# The Effect of Salt Formation on Structure and Charge Distribution in Imines. Part 4.[1] Energy Barriers to Isomerisation about the C–N Bond in 2,6-Dimethyl-4-aryliminopyrans and their Salts: Solvent and Substituent Effects, and Evidence for Isomerisation Mechanisms

By **Michael P. Sammes,** Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Free energies of activation, $\Delta G^{\ddagger}$, have been calculated for isomerisation about the C=N bond in a series of 2,6-dimethyl-4-aryliminopyrans (1), and their hydro- [(2) and (3)] and metho- [(4) and (5)] salts. Independent values were measured from coalescence of two different sets of ^{1}H n.m.r. signals in each compound. The effects of temperature, solvent, and aryl substituent X on $\Delta G^{\ddagger}$ indicate that the metho-salts isomerise by C=N bond rotation, the imines by inversion or a mechanism intermediate between inversion and rotation, and the hydro-salts by the previously unreported deprotonation–imine isomerisation–reprotonation mechanism. Hydro-salts (3) having a $-M$ substituent in the aryl para-position give anomalous results for $\Delta G^{\ddagger}$ at the lower coalescence temperature.

DURING the preparation and characterisation of the imines (1) and their salts (2)—(5), it was observed [2] that their ^{1}H n.m.r. spectra were temperature dependent. Separate signals, observed at low temperatures both for the 2- and 6-methyl groups, and for the 3- and 5-protons of the pyran ring, coalesced into singlets at higher temperatures, the effect arising apparently from rapid isomerisation about the C=N bond on the n.m.r. time scale. The different pathways by which imines and iminium salts might isomerise have been discussed extensively.[3] Thus, evidence has been produced for imine isomerisation by rotation (Scheme 1; path A), in which the C=N π-bond is disrupted while the nitrogen remains in an sp_2 hybridised state in the intermediate;[4] by inversion (path B), in which the C=N bond remains
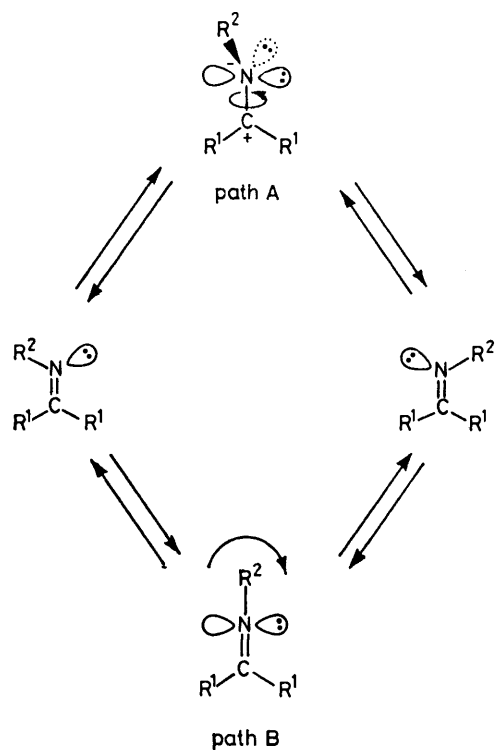
intact while the nitrogen atom is rehybridised to the sp state;[5] and by a spectrum of pathways intermediate between these two extremes.[6] When the group R^1 is strongly electron-withdrawing, an apparent change in mechanism from path A to B has been observed on

path D

path C

path E

SCHEME 2

path A

path B
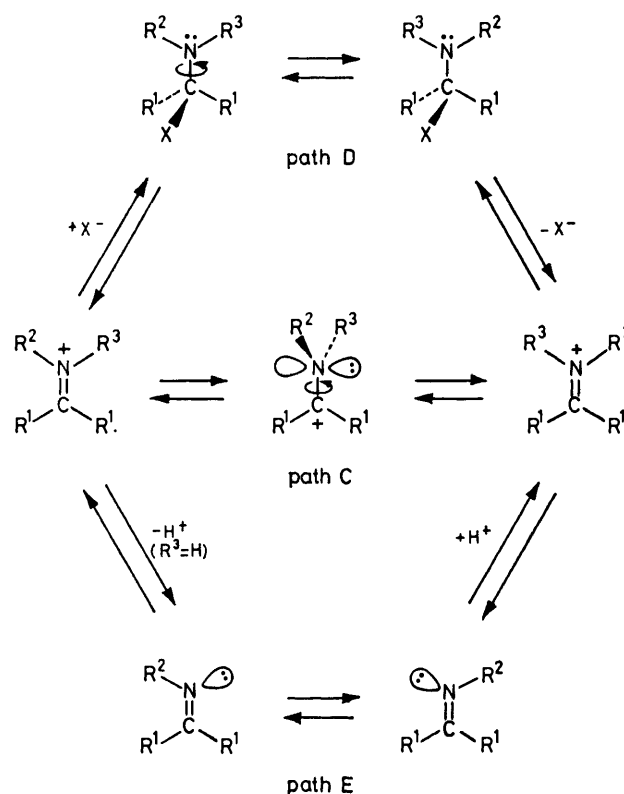
SCHEME 1

varying the electronic properties of R^2 from $+M$ to $-M$.[4,7] Iminium salts may also isomerise by more than one pathway (Scheme 2). Whilst rotation (path C) is the generally favoured process,[3d,8] some examples involving addition of the conjugate anion to the C=N bond, followed by rotation and subsequent loss of the anion (path D) have been reported.[9] For the case

where $R^3 = H$, a third mechanism, namely deprotonation–imine isomerisation–reprotonation (path E) becomes possible, though this pathway has not been demonstrated conclusively, and has even been specifically excluded in one case.* [10] Preliminary measurements by variable temperature ^1H n.m.r. (VTNMR) have indicated [11] that the imine (1a) isomerises by a pathway different from that followed by the salts (2a) and (4a), and evidence from X-ray crystallographic and u.v. measurements,[11] and from ^{13}C n.m.r. data,[1] support the inversion mechanism (path B) for the imine.

