The Effect of Salt Formation on the Molecular Structure and Charge Distribution in Imines: The Crystal and Molecular Structures and the Ultraviolet, Infrared, and the ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectra of 2,6-Dimethyl-4-(*p*-nitrophenylimino)pyran and its Hydrobromide and Methobromide Salts

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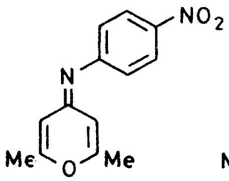
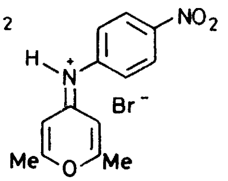
The crystal structures of the title compound (1) and its hydrobromide (2) and methobromide (3) salts have been determined by *X*-ray crystallography in order to investigate the changes which take place in structure (1) on salt formation. Crystals of both (1) and (2) are monoclinic, with space group $P2_1/c$ and $Z = 4$, and having unit cell dimensions respectively $a = 12.021(1)$, $b = 8.117(1)$, $c = 13.562(2)$ Å, $\beta = 115.72(1)°$, and $a = 10.133(2)$, $b = 16.965(4)$, $c = 8.277(2)$ Å, $\beta = 102.55(2)°$. Crystals of (3) are triclinic, space group $P\bar{1}$, and with $Z = 2$ in a unit cell of dimensions $a = 7.929(2)$, $b = 14.480(2)$, $c = 6.549(1)$ Å, $\alpha = 90.12(1)$, $\beta = 98.56(2)$, $\gamma = 95.37(2)°$. Structure (1) was solved by direct methods, and (2) and (3) by the heavy-atom Patterson method; refinements were to *R* 0.041 for 2 165 independent reflections in (1), to *R* 0.047 for 1 855 in (2), and to *R* 0.032 for 2 754 in (3). There is a systematic increase in C=N bond length along the series; all such distances are longer, however, than normal values, as substantiated by $\nu_{C=N}$ frequencies below 1 600 cm^{-1} in the i.r. spectra. Bond parameters for the pyran ring show an increase in pyrylium character on salt formation, the effect being largest in (3). Increased positive charge on the pyran rings in (2) and (3) is confirmed by shifts in their ^{1}H and ^{13}C n.m.r. signals relative to (1), though these reveal no obvious distinction between the two salts. There is a relatively short [2.34(4) Å] linear N–H · · · Br hydrogen bond in the hydrobromide. Structural and spectroscopic data support an inversion mechanism for isomerisation about the C=N bond in the imine (1), consistent with the observed low $\Delta G^‡$ value, while isomerisation in the two salts (with higher $\Delta G^‡$ values) is probably by a different mechanism.

VARIABLE temperature ^{1}H n.m.r. studies by one of us have revealed[1] that for isomerisation about the C=N bond in the imine (1), and its hydrobromide (2) and methobromide (3) salts, $\Delta G^‡$ at the coalescence temperature of the methyl signals is in the order (1) < (3) < (2).† A mechanism involving C=N bond rotation would require the imine (1) to have the *highest* $\Delta G^‡$ value, since the likely intermediate (4) should be of higher energy than that [structure (5)] for the salts (2) and (3).[2] Thus it was proposed that isomerisation in (1) was proceeding by the inversion mechanism *via* intermediate (6) in which the imine nitrogen lone pair interacts with the nitrophenyl ring in the transition state. Such a pathway would be unavailable to structures (2) and (3), though one involving deprotonation–inversion–reprotonation is a possibility for the former. Ease of C=N bond rotation is expected to correlate with bond order, which in turn should be influenced by contributions due to structures such as (4) and (5). In view of the current interest in iminium salt chemistry,[3] the lack of data on the effect of quaternisation on bond lengths and angles in imines, and the continuing interest in establishing mechanisms for C=N bond isomerisation,[4] it seemed desirable to measure the relevant bond lengths and angles in the three compounds, and to obtain additional structural information by spectroscopic methods. We thus report a comparison of the crystal and molecular structures of the imine (1), with its hydrobromide (2) and methobromide (3) salts, together with u.v., i.r., and ^{1}H and ^{13}C n.m.r. data for the three compounds.



(1)



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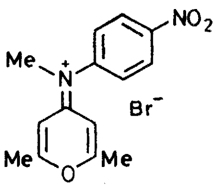

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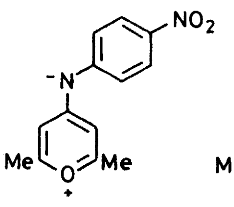

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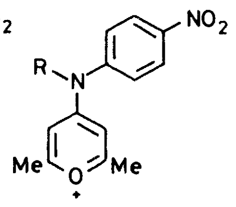

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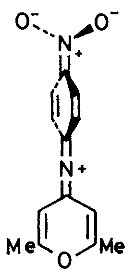

(6)

