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SYNTHESIS AND STRUCTURAL STUDY ON α-SUBSTITUTED-1-STYRYLPYRIDINIUM SALTS

REINVESTIGATION OF KROHNKE CONDENSATION

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Abstract—Kröhnke condensation of several cycloimmonium salts with *p*-dimethylaminobenzaldehyde has been studied. X-Ray diffraction, IR and Raman spectra, ^{1}H- and ^{13}C-NMR and UV spectra of the products are discussed, being compared, when necessary, with the starting pyridinium salts. All compounds showed the *Z* configuration, corresponding to the more stable structure, except one, in which steric factors were predominant.

From a general project on the search for new potential antihelmintic agents, 1-styrylpyridinium salts[1,2] attracted our attention as model compounds. From published synthetic methods,[3,4] Kröhnke condensation[5] seemed to be of interest as a versatile use of pyridinium ylides (Fig. 1). As the stereochemistry of the double bond has not been described, and it seems to be of major importance in order to improve the biological activity of the products,[1] our group has reinvestigated the condensation process of different cycloimmonium salts (Tables 1 and 2) with *p*-dimethylaminobenzaldehyde, to assess the scope of the method and investigate the structure and properties of the resulting compounds.

RESULTS AND DISCUSSION

Synthesis

Reactions (Table 2) were performed in Ac_2O by treating the cycloimmonium salt (Table 1) with an excess of *p*-dimethylaminobenzaldehyde at 130° for 15 min. As can be seen, the method is not generally applicable to any stabilizing group; i.e. when R = R′OCO, H_2NCO or *p*-$O_2NC_6H_4$ no condensation product was isolated, even when lower temperatures were used; also quinolinium and isoquinolinium salts failed to give any positive result. Reaction seems to be specially appropriate with 1-phenacylpyridinium salts (**16–19**, Table 2). Apparently, no isomeric mixture was detected by ^{1}H-NMR of the crude product.

Molecular structure

Figure 2 shows a perspective view of the molecule of **19**, computed from the final atomic coordinates, given with their ESDs in Table 3. Figure 2 also shows the atomic numbering used in the crystallographic study. Bond lengths, and bond and torsion angles are given in Tables 4–6. As can be seen, aromatic rings A, B and C are fairly planar, since their torsion angles vary from −0.2 to 1.5, 0.1 to 1.4 and 0 to 2.7°, respectively.

In the pyridine ring, bond lengths are normal for an aromatic system, but the exocyclic C(9)—N(10) bond could be considered large for a link between sp^2 atoms. However, this can be explained by the rotation of ring A around this bond (Fig. 2). Bond distances in ring C are consistent with an aromatic ring, the torsion angle with C═O being 36.7°. In ring B, C(18)—C(19) and C(21)—C(22) are slightly shorter than the others.

Hence, it is possible to consider that ring B has a partial quinonoid structure. Moreover, as the torsion around C(20)—N(23) is not remarkable and the values of the angles C(9)—C(16)—C(17)—C(18) and C(7)—C(9)—C(16)—C(17) are 13 and 9°, respectively, a conjunction through the styryl moiety can be assumed.

The dihedral angles between the pyridine ring plane (A) and the other two ring planes (B, C) are 151 and 104°, respectively, and the interplanar angle between the two benzene rings (B, C) is 48°. Finally, the nearest contacts between the molecule and the counterion (I^-) are:

$$\text{I----C(2)}\quad(-x+1, y+1/2, -z+1/2) = 3.907(9)\ \text{Å}$$
$$\text{I----C(11)}\quad(x+1, y, z) = 3.660(9)\ \text{Å}$$
$$\text{I----C(12)}\quad(x+1, y, z) = 3.861(11)\ \text{Å}.$$

IR and Raman spectra

Data for the more characteristic IR and Raman bands of **14–19** are given in Table 8; for comparison, the same data of **3–8** are presented in Table 7. In **3** and **4**, four main bands were observed between 1640 and 1475 cm^{-1}, characteristic of the pyridinium cation. In **5–8**, two bands appeared at *ca* 1635 and 1490 cm^{-1}, the others being partially overlapped by the benzene ring vibrations.[15,16]

Due to sample fluorescence, only a few bands were observed in the Raman spectra. The most characteristic band appeared at *ca* 1635 cm^{-1} in all compounds studied, and a strong band at 1607–1585 cm^{-1}, due to a

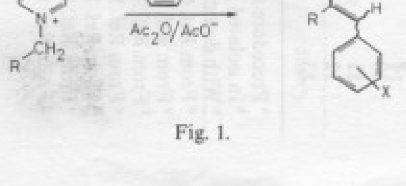


Fig. 1.