It was therefore of interest to measure $\Delta G^{\ddagger}$ for the isomerisation process in a range of imines (1) and their salts (3) and (5) by ^1H VTNMR, observing especially any effects due to the solvent or the nature of the substituent X, since these latter can provide information regarding the pathway being followed.[3a] Further, because the frequency of separation of the two methyl signals in compounds (1)—(5) is generally found to be different from that for the 3- and 5-H signals of the pyran ring, two distinct coalescences can be recorded, giving values of $\Delta G^{\ddagger}$ at two different temperatures. Thus, any temperature dependence in $\Delta G^{\ddagger}$ should be apparent, indicating whether $\Delta S^{\ddagger}$ is close to zero (as has been assumed in some related studies),[8,12] or not.

EXPERIMENTAL

Compounds (1)—(5) were prepared as described previously,[1,2] and recrystallised to constant m.p. Deuteriated solvents were dried, and if necessary redistilled, before use.

^1H N.m.r. spectra were recorded on a JEOL FX 90Q spectrometer, operating at 89.6 MHz, and using a dedicated ^1H insert, solutions in all cases being 0.1M. For a spectral width of 896 Hz, 8 K data points were collected, giving a digital resolution of 0.11 Hz. A pulse angle of 60° with a repetition of 5 s was used to minimise saturation effects. Where possible, two coalescence temperatures (T_c) were determined for each sample, respectively for the 2- and 6-methyl groups and for the 3- and 5-protons of the pyran ring, in all cases the temperature of the probe being increased incrementally from low to high temperature. Repeat runs were carried out for ca. 30% of the samples to establish the reproduceability of T_c; the temperature controller was calibrated with MeOH (low region) and propane-1,3-diol (high region), and was accurate to within ± 2 K.

For salts (3h—k), data were recorded on a JEOL C60 spectrometer operating in the continuous wave mode at 60 MHz (see Results section).

Rate constants, k_c, were determined at T_c, using the approximate expressions $k_c = \pi \Delta \nu / \sqrt{2}$ for the methyl signals,[13] and $k_c = \pi[(\Delta \nu^2 + 6J^2)/2]^{\frac{1}{2}}$ for the 3- and 5-H signals,[14] since coupling $(J$ 2—2.5 Hz) was observable between these latter. Free energies of activation, $\Delta G^{\ddagger}$, were then calculated using the modified Eyring equation, $\Delta G^{\ddagger} = 19.12 \ T_c(10.32 + \log T_c/k_c)$, which assumes a value of unity for the transmission coefficient κ.

* Isomerisation via other processes such as dissociation–recombination, and imine–enamine tautomerism,[3a] are not applicable to the compounds under study here.
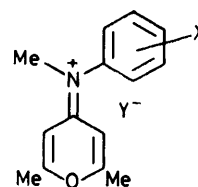
RESULTS

For the imines (1) measurements were carried out in two solvents of high polarity (CD_3NO_2 and CD_3CN) and one of moderate polarity ($CDBr_3$), and reveal a substantial solvent effect. Data are recorded in Table 1, and show that for each compound, within experimental error, $\Delta G^{\ddagger}$ measured at the two coalescence temperatures are the same. Further,
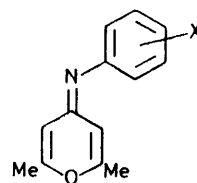
(1)
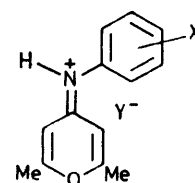
(2) Y = Br
(3) Y = ClO$_4$

(4) Y = Br
(5) Y = ClO$_4$

X		X	
a;	4-NO$_2$	g;	4-Cl
b;	3-NO$_2$	h;	4-F
c;	4-COMe	i;	H
d;	4-CO$_2$Me	j;	4-Me
e;	3-CO$_2$Me	k;	4-OMe
f;	4-Br		

in CD_3NO_2, there is no significant difference in $\Delta G^{\ddagger}$ values for imines (1e—i). The relatively low b.p. of CD_3CN imposed some restrictions on the collection of data, as did the instability of the imines (1h—k) above 380 K. Thus, $\Delta \nu$ for the 3- and 5-H signals began to increase above this temperature, accompanied by darkening of the solution for imines (1h and i), and it was not possible to record T_c for compounds (1j and k). Repeat measurements showed that T_c was reproducible to within ± 1 K. Data for the p-nitro-compound (1a) were also recorded for a solution 0.5M in $CDBr_3$, to evaluate the effect of concentration; this is seen to be small. In the spectra of most of the imines (1) [and of the salts (2)—(5)], long-range coupling (J 0.8 Hz) was observed between 3- or 5-H and the neighbouring methyl protons. This had to be ignored when using the approximate equations (see Experimental) for determining $\Delta G^{\ddagger}$, but was unlikely to introduce an error greater than that imposed by the precision of T_c. For the imine (1a), $J_{3,5}$ was not observable above the freezing point of two of the solvents, so the value (2.14 Hz) found in CD_3CN was used in calculating k_c.