EXPERIMENTAL

The imine (1) and the hydrobromide (2) were prepared as described previously.[5] The methobromide (3) was prepared from the methiodide[5] by ion-exchange *via* a column of Amberlite IRA-401 resin, treated previously with sodium bromide solution. Recrystallisation (absolute EtOH) gave 2,6-*dimethyl*-4-(p-*nitrophenyliminio*)*pyran methobromide* (3), pale yellow prisms, m.p. 232—239 °C (decomp.) (Found:

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† Values (±0.5 kJ mol^{-1}) for compounds (1), (3), and (2) were respectively 66.3, 67.9, and 73.9 kJ mol^{-1} in CDBr$_3$, and 60.9, 67.6, and 69.8 kJ mol^{-1} in CD$_3$NO$_2$. A detailed study of the effect of solvent and of the benzene substituent on $\Delta G^‡$ for isomerisation in imines of types (1)—(3) will be reported elsewhere.[1]

C, 49.5; H, 4.5; N, 8.6. $C_{14}H_{15}BrN_2O_3$ requires C, 49.6; H, 4.5; N, 8.3%). Crystals of the imine (1) were grown by sublimation; those of the salts (2) and (3) by slow evaporation of solutions in a mixture of $CHCl_3$ and CCl_4.

U.v. spectra were recorded on a Beckman Acta CIII instrument, and i.r. spectra on a Perkin-Elmer model 577 spectrophotometer for Nujol mulls, polystyrene being used in calibration. ^{1}H N.m.r. (89.60 MHz) and ^{13}C n.m.r. (22.53 MHz) spectra were run on a JEOL model FX 90Q spectrometer for solutions in $CDCl_3$ with Me_4Si as internal reference.

TABLE 1

Crystal data and details of the structure analysis

	Imine (1)	Hydrobromide (2)	Methobromide (3)
(*a*) Crystal data			
Formula	$C_{13}H_{12}N_2O_3$	$C_{13}H_{13}BrN_2O_3$	$C_{14}H_{15}BrN_2O_3$
M	244.25	325.17	339.20
Crystal system	Monoclinic	Monoclinic	Triclinic
T/K	238	238	233
a/Å	12.021(1) [a]	10.133(2)	7.929(2)
b/Å	8.117(1)	16.965(4)	14.480(2)
c/Å	13.562(2)	8.227(2)	6.549(1)
α/°			90.12(1)
β/°	115.72(1)	102.55(2)	98.56(2)
γ/°			95.37(2)
U/Å^3	1 192.1	1 380.4	740.2
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	4	2
D_c/g cm^{-3}	1.361	1.564	1.522
D_m/g cm^{-3} [b]	1.343	1.538	
μ(Mo-K_α)/cm^{-1}	1.04	31.6	29.3
(*b*) Data collection			
Diffractometer	Syntex P2	Syntex P2	Syntex P3
Radiation [c]	Mo-K_α	Mo-K_α	Mo-K_α
Crystal size/mm	0.24 × 0.38 × 0.47	0.20 × 0.16 × 0.37	0.25 × 0.07 × 0.45
T/K	238	238	233
ω Scan range/°	1.0	1.0	1.0
ω Scan rate/° min^{-1}	1—5	1—5	2—5
2θ Limit/°	55	55	55
Total unique reflections	2 744	3 181	3 434
Absorption correction	No	No	Yes
Transmission coefficients			0.71—1.00
(*c*) Full-matrix refinement			
No. reflections refined $[I > 2\sigma(I)]$	2 165	1 855	2 754
No. variables refined	211	224	241
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.041	0.047	0.032
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.048	0.039	0.030
Peaks in final difference-Fourier/e Å^{-3}	<0.15	0.61 near Br <0.20 elsewhere	<0.17

[a] In this, and all other Tables, estimated standard deviations are given in parentheses. [b] At 298 K. [c] Graphite monochromatised.

Crystal Data, Solution, and Refinement.—Unit cell parameters were refined from at least 45 computer-centred reflections (Mo-K_α radiation, $\lambda = 0.710\,69$ Å). Pertinent crystallographic data and details of the structure refinements are given in Table 1. The structures of the imine (1) and the hydrobromide (2) were completed at the University of Texas at Austin; the mathematical details, and a list of computer programs used can be found elsewhere.[6] The solution and refinement of the methobromide (3) was carried out at the duPont Company with local modifications of the programs supplied by the Enraf–Nonius Corp.;[7] further details may be found in ref. 8.

The structure of the imine (1) was solved by direct methods, the heavy-atom Patterson method being used for the salts (2) and (3). Hydrogen atoms were located by Fourier-difference techniques, except for the methobromide (3) in which their positions were calculated.

The final positional parameters for the three compounds are given in Table 2, and bond distances and angles in Table 3. Thermal parameters (isotropic for H, and anisotropic for other atoms), and final observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22948 (55 pp.).*

RESULTS AND DISCUSSION

Description of the Structures.—Stereodrawings for the three molecules are presented in Figures 1—3. Apart from first-order changes arising from substitution at the nitrogen atom, the three structures are quite similar, with the phenyl ring of each molecule rotated well out of the plane of the pyran ring in order to avoid an interaction between H(5) and the phenyl *ortho*-hydrogen atoms. The dihedral angles between the planes of the two rings for structures (1)—(3) are 60.1, −56.9, and 69.7°, respectively. The rotation is achieved primarily by a twist about the N(9)–C(10) bond, as evidenced by

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* For details see Notices to Authors No. 7 in *J.C.S. Perkin II*, 1980, Index Issue.