Table 1. N-Substituted cycloimmonium salts

Comp.	X^-	R_1	R_2	R_3	R_4	Procedure[a]	Yield (%)[b]	M.p. (°)	Lit. m.p. (°)	Formula	Found (%) (Required) (%) C	H	N
1	Cl	CH_3OCO—	H	H	H	A	85	178–180[c]	178–180[d]	—	—	—	—
2	Cl	H_2NCO—	H	H	H	A	95	208	207–209[d]	—	—	—	—
3	BF_4	NC—	H	H	H	A	70	185	—	$C_7H_7BF_4N_2$	40.86 (40.82)	3.55 (3.42)	13.55 (13.60)
4	I	CH_3SCS—	H	H	H	B	90	158	158[f]	—	—	—	—
5	Br	C_6H_5CO—	H	H	H	A	97	198	199–200[e]	—	—	—	—
6	I	*p*-$CH_3C_6H_4CO$—	H	H	H	C	89	200–203	200–203[g]	—	—	—	—
7	I	*p*-ClC_6H_4CO—	H	H	H	C	72	217–218	217–218[g]	—	—	—	—
8	I	*p*-BrC_6H_4CO—	H	H	H	C	73	233–235	233–235[g]	—	—	—	—
9	Br	*p*-$O_2NC_6H_4$—	H	H	H	A	63	219	222[h]	—	—	—	—
10	Br	C_6H_5CO—	—$(CH{=}CH)_2$—		H	A	90	212	212[i]	—	—	—	—
11	Br	C_6H_5CO—	H	—$(CH{=}CH)_2$—		A	98	204	204–206[i]	—	—	—	—
12	Br	C_2H_5OCO—	H	—$(CH{=}CH)_2$—		A	95	199	199[j]	—	—	—	—
13	Cl	NC—	H	—$(CH{=}CH)_2$—		A	68	214	214[d]	—	—	—	—

[a] Procedure A as described in Ref. 6, B as in Ref. 7, C as in Ref. 8.

[b] In isolated pure product.

[c] With decomp.

[d] From Ref. 6.

[e] From Ref. 9.

[f] From Ref. 7.

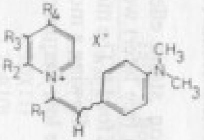
[g] From Ref. 10.

[h] From Ref. 13.

[i] From Ref. 11.

[j] From Ref. 12.

Table 2. Synthesis of N-styrylpyridinium salts



Comp.	X^-	R_1	R_2	R_3	R_4	Yield (%)[a]	M.p. (°)[b]	Formula	Found (%) (Required) (%)		
									C	H	N
—	Cl	$CH_3OCO—$	H	H	H	—[c]					
—	Cl	$H_2NCO—$	H	H	H	—[c]					
14	BF_4	NC—	H	H	H	36	195–196[d]	$C_{16}H_{16}BF_4N_3$	56.76 (57.00)	4.38 (4.78)	12.15 (12.46)
15	I	$CH_3SCS—$	H	H	H	91	201[e,f]	$C_{17}H_{19}IN_2S_2$	46.05 (46.15)	3.85 (4.33)	6.18 (6.33)
16	Br	$C_6H_5CO—$	H	H	H	85	235–237[d]	$C_{22}H_{21}BrN_2O$	64.33 (64.50)	5.11 (5.17)	6.67 (6.48)
17	I	*p*-$CH_3C_6H_4CO—$	H	H	H	64	228[d]	$C_{23}H_{23}IN_2O$	58.81 (58.73)	5.19 (4.92)	5.77 (5.95)
18	I	*p*-$ClC_6H_4CO—$	H	H	H	93	289[d]	$C_{22}H_{20}ClIN_2O$	53.91 (53.84)	3.97 (4.11)	5.75 (5.71)
19	I	*p*-$BrC_6H_4CO—$	H	H	H	74	286[f]	$C_{22}H_{20}BrIN_2O$	49.22 (49.37)	3.45 (3.76)	4.91 (5.23)
—	Br	*p*-$O_2NC_6H_4—$	H	H	H	—[g]					
—	Br	$C_6H_5CO—$	$—(CH{=}CH)_2—$		H	—[c]					
—	Br	$C_6H_5CO—$	H	$—(CH{=}CH)_2—$		—[c]					
—	Br	$C_2H_5OCO—$	H	$—(CH{=}CH)_2—$		—[c]					
—	Cl	NC—	H	$—(CH{=}CH)_2—$		—[c]					