Data for the iminium bromide (2a) were also recorded in three solvents and reveal a substantial solvent effect (Table

TABLE 1

Dynamic ¹H n.m.r. parameters for the imines (1)

Compound	Phenyl sub-stituent	Solvent	2,6-Me₂				3,5-H₂				
			T_c/K [a]	$\Delta\nu$/Hz [b]	k_c/s⁻¹ [c]	$\Delta G^{\ddagger}_{Tc}$ [d]	T_c/K [a]	$\Delta\nu$/Hz [b]	$J_{3,5}$/Hz [b]	k_c/s⁻¹ [c]	$\Delta G^{\ddagger}_{Tc}$ [d]
(1a)	4-NO₂	CD₃NO₂	279	9.96	22.1	60.9	284	14.88	e	35.0	61.0
		CD₃CN	286	11.42	25.4	62.2	294	20.82	2.14	47.7	62.5
		CDBr₃	303	10.13	22.5	66.3	313	26.79	e	60.6	66.0
		CDBr₃ f	299	10.13	22.5	65.4	310	23.73	e	54.0	65.7
(1b)	3-NO₂	CD₃NO₂	351	11.81	26.2	76.8	355	17.58	2.19	40.8	76.4
		CD₃CN	354	12.03	26.7	77.4	362	21.11	2.19	48.4	77.5
		CDBr₃	357	10.72	23.8	78.5	372	28.80	2.20	65.1	78.8
(1c)	4-COMe	CD₃NO₂	322	10.82	24.0	70.5	326	15.61	2.19	36.7	70.2
		CD₃CN	323	11.81	26.2	70.5	330	20.55	2.30	47.3	70.4
		CDBr₃	333	11.70	26.0	72.8	344	26.71	2.20	60.5	72.8
(1d)	4-CO₂Me	CD₃NO₂	328	11.15	24.8	71.8	333	16.03	2.18	37.5	71.7
		CD₃CN	329	12.04	26.7	71.8	334	19.78	2.30	45.7	71.4
		CDBr₃	341	12.03	26.7	74.5	352	26.26	2.19	59.6	74.6
(1e)	3-CO₂Me	CD₃NO₂	370	12.14	27.0	81.1	377	18.03	2.19	41.8	81.3
		CD₃CN	372	10.28	22.8	82.0	380	21.98	2.19	50.3	81.4
		CDBr₃	381	11.92	26.5	83.6	396	28.36	2.19	64.1	84.1
(1f)	4-Br	CD₃NO₂	367	9.84	21.9	81.0	371	10.87	2.19	27.0	81.3
		CD₃CN	369	10.72	23.8	81.2	g	15.47	2.30		
		CDBr₃	380	10.50	23.3	83.8	392	21.65	2.30	49.7	84.1
(1g)	4-Cl	CD₃NO₂	368	9.96	22.1	81.2	372	11.11	2.19	27.4	81.5
		CD₃CN	371	10.88	24.2	81.6	g	15.58	2.30		
		CDBr₃	382	10.72	23.8	84.2	395	21.55	2.19	49.3	84.8
(1h)	4-F h	CD₃NO₂	367	10.18	22.6	80.9	388	10.25	2.29	26.0	85.3
		CDBr₃	400	10.62	23.6	88.3	i	20.55	2.19		
(1i)	H h	CD₃NO₂	370	11.04	24.5	81.3	378	12.25	2.29	29.9	82.5
		CDBr₃	387	11.90	26.4	85.0	i	23.53	2.19		

[a] $T_c \pm 2$ K. [b] $\Delta\nu$ and $J \pm 0.11$ Hz. [c] $k_c \pm 0.1$ s⁻¹. [d] $\Delta G^{\ddagger} \pm 0.5$ kJ mol⁻¹. [e] $J_{3,5}$ Not observed above m.p. of solvent; taken to be 2.14 Hz. [f] 0.5M Solution. [g] $T_c >$ B.p. of solvent. [h] For spectrum in CD₃CN, $T_c >$ b.p. of solvent. [i] Compound decomposes below T_c.

TABLE 2

Dynamic ¹H n.m.r. parameters for the iminium salts (2) and (3)

Compound	Phenyl substituent	Solvent	2,6Me₂				3,5-H₂				
			T_c/K [a]	$\Delta\nu$/Hz [b]	k_c/s⁻¹ [c]	$\Delta G^{\ddagger}_{Tc}$ [d]	T_c/K [a]	$\Delta\nu$/Hz [b]	$J_{3,5}$/Hz [b]	k/s⁻¹ [c]	$\Delta G^{\ddagger}_{Tc}$ [d]
(2a)	4-NO₂	CD₃NO₂	310	5.25	11.7	69.6	340	43.81	1.97	98.0	70.6
		CD₃CN	306	5.47	12.2	68.6	340	45.46	1.97	101.5	70.5
		CDBr₃	325	3.94	8.75	73.9	376	61.43	1.97	136.9	77.3
(3a)	4-NO₂	CD₃NO₂	293	5.47	12.2	65.5	269	6.19	2.19	18.2	59.1
		CD₃CN	297	6.12	13.6	66.2	281	7.50	2.40	21.2	61.5
(3b)	3-NO₂	CD₃CN	322	7.44	16.5	71.5	327	8.65	2.41	23.3	71.7
(3c)	4-COMe	CD₃CN	314	6.78	15.1	69.9	284	7.73	2.40	21.6	62.1
(3d)	4-CO₂Me	CD₃CN	316	6.79	15.1	70.3	274	5.80	1.97	16.8	60.4
(3e)	3-CO₂Me	CD₃CN	339	8.97	19.9	74.9	348	12.50	2.19	30.2	75.7
(3f)	4-Br	CD₃CN	338	7.21	16.0	75.3	343	6.95	1.97	18.8	76.0
(3g)	4-Cl	CD₃CN	340	7.44	16.5	75.6	347	8.08	1.97	20.9	76.6
(3h)	4-F e	CD₃CN	354	5.1	11.3	80.0	371	11.0	2.2	27.3	81.2
(3i)	H e	CD₃CN	351	5.1	11.3	79.3	362	7.2	2.3	20.3	80.1
(3j)	4-Me e	CD₃CN	362	5.1	11.3	81.8	372	6.4	2.6	20.0	82.4
(3k)	4-OMe e	CD₃CN	374	5.3	11.7	84.6	>378	9.4	2.2	24.3	>83.2

[a] $T_c \pm 2$ K. [b] $\Delta\nu$ and $J \pm 0.11$ Hz. [c] $k_c \pm 0.1$ s⁻¹. [d] $\Delta G^{\ddagger}_{Tc} \pm 0.5$ kJ mol⁻¹. [e] 60 MHz Spectrum; $\Delta\nu$ and $J \pm 0.2$ Hz.