TABLE 2

Positional parameters [a]

Atom	Imine (1)			Hydrobromide (2)			Methobromide (3)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Br				0.277 15(5)	0.575 83(3)	0.053 69(5)	−0.131 92(3)	0.199 62(2)	0.034 98(4)
O(1)	0.414 4(1)	0.620 5(1)	0.576 5(1)	0.042 7(3)	0.370 5(2)	0.548 2(3)	0.524 9(2)	0.079 5(1)	0.271 0(2)
O(17)	−0.138 4(1)	0.222 7(2)	−0.141 5(1)	0.725 5(4)	0.731 7(3)	0.960 1(5)	−0.372 0(2)	0.413 3(2)	0.347 6(4)
O(18)	−0.217 7(1)	0.434 9(2)	−0.100 5(1)	0.622 1(4)	0.827 4(3)	0.818 3(5)	−0.248 4(2)	0.477 2(1)	0.106 4(3)
N(9)	0.207 0(1)	0.259 5(2)	0.362 6(1)	0.289 2(4)	0.545 1(2)	0.443 0(4)	0.366 9(2)	0.287 8(1)	0.602 3(3)
N(16)	−0.140 4(1)	0.324 3(2)	−0.075 3(1)	0.635 8(4)	0.758 3(3)	0.849 5(5)	−0.246 0(2)	0.432 8(1)	0.264 8(4)
C(2)	0.404 7(1)	0.464 6(2)	0.611 4(1)	0.065 6(5)	0.379 1(3)	0.391 2(5)	0.621 5(3)	0.111 9(2)	0.449 8(3)
C(3)	0.337 4(2)	0.348 5(2)	0.541 8(1)	0.145 1(5)	0.435 6(3)	0.355 4(5)	0.570 9(3)	0.178 4(2)	0.564 3(3)
C(4)	0.269 5(1)	0.379 0(2)	0.426 2(1)	0.211 5(4)	0.488 4(3)	0.480 6(5)	0.418 4(3)	0.219 7(1)	0.495 9(3)
C(5)	0.282 2(1)	0.545 6(2)	0.394 2(1)	0.187 2(4)	0.478 0(3)	0.642 3(5)	0.319 9(3)	0.183 9(2)	0.307 9(3)
C(6)	0.352 5(1)	0.656 1(2)	0.467 3(1)	0.104 6(5)	0.420 7(3)	0.670 7(5)	0.375 7(3)	0.116 1(2)	0.203 0(3)
C(7)	0.476 5(2)	0.449 2(3)	0.732 1(2)	−0.011 9(8)	0.319 9(4)	0.276 5(8)	0.782 9(3)	0.066 9(2)	0.495 7(4)
C(8)	0.375 1(2)	0.829 1(2)	0.444 9(2)	0.068 7(7)	0.403 7(4)	0.833 3(6)	0.287 2(3)	0.071 9(2)	0.004 9(4)
C(10)	0.125 6(1)	0.287 6(2)	0.252 8(1)	0.371 4(4)	0.598 6(3)	0.554 6(4)	0.213 3(3)	0.330 4(1)	0.523 3(3)
C(11)	0.133 1(2)	0.197 7(2)	0.172 1(1)	0.464 4(4)	0.571 3(4)	0.692 2(5)	0.071 4(3)	0.315 1(2)	0.620 8(4)
C(12)	0.047 7(2)	0.201 3(2)	0.064 3(1)	0.550 0(4)	0.624 3(4)	0.790 0(6)	−0.078 5(3)	0.351 0(2)	0.538 9(4)
C(13)	−0.046 5(1)	0.314 2(2)	0.037 8(1)	0.539 9(4)	0.702 5(3)	0.749 7(5)	−0.082 6(3)	0.400 6(2)	0.360 6(4)
C(14)	−0.056 5(1)	0.416 0(1)	0.115 3(1)	0.446 2(4)	0.730 7(4)	0.616 8(5)	0.059 4(3)	0.419 7(2)	0.266 1(4)
C(15)	0.029 6(1)	0.401 6(2)	0.222 4(1)	0.361 4(4)	0.677 8(3)	0.519 4(5)	0.210 5(3)	0.384 7(2)	0.349 9(3)
C(19)							0.462 8(3)	0.326 4(2)	0.799 0(4)
H(3)	0.327(2)	0.245(2)	0.567(1)	0.162(4)	0.445(2)	0.240(5)	0.643(2)	0.196(1)	0.679(3)
H(5)	0.242(1)	0.575(2)	0.319(1)	0.227(3)	0.509(2)	0.728(4)	0.219(2)	0.204(1)	0.260(3)
H(7A)	0.467(2)	0.347(3)	0.762(2)	0.969(7)	0.272(4)	0.337(8)	0.836(3)	0.084(2)	0.624(4)
H(7B)	0.447(2)	0.536(3)	0.766(2)	0.047(6)	0.297(4)	0.214(8)	0.757(3)	0.000(2)	0.488(4)
H(7C)	0.565(3)	0.472(3)	0.755(2)	−0.065(6)	0.341(4)	0.194(8)	0.860(3)	0.088(2)	0.397(4)
H(8A)	0.461(2)	0.842(3)	0.468(2)	0.122(5)	0.349(3)	0.878(6)	0.183(3)	0.095(2)	−0.034(4)
H(8B)	0.331(2)	0.849(3)	0.367(2)	−0.017(6)	0.393(3)	0.825(7)	0.357(3)	0.084(2)	−0.094(4)
H(8C)	0.355(2)	0.907(2)	0.490(2)	0.103(6)	0.443(3)	0.911(7)	0.262(3)	0.002(2)	0.025(4)
H(9)				0.290(4)	0.552(2)	0.342(5)			
H(11)	0.195(2)	0.110(2)	0.192(1)	0.468(4)	0.519(2)	0.714(4)	0.077(3)	0.285(2)	0.739(3)
H(12)	0.053(2)	0.133(2)	0.007(1)	0.609(5)	0.609(3)	0.889(6)	−0.171(3)	0.342(1)	0.606(3)
H(14)	−0.121(2)	0.493(2)	0.096(1)	0.438(3)	0.785(2)	0.596(4)	0.053(3)	0.454(2)	0.149(3)
H(15)	0.025(1)	0.468(2)	0.279(1)	0.300(4)	0.698(2)	0.423(5)	0.302(3)	0.397(1)	0.292(3)
H(19A)							0.394(4)	0.351(2)	0.876(5)
H(19B)							0.520(4)	0.289(2)	0.874(4)
H(19C)							0.554(5)	0.380(3)	0.780(6)