[a] In isolated pure product.
[b] With decomp.
[c] Tar, with no isolable products.
[d] From MeOH.
[e] Ref. 7 describes 201°.
[f] From EtOH.
[g] Starting pyridinium salt was recovered untransformed in more than 80%.

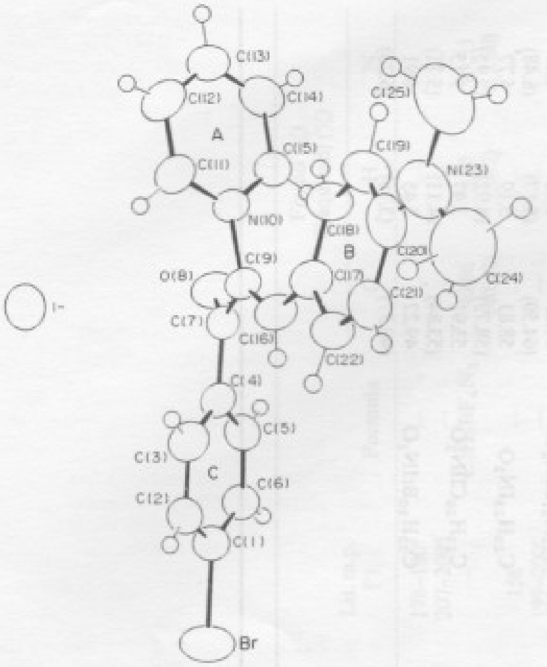


Fig. 2.

benzene ring vibration appeared in **5–8**. A $\nu_{C=O}$ band at 1690–1700 cm^{-1}, in some cases split, also appeared in the IR and Raman spectra of **5–8**. In **14–19** (Table 8), comparing IR data in the solid state and in solution ($CDCl_3$ and DMSO) it can be assumed that there are no essential changes in structure, thus justifying correlation of X-ray data of **19** with IR, Raman and even NMR results (see later). Moreover, from IR data, it can be assumed that **16–18** also adopt the *Z* configuration.

X-Ray data for **19** revealed that the styryl moiety and the carbonyl group are nearly coplanar, suggesting that from the two main canonical forms (Fig. 3) there should be a high contribution of II to the resonance hybrid. II is stabilized by the *p*-dimethylamino group contribution, and this would explain the deep colour of **14–19**. From the above considerations, some analogies in the IR of **14–19** and cycloimmonium ylides[17] could be expected, but no carbonyl ylide absorption bands were detected (near 1500 cm^{-1}). However, in **16–19**, a medium-weak band at 1638–1621 cm^{-1} was assigned to the $\nu_{C=O}$; low frequency and intensity can be explained by the contribution of II (Fig. 3) as is the case with the C=O absorption of analogous *trans-s-trans* chalcones either in the solid state[18] or in $CDCl_3$ solution.[19–21] The strong IR and Raman bands at 1584–1562 cm^{-1}, in some cases accompanied by a shoulder at lower frequencies, was assigned to a vibration of the *p*-dimethylaminophenyl moiety with a large contribution of the $\nu_{C=C}$ vibration. The last band and a second one, weaker, at 1545–1520 cm^{-1}, mainly due to the same ring B, are the most characteristic of **14–19**.

IR and Raman data of the dithioester **15** are in agreement with those for **16–19** and suggest the same *Z* configuration, although lower frequencies of the bands around 1615 and 1560 cm^{-1} are attributable to a less distorted molecule, due to the smaller size of the dithioester group.

Taking into consideration steric effects, and in agreement with NMR data (see later) we tentatively assumed the configuration *E* for **14**. The molecule must be more planar than **16–19**, allowing a more extended conjugation, reflected in the low frequency of the ν_{CN} vibration.