2). The perchlorates (3a—k) had a very low solubility in CDBr₃, but data for the *p*-nitro-compound (3a) show significant differences for CD₃NO₂ and CD₃CN. All other perchlorates were measured in CD₃CN, and salts (3h—k) were studied at 60 MHz since at this frequency Δν would be smaller, and thus T_c would be lower. Even so, for compound (3k), the second value of T_c could not be measured due to boiling of the solvent. The data in Table 2 reveal that ΔG‡ is sensitive to the nature of both the counter ion [as is Δν for 3- and 5-H; compare salts (2a) and (3a)], and the solvent. Further, ΔG‡ is temperature dependent, different values being found from coalescence of the two sets of signals.

Parameters for the metho-salts (4a) and (5) are recorded in Table 3. Though, again, a solvent effect is observable [compare (4a), (5a), and (5c)], the conjugate anion has no significant effect on ΔG‡ for the *p*-nitro-salts (4a) and (5a), in direct contrast to the results for the analogous hydrosalts (2a) and (3a) (Table 2). Further, values of ΔG‡ calculated from the two coalescence temperatures in each compound are the same within experimental error, in analogy with data for the imines (1), but again in contrast to that for the salts (2a) and (3). Only one value of T_c could be determined for the salts (5e—g) due to boiling of the solvent above 380 K.

Finally, as a potentially more quantitative probe into the isomerisation mechanisms, linear free-energy relationships between rate constants and Hammett substituent constants

TABLE 3

Dynamic ^{1}H n.m.r. parameters for iminium salts (4) and (5)

Compound	Phenyl substituent	Solvent	2,6-Me$_2$				3,5-H$_2$				
			$T_c/$K ^{a}	$\Delta\nu/$Hz ^{b}	$k_c/$s^{-1} ^{c}	$\Delta G^{\ddagger}_{Tc}$ ^{d}	$T_c/$K ^{a}	$\Delta\nu/$Hz ^{b}	$J/$Hz ^{b}	$k_c/$s^{-1} ^{c}	$\Delta G^{\ddagger}_{Tc}$ ^{d}
(4a)	4-NO$_2$	CD$_3$NO$_2$	316	21.22	47.1	67.3	333	81.15	e	180.3	67.4
		CD$_3$CN	312	22.42	49.8	66.3	331	95.82	e	212.9	66.5
		CDBr$_3$	317	21.00	46.7	67.6	341	127.1	e	282.3	67.8
(5a)	4-NO$_2$	CD$_3$NO$_2$	317	20.46	45.5	67.7	332	64.48	2.05	143.7	67.8
		CD$_3$CN	313	21.00	46.7	66.7	327	68.88	2.19	153.5	66.6
(5b)	3-NO$_2$	CD$_3$CN	343	21.66	48.1	73.3	359	72.38	2.19	161.2	73.2
(5c)	4-COMe	CD$_3$NO$_2$	346	20.78	46.2	74.1	362	63.62	1.97	141.7	74.2
		CD$_3$CN	339	21.66	48.1	72.4	355	69.31	2.19	154.4	72.5
(5d)	4-CO$_2$Me	CD$_3$CN	343	21.44	47.6	73.3	359	69.30	2.19	154.5	73.4
(5e)	3-CO$_2$Me	CD$_3$CN	370	22.10	49.1	79.2	>381 ^{f}	73.25	2.18	163.2	>77.9
(5f)	4-Br	CD$_3$CN	367	19.69	43.7	78.9	>381 ^{f}	66.46	2.19	148.1	>78.2
(5g)	4-Cl	CD$_3$CN	368	20.34	45.2	79.0	>368 ^{f}	67.12	2.19	149.6	>75.4

^{a} $T_c \pm 2$ K. ^{b} $\Delta\nu$ and $J \pm 0.11$ Hz. ^{c} $k_c \pm 0.1$ s^{-1}. ^{d} $\Delta G^{\ddagger}_{Tc} \pm 0.5$ kJ mol^{-1}. ^{e} Broad signal; $J_{3,5}$ not observed. ^{f} $T_c >$ B.p. of solvent.

were sought. Assuming $\Delta S^{\ddagger}$ to be zero,* log k was calculated from each value of $\Delta G^{\ddagger}$ in Tables 1—3, at an arbitrary intermediate temperature of 370 K. Values of log k were plotted against each of the Hammett substituent constants [16] σ, σ^-, and σ^+ for each series of compounds (1), (3), and (5), both with inclusion and with exclusion of data for those with *meta*-substituents. In all cases, the best fit was with σ^- constants (using σ values for all but $-M$ substituents); results from least squares regression analyses are given in Table 4. For the imines (1), exclusion of data

TABLE 4

Least-squares ' best fit ' correlations between log k at 370 K, and Hammett substituent constants ^{a}

