cis–trans-Isomerism in *N*-Arylformamidinium Salts

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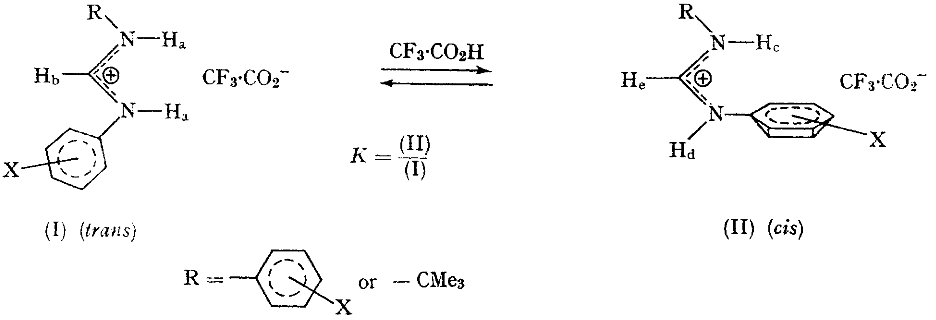
THERE is now a number of examples of geometrical isomerism about single and double bonds in which the isomer with the larger groups *cis*-oriented predominates.[1] The cause of this thermodynamically preferred *cis*-orientation is not settled. We report here an example of *cis–trans*-isomerism which is highly sensitive to electrical effects in the substituents.

Protonation of *NN'*-disubstituted formamidines occurs on the imino-nitrogen, giving a conjugate acid which can exist in either a *trans*-(I) or *cis*-(II) configuration. Nuclear magnetic resonance (n.m.r.) spectra of these formamidines in trifluoroacetic acid (TFA) give distinguishable signals for he protons H_a–H_e which can be assigned on the basis of line shape and coupling constants (*e.g.*, $J_{\mathrm{H_aH_b}} \simeq J_{\mathrm{H_cH_e}} \simeq 14$, $J_{\mathrm{H_dH_e}} \simeq 6$ c./sec.; H_a, H_c, and H_d are doublets broadened by quadrupole coupling, H_b is a triplet, and H_e is a quartet). Steric interaction between the *endo**-aryl and NH_c groups in (II) will force the aryl ring to orient such that H_c lies above the aryl-π system. Accordingly, H_c shows an upfield shift of about one p.p.m. relative to the H_a resonance because of the ring anisotropy. Integration of appropriate n.m.r. signals provides a ready measure of the equilibrium concentrations of (I) and (II). In the case of R = t-butyl, the large steric requirements of the t-butyl group force it to take up the *exo**-position in all cases (see below).



(I) (*trans*)

(II) (*cis*)

The results (Table) show a striking aryl-substituent effect upon the equilibrium. In the case of the symmetrically substituted salts, the *cis*-configuration is favoured by an entropy factor which is not present in the *N*-aryl-*N'*-t-butylformamidinium salts. Nevertheless, the substituent effect is similar in both series. The equilibrium constants for *meta*- and *para*-substituted compounds are correlated by a Hammett plot which yields ρ-values of $-0{\cdot}75$ ($r = 0{\cdot}917$) and $-0{\cdot}83$ ($r = 0{\cdot}989$) for the diaryl and aryl, and t-butyl series, respectively. The effect of electron-donating groups in stablizing the *cis*-configuration is also mirrored in the methyl-substituted arylformamidines which show an increase in the *cis*-isomer populations as the number of methyl groups increases (see Table). *ortho*-Alkyl groups are particularly effective.

The striking substituent dependence rules out a simple steric effect. This conclusion is emphasized by the finding that the conjugate acid of *NN'*-di-t-butylformamidine exists wholly in the *trans*-configuration in aqueous acid and TFA. A tempting hypothesis, which is consistent with the foregoing observations, is that there exists an attractive N–$H_c \cdots \pi$-interaction. Such interactions are known to be sensitive to steric and substituent effects.[2] However, this interaction cannot be of overriding significance because it is found that in the *N*-2,6-dimethylaryl-*N'*-t-butylformamidine series, the equilibrium is essentially independent of substituent effects varying from 85–90% *cis*- for X=H, 4-Br, 3-NO_2. Therefore, the substituent effect appears to be associated with a resonance interaction of the coplanar *trans*-configuration.

Because of the polar nature of the substituents about the partial C$\overset{\text{---}}{=}$N bond, it appears likely

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* The positions occupied by H_a and H_c will be referred to as the *endo*-positions and those occupied by H_a and R are denoted as the *exo* positions.

TABLE

cis–trans *Equilibrium constants*† *for* NN′-*diarylformamidinium* (K) *and* N-*aryl*-N′-*t*-*butylformadinium* (K′) *trifluoroacetates*

Substituent (X)	*K*	*K′*	Substituent (X)	*K*	*K′*
H	1·00	0·48	4-Methoxy	1·90	1·00
3-Acetyl	0·65	0·28	2-Methyl	2·50	2·20
4-Acetyl	0·25	0·09	3-Methyl	1·10	0·62
3-Trifluoromethyl	0·65	0·25	4-Methyl	1·40	0·68
4-Trifluoromethyl	0·40	0·20	2,4-Dimethyl	3·0	2·1
3-Chloro	0·65	0·38	2,6-Dimethyl	large‡	—
4-Chloro	0·85	0·32	2,4,5-Trimethyl	large‡	2·4

† N.m.r. spectra of 10 mole % solute in TFA were determined with a Varian A-60 instrument at 38 ± 2° for the diaryl series and with an HA-60 instrument for the aryl, t-butyl series; equilibrium constants are estimated to be accurate to ± 0·02 units for the aryl, t-butyl series and ± 0·10 units for the diaryl series.

‡ In these cases no *trans*-isomer could be detected: $K \geqslant 20$.

that the *cis*-configuration is stabilized by favourable dipolar interactions.

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