Table 3(a). Atomic parameters for non-hydrogen atoms. Coordinates and thermal parameters as $U_{EQ} = (1/3), \sum(U_{IJ} A_I^* A_J^* A_I A_J \cos(A_I, A_J)) \times 10^4$

Atom	*X/A*	*Y/B*	*Z/C*	U_{EQ}
I	0.81046(8)	0.10964(6)	0.36875(3)	684(3)
Br	0.39180(15)	0.02445(11)	0.05776(4)	847(5)
C1	0.38107(103)	0.03270(87)	0.13917(35)	564(32)
C2	0.30071(110)	−0.05605(82)	0.16203(38)	591(32)
C3	0.29561(106)	−0.05053(79)	0.22176(38)	537(31)
C4	0.36710(96)	0.04322(76)	0.25600(34)	496(28)
C5	0.44580(103)	0.13096(81)	0.23187(37)	529(30)
C6	0.45596(104)	0.12658(87)	0.17272(40)	576(33)
C7	0.35605(91)	0.04278(73)	0.32084(33)	475(27)
O8	0.36502(74)	−0.05090(52)	0.34742(24)	612(22)
C9	0.32284(92)	0.15510(76)	0.34863(32)	474(27)
N10	0.34922(78)	0.14373(56)	0.41336(26)	456(22)
C11	0.24126(105)	0.08120(85)	0.43647(38)	554(32)
C12	0.26456(133)	0.07093(96)	0.49738(45)	684(40)
C13	0.39426(132)	0.12143(103)	0.53248(40)	678(38)
C14	0.50361(129)	0.18327(99)	0.50829(45)	691(39)
C15	0.48060(107)	0.19444(86)	0.44741(39)	577(33)
C16	0.26489(107)	0.25423(85)	0.32190(36)	533(30)
C17	0.20790(95)	0.36494(71)	0.34170(34)	494(28)
C18	0.17165(112)	0.38441(86)	0.39729(38)	595(33)
C19	0.11901(113)	0.49291(87)	0.41224(39)	617(35)
C20	0.09847(96)	0.58923(79)	0.37365(45)	599(34)
C21	0.13071(110)	0.56910(86)	0.31647(43)	604(34)
C22	0.18261(105)	0.45917(82)	0.30192(38)	552(32)
N23	0.05211(105)	0.69856(74)	0.38858(42)	782(36)
C24	0.00390(179)	0.79002(103)	0.34560(67)	1004(61)
C25	0.01572(144)	0.71735(103)	0.44684(63)	1013(57)

Table 3(b). Atomic parameters for hydrogen atoms. Coordinates and thermal parameters as $\exp(-8\pi^2 U(\sin\theta/\lambda)^2)\times 10^3$

Atom	X/A	Y/B	Z/C	U
H251	0.107(14)	0.694(11)	0.475(5)	96
H252	−0.099(14)	0.682(11)	0.441(5)	96
H253	−0.007(14)	0.797(11)	0.450(5)	96
H2	0.236(0)	−0.136(0)	0.142(0)	59
H3	0.244(11)	−0.118(9)	0.237(4)	54
H5	0.489(12)	0.193(9)	0.253(5)	51
H6	0.498(12)	0.191(9)	0.156(4)	57
H11	0.156(12)	0.047(9)	0.410(4)	58
H12	0.182(13)	0.033(10)	0.509(5)	68
H13	0.406(12)	0.121(10)	0.573(5)	67
H14	0.585(13)	0.227(10)	0.526(5)	68
H15	0.562(12)	0.238(9)	0.429(4)	59
H16	0.264(12)	0.260(9)	0.286(4)	52
H18	0.177(12)	0.319(9)	0.424(4)	58
H19	0.095(0)	0.504(0)	0.453(0)	61
H21	0.130(12)	0.632(9)	0.288(4)	59
H22	0.219(11)	0.445(9)	0.265(4)	54
H241	0.022(0)	0.751(0)	0.312(0)	92
H242	0.107(15)	0.827(12)	0.337(6)	92
H243	−0.090(14)	0.837(11)	0.362(5)	92

^{1}H- *and* ^{13}C-NMR *spectra*

The ^{1}H- and ^{13}C-NMR data for **14–19** are presented in Tables 9 and 10, respectively. By comparing NMR data of **14–19** with those from several previously described chalcones,[22–24] some considerations can be deduced.