Compound	Solvent	No. of data	Scale ^{b}	Slope ρ	σ_{slope} ^{c}	r ^{d}
(1)	CDBr$_3$	16	σ^-	2.62	0.16	0.974
		12	*σ^-*	*2.64*	*0.11*	*0.991*
(1)	CD$_3$CN	12	σ^-	2.97	0.30	0.954
		8	*σ^-*	*2.83*	*0.15*	*0.972*
(1)	CD$_3$NO$_2$	18	σ^-	2.56	0.22	0.948
		14	*σ^-*	*2.64*	*0.16*	*0.978*
(3) ^{e}	CD$_3$CN	11	σ^-	1.80	0.12	0.981
		9	*σ^-*	*1.80*	*0.13*	*0.981*
(5)	CD$_3$CN	11	σ^-	1.89	0.09	0.990
		8	*σ^-*	*1.83*	*0.10*	*0.991*

^{a} For figures in italics, data for *meta*-substituted compounds have been excluded. ^{b} σ Values used, except for substituents a, c, d, and h. ^{c} Standard error. ^{d} Correlation coefficient. ^{e} Data used only from coalescence of methyl signals.

for the *meta*-substituted compounds led to a significant improvement in the correlations. In contrast, a similar operation with the salts (3) and (5) had little effect. The values of ρ are seen to be larger in the imines (1) than in the salts (3) and (5), the latter two having very similar values for this parameter.

DISCUSSION

For the purposes of the discussion, it is convenient to consider first the metho-salts (4) and (5), then the imines (1), and finally the hydro-salts (2) and (3).

The Metho-salts (4) *and* (5).—Kessler and Leibfritz concluded that isomerisation in the guanidinium salts (6) was by rotation,[8] and Krebs assumed this to be the

* A similar assumption was made by Kessler with a series of arylimine metho-salts (6).[8] Where $\Delta S^{\ddagger}$ has been determined for analogous isomerisation processes, it has been found to be small, both for imines,[4,6,9b] and for iminium salts.[15]

mechanism in the two related series of iminium salts (7) [17] and (8).[18] For the salts (4) and (5) the mechanism must also be by rotation (path C; Scheme 2) since the alternative path D is excluded by the non-dependence
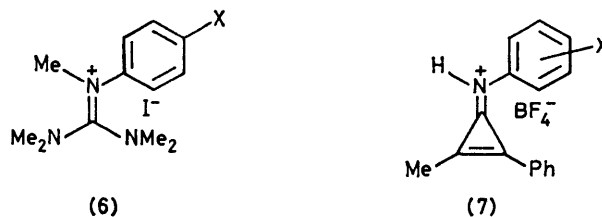

(6)

(7)

(8)

of $\Delta G^{\ddagger}$ on the nature of the conjugate anion.† The presumed intermediate, C—N single-bonded, species (9) would achieve stabilisation through considerable pyrylium character, a partial development of this being apparent even in the ground-state of the salt (4a), as evidenced by the long C=N bond (1.334 Å),[11] and the pyran ring ^{13}C chemical shift values.[1,11] The absence of a solvent effect on changing from the very polar CD$_3$-NO$_2$ to CDBr$_3$ is also consistent with a single-step intramolecular process with no charge separation in the transition state. The small stabilising effect observed with CD$_3$CN is unexpected, but might arise from a charge-transfer interaction between the nitrile lone-pair, and the pyrylium ring in the intermediate (9).

The observation that $\Delta G^{\ddagger}$ is constant within experimental error, even when δT_c is as large as 24 K [as for the salt (4a) in CDBr$_3$; Table 3], seems to justify putting

† A pathway analogous to E, in which the N-methyl group is attacked reversibly by a nucleophilic anion, can be excluded on similar grounds.
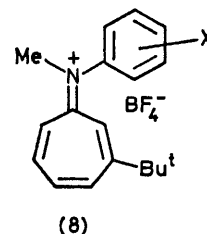
$\Delta S^{\ddagger} = 0$ for the purposes of the Hammett correlation. The correlation with σ^- constants proves to be good (r 0.99, ρ 1.7—1.9; Table 4), indicating that the transition state is stabilised by through-conjugation to electron-withdrawing substituents on the benzene ring. This implies an interaction between the nitrogen lone pair and the aryl ring in intermediate (9), further supportive evidence coming from the high energy barrier to rotation

(9a)   (9b)   (10)
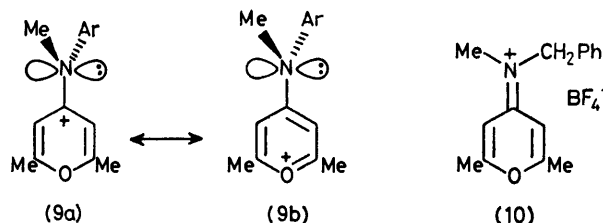
[94.1 kJ mol⁻¹ in (MeO)₃PO] in the N-benzyl derivative (10),[19a] in which such an interaction is impossible. Both u.v. spectra,[11] and ^{13}C chemical shifts,[1] contra-indicate through-conjugation in the salt (4a) at room temperature, and X-ray diffraction data [11] show the aryl ring to be rotated by nearly 70° from the most favourable conformation, due to steric effects. However, in the intermediate (9), the aryl ring could become coplanar with the N—Me bond, thus permitting an interaction with the nitrogen lone pair. Krebs found linear correlations with data for the salts (7) and (8) using Hammett σ^+ constants, though for the p-NO₂ compounds he found it necessary to use the σ^- value,[17] or to ignore the result.[18] It is hard to see how the rotational transition state could be stabilised by through-conjugation with electron-releasing substituents. Using the published rate constants,[17] or values calculated from data [18] for $\Delta G^{\ddagger}$ as above, however, I find good correlations with combined σ and σ^- constants as in this work [r 0.984, ρ 1.31 for salts (7); and r 0.990, ρ 2.62 for salts (8)],* suggesting an analogous stabilisation of the transition state by electron-withdrawing substituents. The relative magnitudes of the ρ values, (6) < (7) < (5) < (8), might reflect more or less steric inhibition to conjugation between the aryl ring and the nitrogen lone pair in the transition states.

