E- AND Z-(C-ARYL)KETIMINES.   AN ALTERNATIVE

EXPLANATION TO THE "n-π REPULSIVE INTERACTION"

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The effective "size" of a lone pair of electrons on an sp^3 nitrogen atom
in saturated N-heterocycles, and thus its steric interaction with adjacent
groups, which might affect conformational equilibria, has received considerable
attention in recent years.[1]   Allinger has presented a discussion which favors
ignoring the lone pair altogether, and considering only the other substituents
on the nitrogen atom in determining conformational equilibria of saturated
N-heterocycles.[1]

Recently it was proposed that an important factor in determining the E- to
Z-isomer ratios of ketimines[2] of type (1) and aldimines[3] is an "n-π repulsive
interaction" between the lone pair of electrons on the sp^2-nitrogen atoms and
the π-electrons of the aryl ring. It was also suggested[2] that similar consider-
ations might apply to E- to Z-isomer stabilities in diaryloximes and alkylaryl
hydrazones.   Thus it was rationalized[2] that (1b) and (c) (Table) gave large

1,E   1,Z   2
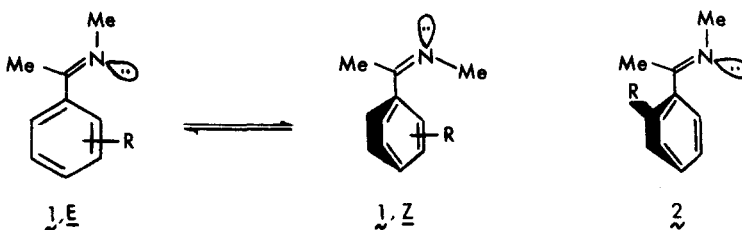
Table

Chemical shift and equilibrium composition data of E and Z isomers of (1).[a]

R	E (δ,p.p.m.) N-Me	E (δ,p.p.m.) C-Me	Z (δ,p.p.m.) N-Me	Z (δ,p.p.m.) C-Me	% Z isomer
a H[b,c]	3.27	2.10	2.97	2.19	7
b 2-Me[b]					76
c 2-MeO[b]					58
d 4-Me[c]	3.30	2.14	3.07	2.23	7
e 4-MeO[c]	2.28	2.12	3.10	2.26	3
f 2-Ph[d]	3.15	1.52	2.90	1.90	58
g 4-Ph[c]	3.34	2.17	3.12	2.30	4
h 4-NO$_2$[c]	3.40	2.26	3.06	- [e]	1
i 2,4-(MeO)$_2$[c]	3.27	2.15	2.99	2.24	51
j 2-CF$_3$[c]	3.34	2.18	2.94	2.31	71

[a] Spectra determined on a Varian A60 instrument at 300°K using 20% (w/v) deuteriochloroform solutions and TMS as internal standard. All new compounds gave satisfactory spectroscopic and analytical data. Homoallylic[3] coupling constants for the E isomers were in the range of 0.8-0.9 Hz and for the Z isomers, 1.3-1.5 Hz. [b] Ref. 1. [c] This work. [d] Ref. 4. [e] Presumably under the C-Me absorption of the E isomer.

amounts of the $\underline{Z}$-isomer ($\underline{cf}$. $\underline{1a}$) due to repulsion of the sp^2-nitrogen lone pair of electrons and the π-electrons on the aryl ring in conformation ($\underline{2}$).

Consideration of the isomer composition data presented in the Table shows that this "n-π repulsive interaction" is, at best, of minimal importance in determining $\underline{E}$- and $\underline{Z}$-isomer ratios of imines ($\underline{1}$). Comparison of 2- and 4-substituted aryl imines ($\underline{1b}$ and $\underline{d}$, $\underline{c}$ and $\underline{e}$, $\underline{f}$ and $\underline{g}$) reveals that indeed 2-substitution does markedly enhance the amount of the $\underline{Z}$-isomer. Were the "n-π repulsion" operative, however, an electronic effect should be observable, in which the substituent affects the extent of such an interaction by either electron withdrawal or donation. Comparison of ($\underline{1c}$) and ($\underline{1i}$), and particularly ($\underline{1b}$) and ($\underline{1j}$), shows that such effects are minimal ($\underline{e}$.$\underline{g}$. $\Delta\Delta G(\underline{1b}, \underline{Z}-\underline{E})-(\underline{1j}, \underline{Z}-\underline{E})$ = 0.15 kcal mol^{-1}).

The data may be better rationalized by postulating that $\underline{E}$-isomers of ($\underline{1}$) without 2-substituents may exist with the aryl ring and the C=N group coplanar, whereas the $\underline{Z}$-isomers cannot. Examination of CPK space-filling models supports this hypothesis. Thus the $\underline{E}$-isomers are more stable than $\underline{Z}$-isomers ($\underline{e}$.$\underline{g}$. $\Delta G(\underline{1a}, \underline{Z}-\underline{E})$ = 1.5 kcal mol^{-1}, $\Delta G(\underline{1h}, \underline{Z}-\underline{E})$ = 2.7 kcal mol^{-1}) by virtue of the resonance interaction available only to the former. Substitution at the 2-position has a drastic effect on the conformation of the $\underline{E}$-isomer, forcing the aryl ring and the imine linkage out of coplanarity ($\underline{2}$), thereby sterically blocking resonance interaction between the two. In contrast, the same substitution in the $\underline{Z}$-isomer has very little effect except to restrict somewhat the oscillation about the aryl-$\underline{C}$-imine-$\underline{C}$ bond. In the absence of a resonance effect favoring the $\underline{E}$-isomers of 2-substituted imines (conformations $\underline{1}(\underline{Z})$ and $\underline{2}$ are important), the relative energies of the $\underline{E}$ and $\underline{Z}$ isomers depend primarily on the non-bonded steric interactions of the three groups about the C=N bond,[2,6,7] although factors such as the degree of oscillational freedom of the C=N linkage about the aryl-$\underline{C}$-imine-$\underline{C}$ bond might play a minor role.

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References

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6. It is important to recognize that the steric interactions of the aryl group involve presenting the _face_ of the aryl ring to the _N_—Me group. Thus the aryl group is smaller than might otherwise be expected [see E. L. Eliel, _Angew. Chem. Int. Ed. Engl_., 4, 761 (1965)].

7. For example, examination of CPK models of the imines $1-C_{10}H_7C(R)=NMe$, $(R=Me,Et)^2$, shows that the C=N and 1-naphthyl systems cannot be coplanar, and _E/Z_ isomer ratios are about what would be expected based on the sizes[6] of the three groups attached to the C=N linkage (_Z_-isomer predominates).