(a) The π-releasing effect of the NMe_2 group is increased by the σ-attracting effect of the pyridinium group, and the resonance form II will contribute greatly to the electronic distribution in the ground state. This is supported by H-2′(6′), H-3′(5′), C-2′(6′) and C-1′ chemical shifts, although the diamagnetic anisotropy contribution of the pyridinium ring on H-2′(6′) should be considered.

(b) The vinyl moiety is only slightly affected by the pyridinium σ-attracting effect, and, as expected, the polarization of the C=C bond is predominantly caused by the carbonyl group.

Table 4. Bond distances (Å)

Br—C1	1.904(8)	C1—C2	1.373(16)
C1—C6	1.383(13)	C2—C3	1.391(21)
C3—C4	1.380(12)	C4—C5	1.372(13)
C4—C7	1.520(11)	C5—C6	1.388(13)
C7—O8	1.214(10)	C7—C9	1.472(12)
C9—N10	1.470(10)	C9—C16	1.319(12)
N10—C11	1.347(12)	N10—C15	1.345(10)
C11—C12	1.384(14)	C12—C13	1.345(14)
C13—C14	1.365(16)	C14—C15	1.384(14)
C16—C17	1.444(13)	C17—C18	1.398(13)
C17—C22	1.390(12)	C18—C19	1.368(14)
C19—C20	1.391(13)	C20—C21	1.421(15)
C20—N23	1.357(13)	C21—C22	1.377(14)
N23—C24	1.429(16)	N23—C25	1.457(18)

Table 5. Bond angles (°)

Br—C1—C6	118.7(7)	Br—C1—C2	118.3(7)
C2—C1—C6	123.0(9)	C1—C2—C3	118.0(8)
C2—C3—C4	120.2(8)	C3—C4—C7	116.9(8)
C3—C4—C5	120.6(8)	C5—C4—C7	122.5(8)
C4—C5—C6	120.6(8)	C1—C6—C5	117.6(9)
C4—C7—C9	118.9(7)	C4—C7—O8	119.4(7)
O8—C7—C9	121.5(7)	C7—C9—C16	127.5(7)
C7—C9—N10	111.5(7)	N10—C9—C16	120.8(7)
C9—N10—C15	119.3(7)	C9—N10—C11	118.5(7)
C11—N10—C15	122.2(7)	N10—C11—C12	118.8(9)
C11—C12—C13	120.2(10)	C12—C13—C14	120.2(9)
C13—C14—C15	119.9(10)	N10—C15—C14	118.6(9)
C9—C16—C17	134.2(8)	C16—C17—C22	117.7(7)
C16—C17—C18	125.3(8)	C18—C17—C22	117.0(8)
C17—C18—C19	121.1(8)	C18—C19—C20	122.5(9)
C19—C20—N23	123.2(9)	C19—C20—C21	116.7(8)
C21—C22—N23	120.1(9)	C20—C21—C22	120.2(9)
C17—C22—C21	122.5(8)	C20—N23—C25	119.6(9)
C20—N23—C24	122.1(10)	C24—N23—C25	116.9(9)

Table 6. Some torsion angles (°)

C3—C4—C7—O8	36.7(11)
C3—C4—C7—C9	−138.9(8)
C5—C4—C7—O8	−142.4(9)
C5—C4—C7—C9	42.0(12)
C4—C7—C9—N10	−168.3(7)
C4—C7—C9—C16	16.7(13)
O8—C7—C9—N10	16.2(11)
O8—C7—C9—C16	−158.9(9)
C7—C9—C16—C17	171.1(9)
C7—C9—N10—C11	−72.6(9)
C7—C9—N10—C15	106.6(8)
N10—C9—C16—C17	−3.6(15)
C16—C9—N10—C15	−78.0(11)
C16—C9—N10—C11	102.8(10)
C9—C16—C17—C18	−13.5(16)
C9—C16—C17—C22	168.4(10)
C16—C17—C18—C19	179.7(9)
C17—C18—C19—C20	0.1(15)
C18—C19—C20—N23	−177.5(9)
C19—C20—N23—C24	−168.6(10)
C19—C20—N23—C25	−2.3(15)
C21—C20—N23—C24	12.3(15)
C21—C20—N23—C25	178.6(10)

Average torsion angle in ring A = 0.91°.
Average torsion angle in ring B = 1.46°.
Average torsion angle in ring C = 0.65°.