The observation that the inclusion of *meta*-substituted compounds has no significant effect on the Hammett correlations for the salts (5) [or for the salts (3)], contrasts directly with results from ^{13}C chemical shift correlations.[1]

The Imines (1).—It had earlier been concluded [11] that the imine (1a) was isomerising by a mechanism different from that for the methobromide (4a), since the $\Delta G^{\ddagger}$ value for the former was the smaller of the two in two different solvents.† The rotational intermediate (11) for the imines should be of higher energy than that (9) for the metho-salts for any given group X, as a result

* Compare r 0.98, ρ 1.09 for the guanidinium salts (6).[8]
† A direct comparison is permissible, since $\Delta G^{\ddagger}$ for both compounds is shown to be independent of temperature within experimental error.

of the required charge separation in the former. The intermediate for inversion (12), however, might be of higher or lower energy than the corresponding (9), for, since both the mechanism and the effect of X will be different, no meaningful predictions can be made. A

(11a)   (11b)

(12a)   (12b)   (12c)
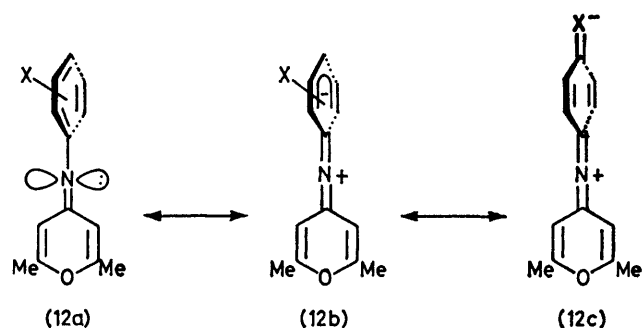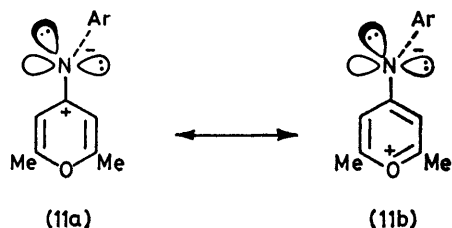
comparison between the data in Tables 1 and 3 shows that in all solvents studied, $\Delta G^{\ddagger}$ for the imines (1) has a lower value than that for the corresponding metho-salts (4) or (5) only when X is a $-M$ substituent in the p-position. In all other cases, $\Delta G^{\ddagger}$ for the imines is larger. Therefore for imines (1a, c, and d), the rotational pathway A can be excluded, and the mechanism taken to be inversion (path B) (or inversion with some rotational character). For the remaining imines, rotation is not excluded, but nor either are the alternative mechanisms. The temperature independence of $\Delta G^{\ddagger}$, over a range of up to 15 K in compounds (1a—g) suggests that $\Delta S^{\ddagger}$ is small. Belsky and his co-workers [20] found a large negative value for $\Delta S^{\ddagger}$ (-110 J mol⁻¹ K⁻¹) for the rotational barrier in the related heterofulvene (13) in CD₃CN. A


(13)
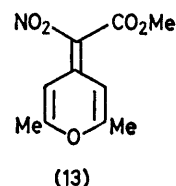
similar value for the pure rotational pathway A in the imines (1) would show up in Table 1 as $\delta\Delta G^{\ddagger} > 0.5$ kJ mol⁻¹. This is not apparent.

In contrast to Kessler's results for tetramethyl-(phenyl)guanidine,[10] $\Delta G^{\ddagger}$ for the imines (1) is solvent dependent, being 2—5 kJ mol⁻¹ smaller in CD₃NO₂ and CD₃CN than in the less polar CDBr₃, and indicating that the transition state has some polar character. Since the pure rotational intermediate (11) has to be excluded for

compounds (1a, c, and d), the solvent effect must be accounted for by charge separated forms such as (12b), or a structure intermediate between (12b) and (14a) [the latter derived from (11)]. This could apply equally to the remaining imines, though the pure rotational intermediate (11) cannot be excluded with certainty.

For effective stabilisation of the inversion intermediate (12) by interaction of the nitrogen lone pair with the aryl ring, it is necessary for the two rings to be

(14a)   (14b)
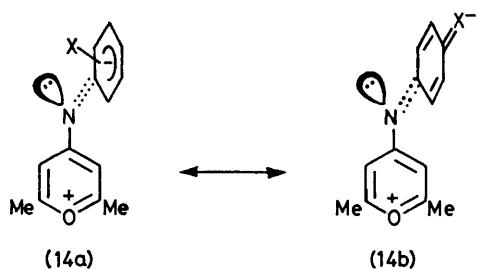
orthogonal. X-Ray diffraction measurements [11] show the torsion angle in the ground state of the imine (1a) to 60°, so little extra rotation is required. U.v. data, in fact, show a significant interaction between the nitrogen lone-pair and the nitroaryl ring at room temperature, λ_{max} shifting from 344 to 287 nm on conversion of the imine into the methobromide (4a).[11] Loss of this interaction on salt-formation is also apparent from ^{13}C chemical shift changes for C-1, -2, -4, and -6 of the aryl ring.[1] However, if δ ^{13}C values reflect charge densities, the magnitude of the lone-pair interaction in the ground state (though not necessarily in the inversion transition state) is independent of the nature of X when measured from substituent chemical shifts.[1]