[a] Hydrogen atoms are numbered in accord with the carbon or nitrogen atom to which they are attached.

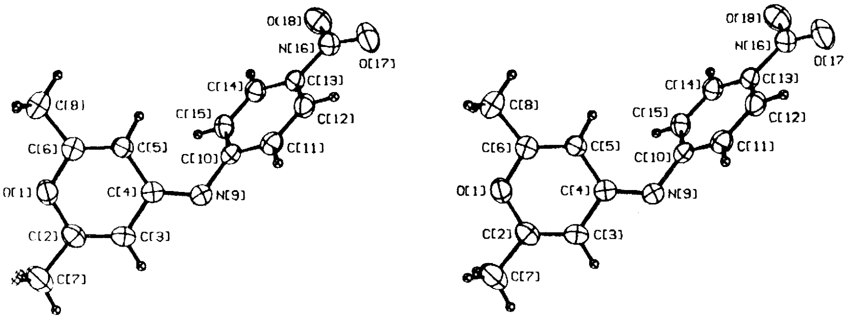


FIGURE 1 ORTEP stereo-drawing of the amine (1), showing the atom numbering scheme used

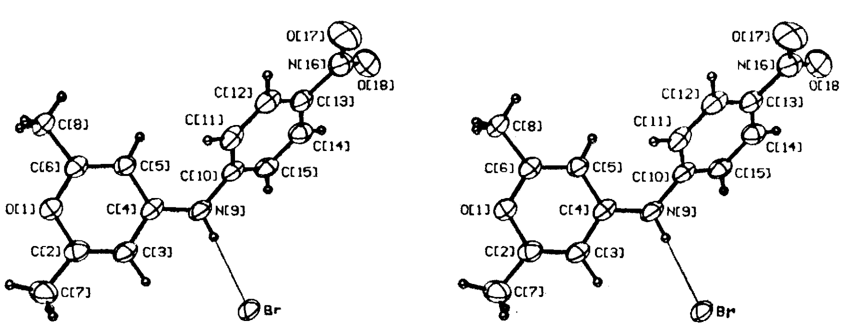


FIGURE 2 ORTEP stereo-drawing of the hydrobromide salt (2)

TABLE 3

Interatomic distances (Å) and bond angles (°). Chemically equivalent values for the three structures have been paired

