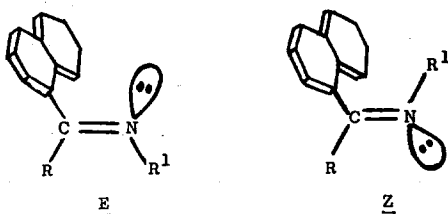
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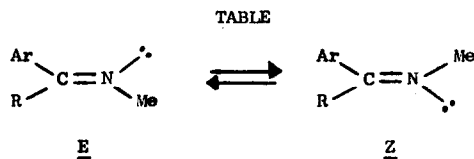
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Acyclic imine stereochemistry is characterised by a rapid equilibration of E and Z-stereoisomers in solution at ambient temperature.² Although there have been few systematic investigations of the equilibrium, the E to Z-isomer ratios have generally been rationalised in terms of non-bonded interactions between the nitrogen substituent and the proximate carbon substituent.³ However, results are now presented which indicate that interactions involving the nitrogen lone pair electrons may be important in determining imine stereochemistry (Table).

The isomer ratios for imines 1 - 5 can be rationalised in terms of nonbonded interactions between the N-methyl group and the neighbouring alkyl or aryl moieties. On the basis that the 1-naphthyl group is more bulky than phenyl, imines 7 and 8 might be expected to exhibit less of the Z-isomer at equilibrium than 2, and 3 respectively; however, the proportion of the Z-isomer increases on substitution of 1-naphthyl for phenyl (Table). Additionally, comparison of the results for imines 7 and 9 shows that the proportion of the Z-isomer increases dramatically on changing the aryl moiety from 2-naphthyl to 1-naphthyl, even though the latter imine is more hindered. It is clear that additional factors should be considered. The 1-naphthyl ring in 7 and 8 is probably twisted out of the molecular plane in the preferred conformation (Figure).



R = Me, Et
R¹ = Me



Compound	Ar	R	Isomer Ratio ^a (%)	
			<u>E</u>	<u>Z</u>
1	Ph	H	100	0
2	Ph	Me	93	7
3	Ph	Et	74	26
4	Ph	Pr	70	30
5	Ph	Pr ⁱ	5	95
6	Ph	Bu ^t	0	100
7	1-C ₁₀ H ₇	Me	23	77
8	1-C ₁₀ H ₇	Et	0	100
9	2-C ₁₀ H ₇	Me	96	4
10	2-Me-C ₆ H ₄	Me	24	76
11	2-MeO-C ₆ H ₄	Me	42	58

^a Isomer ratios were determined as 0.5 molar solutions in deuteriochloroform solution at 35° by n.m.r.; sufficient time was allowed for the imines to attain equilibrium.

Non-bonded interactions between the 1-naphthyl moiety and the N-methyl group in this conformation of the Z-isomer will be reduced; however from an examination of space-filling models it appears unlikely that the latter steric interaction could be less than that between the C-methyl and N-methyl groups in 7E. In explanation of this anomaly it is proposed that the E configuration may be destabilised by an "n- π repulsive interaction" between the non-bonding nitrogen lone pair electrons and the π -electrons of the proximate aryl ring. This effect should be maximum in conformation E where the lone pair can interact with the aromatic π -electron cloud. This interpretation appears to be supported by the isomer ratios for imines 10 and 11 which also possess an ortho substituted ring; a similar effect is probably responsible for the significant amount of Z-isomer found in aldimines derived from 9-

anthraldehyde.⁴ Comparison of the equilibrium constants for 2 and 10 or 9 and 7 enables the ortho effect in 7 or 10 to be estimated at ca 2.5 k.cal./mole. An intermolecular n- π repulsion effect has been used to interpret benzene induced solvent shifts in the n.m.r. spectra of compounds possessing lone pairs of electrons.⁵

The ortho effect should be observable in other mobile systems containing a trivalent nitrogen atom and a neighbouring aryl ring.⁶ Indeed the E to Z isomer ratios in some diaryloximes⁷ and alkylaryl hydrazones⁸ have been rationalised in terms of a twisted conformation of the ortho substituted ring (cf. figure) and of steric interactions involving the hydroxyl or dimethylamino group. It is possible that repulsion between the lone pair electrons on the nitrogen or oxygen atoms and the proximate aryl rings are also important factors in the equilibrium stereochemistry of these oximes and hydrazones.

The stereochemistry of the imines was assigned from the n.m.r. spectra on the basis of the N-methyl signal positions,¹⁰ the magnitude of coupling constants,³ and benzene induced solvent shifts on the C-alkyl signals.⁵ The assignments are supported by the observation that the proportion of the E-isomer decreases with increasing size of the group R (Table) in both the phenyl series (1→6) and the 1-naphthyl series (7 and 8). The observation of two N-methyl signals in each of the n.m.r. spectra of compounds 3 (6.66 (E) and 6.97 (Z)) and 4 (6.63 (E) and 6.96 (Z)) in deuteriochloroform solution is in contrast to a previous report by Lambert *et al.*⁹

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