Although evidence so far presented is consistent with an inversion mechanism for imines (1a, c, and d), additional data give strong support for an intermediate pathway with some rotational character. Thus, the C=N bond in the imine (1a) is very long (1.300 Å compared with 1.269 Å in benzylidene-p-nitroaniline),[11] this being consistent with the low i.r. stretching frequency (1 567 cm^{-1}).[21] The effect of changing the solvent from CDCl$_3$ to the more polar CD$_3$CN, which results in a lowering of $\Delta G^{\ddagger}$, is seen in the [13]C n.m.r. spectra of all of the imines (1) as an increase in pyrylium character in the oxygen ring, and a build up of negative charge at nitrogen.[1] Finally, correlations between ^{13}C chemical shifts and Taft dual substituent parameters, for C-2 and -6 of the pyran ring, show the best correlation with σ_R^- constants,[1] giving evidence for a conjugative interaction between the para-substituent X and the pyran ring. Though these [13]C n.m.r. data relate to the ground state, and not to the transition state for the isomerisation process, they are nevertheless supportive of a rotational contribution to the mechanism.

Finally, the Hammett correlations in Table 4 give important additional information. Good straight lines are obtained from the plots if data for the meta-substituted compounds and the imines (1h and i) are

excluded. The ρ value (2.83 in CD$_3$CN) is a good measure of the slope, and is larger than values reported earlier (1.30—2.21) [19a] for other imines, indicating a greater effect due to the substituent X in the transition state. As stated earlier, $\Delta G^{\ddagger}$ values for imines (1e—i) in CD$_3$-NO$_2$ are the same within experimental error, a similar trend being apparent in CDBr$_3$ if the value for the 4-F compound (88.3 kJ mol^{-1}; unreliable on account of partial decomposition) is neglected. For the data in CD$_3$NO$_2$, this discontinuity in the plot results in a poorer correlation, and gives an artificially low ρ value. The implication is that when substituent X has a $-M$ effect in the para-position, the transition state can achieve stabilisation via structure (12c), or one intermediate between (12c) and (14b), giving a good correlation with σ^-. For all other imines, with the exception of (1b), the nature of the substituent X has little influence on $\Delta G^{\ddagger}$, and the line has a much smaller slope, suggesting that a different mechanism is operating. Herkstroeter [7] observed a discontinuity in similar Hammett plots for a series of aryl imines bearing a $-M$ substituent at the imine carbon atom, and interpreted it in terms of a change in mechanism from inversion (or intermediate) to rotation. It is possible that a similar explanation applies here, but no analogous discontinuities have been observed with other series of aryl imines having, as in compounds (1), $+M$ substituents at the imine carbon atom. Clearly, data for imines (1) having Me, MeO, and Me$_2$N groups at the aryl para-position are needed, but these compounds are thermally unstable below the coalescence temperature. Complete line shape analysis of VTNMR spectra are planned in an attempt to obtain values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The Iminium Salts (2) *and* (3).—The sensitivity of $\Delta G^{\ddagger}$ to the solvent, to the nature of the counter ion, and to the temperature, shows that the isomerisation mechanism in the hydro-salts (2) and (3) is different from that in the metho-salts (4) and (5), and rules out the rotational pathway C for these salts. Path D can also be eliminated for the perchlorate salts (3), due to the low nucleophilicity of the anion, and while it remains a possibility for the bromide (2a), there is no obvious reason why this salt should behave differently in this respect from the methobromide (4a). The differences between $\Delta G^{\ddagger}$ values for the salts (2a) and (3a) are more likely to arise from the strong N–H . . . Br hydrogen bond, present in the former,[1,11,21] but not in the latter, and revealed in solution from its large anisotropic effect on the chemical shift of H-3 [compare $\Delta \nu$ for salts (2a) and (3a); Table 2]. It is therefore necessary to consider the data in terms of the deprotonation–isomerisation–reprotonation pathway E, a route which has not previously been demonstrated.

Path E has several possible variants. Thus, any one of the three steps, deprotonation, imine isomerisation, or reprotonation might be rate limiting (though the last is unlikely to be); and the second step could proceed by inversion, rotation, or an intermediate mechanism. With so many alternatives, there is the further possibility

that a change in substituent X or of solvent may lead to a change in mechanism among the variants. Data can therefore only be interpreted as consistent or inconsistent with path E in a general sense. The decrease in $\Delta G^{\ddagger}$ with increasing solvent polarity, for example, can be rationalised in terms of the stabilisation of a polar transition state in the second step, or in terms of the ability of the solvent to deprotonate the cation.*

The most notable feature in the data for these salts is the temperature dependence of $\Delta G^{\ddagger}$. Although δT_c for the two sets of coalescing signals is generally larger in this series than for the imines or metho-salts, making any temperature effect more noticeable, the difference in $\Delta G^{\ddagger}$ values is greater than experimental error even when δT_c is as small as 5 K [see salt (3f)]. With the exclusion of data for salts (3a, c, and d) (see below) a crude estimate of $\Delta S^{\ddagger}$ from substitution of values of ΔG_{T_c} and T_c in the equation $\Delta G_{T_c}{}^{\ddagger} = \Delta H^{\ddagger} - T_c \Delta S^{\ddagger}$ gives a figure of -100 ± 60 J mol^{-1} K^{-1}. Large negative values of $\Delta S^{\ddagger}$ have been explained in terms of charge separated intermediates in rotational processes,[20,22] and are thus consistent with path E. More significantly, Berg and Sjöstrand [22] have observed $\Delta S^{\ddagger}$ -107 J mol^{-1} K^{-1} for the acid-catalysed rotation of a keten dithioacetal, and indicate that this result is consistent with proton exchange in the rate determining step.