	Imine (1)	Hydrobromide (2)	Methobromide (3)
(*a*) Distances			
O(1)–C(2)	1.375(2)	1.369(5)	1.356(2)
O(1)–C(6)	1.369(2)	1.364(5)	1.357(2)
C(2)–C(3)	1 331(2)	1 327(7)	1 345(3)
C(5)–C(6)	1 332(2)	1 337(7)	1 341(3)
C(2)–C(7)	1.488(3)	1.481(8)	1.482(3)
C(6)–C(8)	1.488(3)	1.489(7)	1.492(3)
C(3)–C(4)	1.441(2)	1.420(6)	1.413(3)
C(4)–C(5)	1.449(2)	1.416(6)	1.425(2)
C(4)–N(9)	1.300(2)	1.322(6)	1.334(2)
N(9)–C(10)	1.401(2)	1.424(6)	1.444(2)
N(9)–C(19)			1.475(3)
C(10)–C(11)	1.396(2)	1.386(6)	1.375(3)
C(10)–C(15)	1.395(2)	1.375(7)	1.381(3)
C(11)–C(12)	1.380(3)	1.381(7)	1.377(3)
C(14)–C(15)	1.375(3)	1 373(7)	1 383(3)
C(12)–C(13)	1.378(2)	1.367(9)	1.370(3)
C(13)–C(14)	1.384(2)	1.369(6)	1.370(3)
C(13)–N(16)	1.461(2)	1.473(7)	1.470(3)
N(16)–O(17)	1.228(2)	1.224(6)	1.217(2)
N(16)–O(18)	1.229(2)	1.220(8)	1.220(2)
(*b*) Angles *			
C(2)–O(1)–C(6)	118.7(1)	119.1(3)	119.6(1)
O(1)–C(2)–C(3)	121.6(2)	121.4(4)	121.5(2)
O(1)–C(6)–C(5)	122.3(1)	122.0(4)	121.8(2)
O(1)–C(2)–C(7)	111.2(2)	110.8(4)	112.3(2)
O(1)–C(6)–C(8)	111.0(2)	112.3(4)	112.0(2)
C(3)–C(2)–C(7)	127.2(2)	127.8(4)	126.3(2)
C(5)–C(6)–C(8)	126.7(2)	125.6(4)	126.2(2)
C(2)–C(3)–C(4)	122.2(1)	120.7(4)	120.5(2)
C(4)–C(5)–C(6)	121.4(2)	119.9(4)	120.1(2)
C(3)–C(4)–C(5)	113.8(1)	116.8(4)	116.5(2)
C(3)–C(4)–N(9)	119.1(1)	120.2(4)	122.2(2)
C(5)–C(4)–N(9)	127.1(2)	123.0(4)	121.4(2)
C(4)–N(9)–C(10)	121.4(1)	127.4(4)	120.4(2)
N(9)–C(10)–C(11)	119.1(1)	120.9(5)	119.3(2)
N(9)–C(10)–C(15)	121.9(1)	118.8(4)	119.6(2)
C(11)–C(10)–C(15)	118.7(2)	120.3(4)	121.1(2)
C(10)–C(11)–C(12)	120.9(2)	119.3(5)	119.5(2)
C(10)–C(15)–C(14)	121.0(2)	120.5(4)	119.3(2)
C(11)–C(12)–C(13)	118.6(2)	119.1(4)	119.0(2)
C(13)–C(14)–C(15)	118.6(2)	118.5(5)	118.7(2)
C(12)–C(13)–C(14)	122.2(2)	122.3(5)	122.3(2)
C(12)–C(13)–N(16)	119.0(1)	118.9(4)	118.9(2)
C(14)–C(13)–N(16)	118.9(1)	118.8(5)	118.8(2)
C(13)–N(16)–O(17)	118.6(1)	118.2(5)	118.0(2)
C(13)–N(16)–O(18)	118.7(1)	118.4(4)	118.5(2)
O(17)–N(16)–O(18)	122.7(2)	123.5(5)	123.5(2)

* For the methobromide C(4)–N(9)–C(19) = 123.5(2)° C(10)–N(9)–C(19) = 116.1(2)°.

the fact that C(10) lies almost in the plane of the pyran ring; the C(5)–C(4)–N(9)–C(10) torsion angles being respectively −10.7, 7.2, and −3.3°.

An almost linear hydrogen bond is found between H(9) and the Br^- ion in the salt (2), relevant bond lengths and angles being given in Table 4. The average N · · · Br distance for 51 compounds having N–H · · · Br hydrogen bonds is reported [9] as being 3.37(15) Å, indicating that in the present example, the bond is relatively short.

TABLE 4

Distances and angles at the hydrogen bonding site in the hydrobromide (2)

Distances (Å)		Angles (°)	
N(9)–H(9)	0.85(4)	C(4)–N(9)–H(9)	118(3)
N(9) · · · Br	3.221(4)	C(10)–N(9)–H(9)	115(3)
H(9) · · · Br	2.38(4)	N(9)–H(9) · · · Br	177(4)

The torsion angle C(3)–C(4)–N(9)–H(9) is 7.9°.

The Br^- ion in the methobromide (3) makes a number of close approaches to the hydrogen atoms in the cation (Table 5), but none as close as that in the hydrobromide (2). The *N*-methyl group lies almost exactly in the plane of the pyran ring, the C(3)–C(4)–N(9)–C(19) torsion angle being 0.2°.

The changes of greatest interest, resulting from quaternisation at N(9), should be manifest mainly in the C(4)–N(9) bond length and in the parameters of the pyran ring, with smaller changes elsewhere. These will now be considered.