For salts (3a, c, and d), $\Delta G^{\ddagger}$ calculated from coalescence of H-3 and -5 is anomalously low. The anomaly lies not in $\Delta S^{\ddagger}$, but in the value of the rate constant, which is calculated as being larger at the lower value for T_c than at the higher in these three compounds (all of which have a $-M$ substituent X in the *para*-position). Kost and his co-workers [23] have shown that the approximate equation for determining k_c, and hence $\Delta G^{\ddagger}$, from coalescing AB quartets gives acceptable agreement with values from complete line shape analysis as long as $\Delta \nu > J$. Also, it is necessary that $b_E / \Delta \nu \leqslant 0.4$, where b_E is the line width at zero exchange.[24] These requirements are met for all data in Table 2, and while the ratio $\Delta \nu / J$ is smallest in salts (3a, c, and d), its value is little different from that of the 4-Br compound (3f) which behaves 'normally'. There is no obvious explanation for these anomalous $\Delta G^{\ddagger}$ values (which are quite reproduceable), and since few reports have appeared in which $\Delta G^{\ddagger}$ has been calculated from two or more coalescence temperatures in the same compound,[24] there seems to be no precedent. Complete line shape analysis of signals, both in the ^{1}H and ^{13}C n.m.r. spectra are planned.

* This would be more difficult in (2a) due to the N–H $\cdots$ Br hydrogen bond, though a comparison with (3a) can only be made if the same step is rate-limiting in both compounds.

In view of the above, Hammett correlations (Table 4) were determining using only log k_c calculated from methyl coalescences. The similarity between ρ values for salts (3) and (5) must be coincidental, since the isomerisation mechanisms are different. A positive value for the former, however, is supportive of a charge-separated intermediate in which an interaction involving the substituent X is important.

REFERENCES

[1] Part 3, M. P. Sammes, *J. Chem. Res.*, 1981, (S) 200, (M) 2455.

[2] M. P. Sammes and K. L. Yip, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1373.

[3] (a) H. Kessler, *Tetrahedron*, 1974, **30**, 1861; (b) J. M. Lehn, *Fortschr. Chem. Forsch.*, 1970, **15**, 311; (c) E. Carlson, F. B. Jones, and M. Raban, *Chem. Commun.*, 1969, 1235; (d) R. Mérenyi, in ' Iminium Salts in Organic Chemistry,' eds. H. Böhme and H. G. Viehe, Wiley–Interscience, New York, 1976, part 1, p. 78.

[4] See *e.g.* G. E. Hall, W. J. Middleton, and J. D. Roberts, *J. Am. Chem. Soc.*, 1971, **93**, 4778.

[5] See *e.g.* (a) G. Binsch, E. L. Eliel, and H. Kessler, *Angew. Chem. Int. Ed. Engl.*, 1971, **10**, 570; (b) C. Brown, B. T. Grayson, and R. F. Hudson, *J. Chem. Soc., Perkin Trans. 2*, 1979, 427.

[6] M. Raban and E. Carlson, *J. Am. Chem. Soc.*, 1971, **93**, 685.

[7] W. G. Herkstroeter, *J. Am. Chem. Soc.*, 1973, **95**, 8686.

[8] H. Kessler and D. Leibfritz, *Chem. Ber.*, 1971, **104**, 2158.

[9] See *e.g.* (a) G. J. Martin and S. Poignant, *J. Chem. Soc., Perkin Trans. 2*, 1974, 642; (b) W. B. Jennings, S. Al-Showiman, M. S. Tolley, and D. R. Boyd, *ibid.*, 1975, 1535.

[10] H. Kessler and D. Leibfritz, *Tetrahedron*, 1969, **25**, 5127.

[11] M. P. Sammes, R. L. Harlow, and S. H. Simonsen, *J. Chem. Soc., Perkin Trans. 2*, 1981, 303.

[12] (a) D. Y. Curtin, E. J. Grubbs, and G. C. McCarty, *J. Am. Chem. Soc.*, 1966, **88**, 2775; (b) J. D. Andose, J. M. Lehn, K. Mislow, and J. Wagner, *ibid.*, 1970, **92**, 4050.

[13] J. A. Pople, W. G. Schneider, and H. J. Bernstein, ' High-resolution Nuclear Magnetic Resonance,' McGraw–Hill, New York, 1959, p. 223.

[14] R. J. Kurland, M. B. Rubin, and M. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

[15] (a) J. Riand, M. Th. Chenon, and N. Lumbroso-Bader, *Can. J. Chem.*, 1980, **58**, 466; (b) M. Th. Chenon, S. Sib, and M. Simalty, *Org. Magn. Reson.*, 1979, **12**, 71.

[16] Values taken from C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, 1964, **2**, 323.

[17] A. Krebs and J. Breckwoldt, *Tetrahedron Lett.*, 1969, 3797.

[18] A. Krebs, *Tetrahedron Lett.*, 1971, 1901.

[19] ' Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, London, 1975; (a) quoted as 'Unpublished results, 1973,' by J. P. Brown and L. M. Jackman, Table XII, p. 232; (b) Table XXIII, p. 247.

[20] I. Belsky, H. Doduik, and Y. Shvo, *J. Org. Chem.*, 1977, **42**, 2734.

[21] M. P. Sammes, *J. Chem. Res.*, 1981, (S) 122; (M) 1648.

[22] U. Berg and U. Sjöstrand, *Org. Magn. Reson.*, 1978, **11**, 555.

[23] D. Kost, E. H. Carlson, and M. Raban, *J. Chem. Soc., Chem. Commun.*, 1971, 656.

[24] F.-H. Marquardt, *J. Chem. Soc. (B)*, 1971, 366.