TABLE 5

Contacts between the methyliminium cation and the bromide ion in the salt (3) which are less than 3.5 Å

Br · · · H(3)	2.71(2)	Br · · · H(11)	2.93(2)
Br · · · H(7A)	3.13(2)	Br · · · H(12)	3.48(2)
Br · · · H(7C)	2.88(2)	Br · · · H(19B)	3.19(3)
Br · · · H(8C)	3.00(3)		

The C(4)–N(9) *bond length.* There is a systematic increase in the length of the C(4)–N(9) bond in going from structure (1) to (3), showing (Table 3) an apparent decrease in bond order, as anticipated. For a series of benzylideneanilines,[10] the C=N distance is 1.269(14) Å, and for three benzylidenimine sulphides [11] 1.269(4) Å. Hence, even in the case of the imine (1), the C=N bond

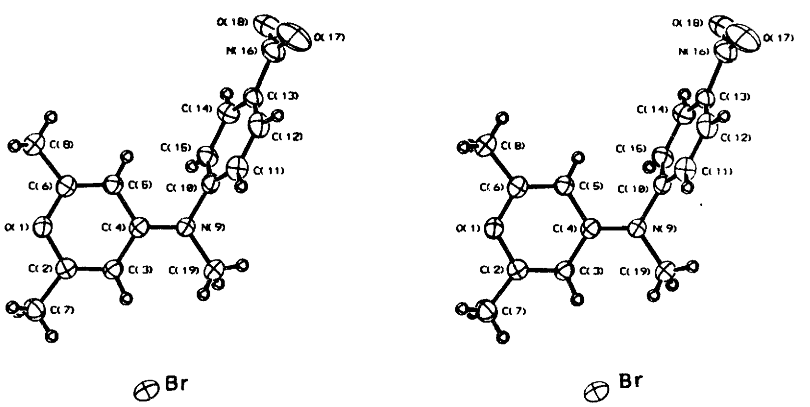


FIGURE 3 ORTEP stereo-drawing of the methobromide salt (3), showing the atom numbering scheme used

(1.300 Å) shows significant lengthening relative to a ' normal ' conjugated imine. Very few C=N distances have been reported for iminium salts, but 1.290(3) is the average for four examples,[12,13a] indicating also significant lengthening in the salts (2) and (3).

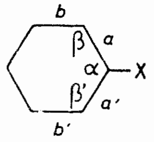
Pyran ring parameters. The methobromide (3) shows a decrease in O(1)–C(2) and C(3)–C(4), and an increase in C(2)–C(3) bond lengths * relative to the imine (1) (Table 3). Additionally, the C(3)–C(4)–C(5) angle opens by nearly 3°, and there is a smaller decrease in the angle * C(2)–C(3)–C(4). The observed differences between 4-oxopyran-type [14,15] and pyrylium salt [16] structures are rather larger, the latter having C(2)–O(1)–C(6) and C(3)–C(4)–C(5) angles greater by 4—5°, O(1)–C(2) and C(3)–C(4) bonds * shorter by respectively 0.01 and 0.04—0.05 Å, and C(2)–C(3) bonds * larger by 0.03 Å relative to 4-oxopyrans.

For the hydrobromide (2), significant differences from the imine (1) are found only in bond parameters associated with C(4), those in the lower half of the molecule being essentially the same for both structures. Thus, from the *X*-ray data, delocalisation of positive charge in the heterocyclic ring appears to be more effective in the methobromide (3) than in the hydrobromide (2), which is consistent with the difference in their C=N bond lengths.

Additional Structure Changes on Quaternisation.—Other parameters associated with N(9). Protonation at N(9) results in an increase by 6° in the C(4)–N(9)–C(10) angle, due presumably to a lessening in the interaction between the nitrogen lone-pair, and the adjacent bonding electrons. Steric repulsion between the methyl group and the two rings would account for the *decrease* in this angle in the methobromide (3).

The N(9)–C(10) distance, which in structure (1) matches closely the corresponding value (1.400 Å) in benzylidene-*p*-nitroanilines,[10,17] increases in length systematically in the three structures, in parallel with the C(4)–N(9) distance. This will be discussed later. The imine (1), having the shortest C(4)–N(9) and N(9)–C(10) bond lengths, experiences the largest steric repulsion between the two rings. This is relieved to some extent by the opening of the angle C(5)–C(4)–N(9) at the expense of C(3)–C(4)–N(9), and of N(9)–C(10)–C(15) at the expense of N(9)–C(10)–C(11).

The nitrophenyl ring. Domenicano *et al.*[18] have recently rationalised the effect of monosubstitution, and *para*-disubstitution on the bond angles, and some bond lengths, in the benzene ring in terms of small changes in hybridisation state of the ring atom bearing the substituent, and also of intramolecular non-bonded interactions. According to their treatment, an increase in electronegativity in a substituent X [structure (7)] causes a lengthening in the C–X bond, due to an increase in the bond *p* character. The concurrent reduction in *p* character in the bonds *a* and *a'* results in a decrease in their lengths, and an opening of the angle α. A decrease in the angles β and β' follows to maintain the ring geometry. For a substituent X which can conjugate with the ring, whether as a π donor or as a π acceptor, the effect is exactly the opposite, since conjugation results in a shortening of the C–X bond, which in turn reflects greater *s* character in the bond.† For structure (3), the atom N(9) is more electronegative than it is in structure (1), due to the positive charge. Additionally, conjugation between the C=N bond and the benzene ring in (3) is disfavoured on account of the large dihedral angle between the respective planes, whereas in structure (1), conjugation between the N(9) *lone pair* and the benzene ring is possible. For structure (2), the atom N(9) should be somewhat less electronegative than in (3) as a result of the electron-donating Br^- ion in the hydrogen bond. Hence the observed changes in the N(9)–C(10), C(10)–C(11), and C(10)–C(15) bond lengths, and in the C(11)–C(10)–C(15), C(10)–C(11)–C(12), and C(10)–C(15)–C(14) angles for the series (1)—(3) are fully consistent with the analysis given in ref. 18. Furthermore, and perhaps not surprisingly, the bond parameters associated with C(4) in the pyran ring follow this same pattern. It was also noted [18] that distortion of exocyclic bond angles by steric factors has little effect on the distances *a* and *a'* [structure (7)]. This too is borne out in structure (1) for both rings.



(7)

The three structures thus reflect the changes in electronegativity at N(9) on quaternisation, the greatest difference being observed between the imine (1) and the methobromide (3).

Spectroscopic Measurements.—I.r. spectra. Recently, the C=N stretching vibration in a series of iminium salts was assigned [5] to an intense band near 1 660 cm^{-1}. We now find that replacement of the NH proton in the salt (2) by deuterium causes no change in this frequency. Instead, an intense peak at 1 583 cm^{-1} showing a second-order isotopic shift to 1 545 cm^{-1} on deuteriation is assigned to $\nu_{C=N}$,‡ the 1 660 cm^{-1} bond being correlated with the pyran ring C=C vibration. By analogy, an intense, somewhat broad peak in the methobromide (3) at 1 549 cm^{-1} is also assigned to the C=N mode,§ the lower frequency relative to the hydrobromide (2) being consistent with the increased bond length found by *X*-ray crystallography. The imine (1) is more of a problem, but the peak at 1 678 cm^{-1} assigned previously [5] to $\nu_{C=N}$ is now more appropriately correlated with the pyran ring, and an intense absorption at 1 567 cm^{-1} reflects

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* Applies also to chemically equivalent bond parameters.

† The same predictions are made when the system is treated in terms of valence shell electron pair repulsions.[18]

‡ Similarly, a shift from 1 589 to 1 540 cm^{-1} is observed for the analogous perchlorate salt.

§ Found at 1 554 cm^{-1} in the perchlorate salt. The NO_2 vibrations appear at 1 518 and 1 350 cm^{-1}.

better the relatively low C=N bond order found in the structure. Synthesis of ^{15}N substituted compounds is under way to check these assignments.

The presence of the N–H · · · Br hydrogen bond is confirmed by an absorption at 2 710 cm^{-1}, showing a substantial broadening, intensification, and low frequency shift relative to free N–H vibrations found [5] in the perchlorate salt above 3 050 cm^{-1}.

U.v. spectra. The imine (1) is bright yellow both as a solid and in solution, the colour being discharged on quaternisation at N(9). The effect is shown quantitatively in the u.v. spectra (Table 6) and appears to substantiate the proposed interaction between the N(9) lone pair and the nitrophenyl ring. The bond at 344 nm in the imine, which trails into the visible region, both sharpens and undergoes a hypsochromic shift on protonation at N(9). A further small shift is found both in a more (×9) concentrated solution of the salt (2), and on the addition of excess HBr, reflecting a suppression in the degree of dissociation into the conjugate base (1). Methylation at N(9), however, results in a much larger hypsochromic shift, showing that some interaction may still be occurring in salt (2) between the N–H bonding electrons and the π electrons of the nitrophenyl ring, at least in solution.

^{1}H *N.m.r. spectra.* These were recorded below the coalescence temperature of the protons associated with the pyran ring (Table 7). The H(3) and H(5) signals were assigned on the assumption that the anisotropic effect of the nitrophenyl ring would cause a high-field shift for H(5).[19] Similar, though less certain, reasoning permits assignment of the H(7) and H(8) signals. The substantial low-field shifts for H(3), H(5), H(11), and H(15) on quaternisation, which must arise from a combination of through-bond and anisotropic effects, are consistent with increased positive charge at N(9). The low-field shifts experienced by H(7) and H(8) indicate an increase in positive charge at C(2) and C(6) also.

TABLE 6

U.v. spectral data for compounds (1)—(3)

Compound	Concentration [a] (mol dm^{-3})	$\lambda_{max.}$/nm (log ϵ)		
(1)	7.37 × 10^{-5}		242.5 (4.121)	344.0 (4.207)
(2)	7.63 × 10^{-5}	219.2 (4.046)	246.0 (4.022)	324.8 (4.199)
(2)	6.80 × 10^{-4}	218.9 (4.039)	256.0 (4.006)	318.4 (4.298)
(2) [b]	7.13 × 10^{-5}	*c*	256.2 (4.006)	318.6 (4.299)
(3)	6.84 × 10^{-5}		245.0 (4.143)	287.0 (4.294)

[a] In 95% EtOH. [b] Solution 0.1M in HBr. [c] Band masked by intense end-absorption.

^{13}C *N.m.r. spectra.* All signals, except those for C(7) and C(8) have been assigned unambiguously by a combination of off-resonance and single-frequency ^{1}H decoupling experiments (observing both first- and second-order couplings), by observing which signals coalesce at higher temperatures, and by comparison with spectra of analogous molecules containing different substituents in place of NO$_2$.

Two unexpected features are the relatively small high-field shift for the C(4) signal on quaternisation at N(9), and the large and irregular variation in δ for the C(10) signal. While protonation of imines is expected to cause a large low-field shift in the α-carbon atom, in practice the observed shift is often in the opposite direction, and may be close to zero.[13b] The explanation is that quaternisation at the nitrogen atom causes a decrease in the paramagnetic contribution to the chemical shift through loss of the low energy $n \longrightarrow \pi^*$ transition, and through a reduction in the C–N bond order.[13b] This effect compensates for the low field shift caused by charge-density changes. Hence, for the C(4) atoms in salts (2) and (3) the net effect is a small low-field shift, whereas for the C(10) atoms it appears to be a substantial shift to high field.

TABLE 7

N.m.r. spectral data (CDCl$_3$) for compounds (1)—(3). Atoms are numbered according to the scheme for molecular structures

	Compound		
	(1)	(2)	(3)
(*a*) ^{1}H Resonances (δ)			
H(3)	6.06	7.90	7.87
H(5)	5.76	6.92	6.28
H(7), H(8)	2.25, 2.15	2.60, 2.56	2.74, 2.47
H(11), H(15)	6.89	7.74	7.83
H(12), H(14)	8.17	8.32	8.45
H(19)		13.42 [a]	3.94
(*b*) ^{13}C Resonances (δ)			
C(2)	162.16	172.60	172.17
C(6)	160.55	169.84	169.94
C(3)	110.82	106.94	105.37
C(5)	102.50	102.23	104.45
C(4)	155.37	159.16	160.46
C(7), C(8)	19.58, 19.82	20.48, 21.24	20.91 [b]
C(10)	158.45	140.69	146.87
C(11), C(15)	121.65	124.87	127.96
C(12), C(14)	125.25	125.47	126.50
C(13)	143.02	146.65	148.11
C(19)			43.66

[a] Signal for H(9). [b] Signals coalesced below probe temperature (305 K).

Chemical-shift changes for C(5) are complicated by steric compression, this effect being most marked for the imine (1) in agreement with crystal structure parameters. The high-field shift at C(3) on salt formation, however, is inconsistent with differences observed between pyrone and pyrylium salt ^{13}C n.m.r. spectra. Thus the C(3) and C(5) signals in the 2,4,6-trimethylpyrylium cation are to *lower* field (δ 124.9) [20] than those for 2,6-dimethyl-4-oxopyran (δ 113.7).[21] This apparent anomaly probably arises from an electric field effect involving the nitrogen atom.[22]

Finally, salts (2) and (3) show δ values for C(2) and C(6) *ca.* 10 p.p.m. larger than those for imine (1), demonstrating further the greater degree of positive charge at these atoms in the salts.* A useful comparison

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* ^{13}C Chemical shifts for simple pyrylium salts correlate well with total charge densities at the appropriate carbon atoms.[20]

is with the analogous chemical shifts in 2,6-dimethyl-4-oxopyran (δ 165.3 p.p.m.),[21] and in the 2,4,6-trimethylpyrylium cation (δ 180.15 p.p.m.).[20]

Conclusions.—The longer C(4)–N(9) distance in the methobromide (3) as compared with the hydrobromide (2), together with the differences in the pyran ring parameters, support a greater contribution from resonance structure (5) in this salt, which in turn is consistent with the observed lower $\Delta G^{\ddagger}$ value for rotation about the C=N bond. This distinction between the two salts is not apparent from their ^{1}H and ^{13}C n.m.r. spectra, however, although these do reveal greater positive charge density on the pyran ring relative to the imine (1), but less than that found in pyrylium salts.[20] The shorter C(4)–N(9) and N(9)–C(10) distances in the imine (1), with associated steric interaction between the two rings, support a higher energy barrier for rotation about the C=N bond in this compound. Thus isomerisation in the imine (1) must follow a different mechanism to account for the lower $\Delta G^{\ddagger}$ value relative to salts (2) and (3). Evidence for interaction between the N(9) lone pair and the π system of the benzene ring strongly supports a lateral-shift process *via* the intermediate (6).

Two of us (R. L. H. and S. H. S.) thank the Robert A. Welch Foundation for support of the crystallographic investigations carried out at the University of Texas at Austin.

[0/649 *Received*, 1*st May*, 1980]

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