Table 7. IR and Raman frequencies (cm^{-1}) of the N-substituted cycloimmonium salts (**3–8**)

				Pyridinium ring					Other	
Comp.	Medium	ν C=O	Benzene ring	**8a**	**8b**	**19a**	**19b**	**1**	ν C≡N	ν C=S
3	KBr			1626 m[a] 1615 m	1588 vw	1504 w	1493 m 1480 m		2215 m	
	Solid (Raman)			1625 m	1587 w			1034 m	2215 vs	
	$(CH_3)_2SO$									
4	KBr			1640 vs	1580 vw	1500 vw	1494 s	1021 vw		1170 s
	Solid (Raman)			1635 w	1580 m	1501 vw		1020 vs		1170 vs
5	KBr	1690 vs	1593 s 1578 m 1503 s 1448 s	1635 s			1492 s			
	Solid (Raman)	1697 s	1592 s 1575 vw	1632 w						
	$(CH_3)_2SO$	1697 vs	1596 m 1580 m	1635 vs			1492 s			
6	KBr	1696 vs 1675 vs	1611 vs 1570 w	1636 s	1580 w	1504 m	1495 vs	1028 vw		
	Solid (Raman)	1691 s 1675 w	1607 vs	1635 m	1580 vw			1028 s		
	$(CH_3)_2SO$	1692 vs	1607 s	1634 m			1493 s			
7	KBr	1695 vs	1592 s 1573 w	1635 s		1501 m	1485 s	1025 vw		
	Solid (Raman)	1693	1590	1640						
8	KBr	1697 vs	1590 s	1638 m	1574 w	1502 w	1488 m			
	Solid (Raman)	1693 s	1585 s	1631 vw				1033 m		

[a] Abbreviations: s, strong; m, medium; w, weak; v, very.

(c) The carbonyl group acts as an insulator of the conjugation and the electronic distribution of the enone moiety is unaffected by ring C substituents.

(d) The pyridinium ring data for **14–19** are in close agreement with those reported for pyridinium salts;[25–28] consequently, the pyridinium ring must be twisted with respect to the styryl plane, and no conjugative effect is observed.

(e) In the case of **14**, the δ-values for C-2(6), C-3(5), C-4, H-3(5) and H-4 appeared at higher field than the corresponding δ-values of **15–19**, indicating an extended conjugation, which is corroborated by the δ-values of H-2′(6′) and H-3′(5′) in **14**. These results are interpreted in the sense that **14** adopts the *E* configuration.

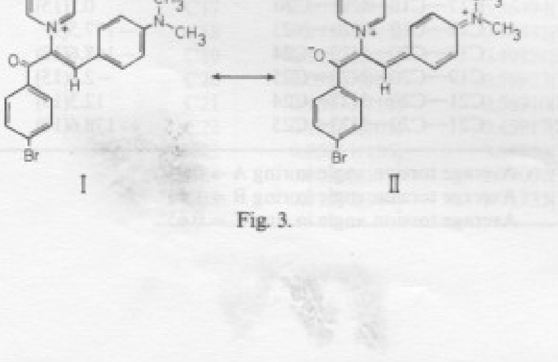


Fig. 3.

UV–vis *spectra*

UV–vis spectroscopy data for **14–19** are presented in Table 11. All compounds showed two absorptions: one, in the visible between 424.7–491.5 nm (log ε: 4.47–4.64) and the other between 260.9–269.1 nm (log ε: 4.18–4.44). Similar absorptions have been described for chalcones.[29]

CONCLUSIONS

Six pyridinium salts were condensed, in boiling Ac_2O, with *p*-dimethylaminobenzaldehyde as a model of Kröhnke synthesis of 1-styrylpyridinium salts.

No previous data have been published on the stereochemistry of the reaction, and as no isomeric mixtures were detected in the crude material, it should be accepted that the process is stereospecific.

From the structural study, it seems that all products have the *Z* structure in the styryl moiety, corresponding to the more conjugated—and stable—system, except for **14**, in which steric effects may be predominant.

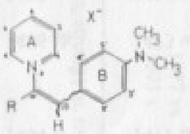
There is an indirect precedent in the literature, as a paper from Ahlbrecht and Kröhnke[30] described an enolate attack to a 1-styrylpyridinium salt, being the process described as regioselective over the 4-position of the pyridinium ring, thus suggesting that the 2-position was sterically hindered, as would correspond to a *Z* isomer.

Table 8. IR and Raman frequencies (cm^{-1}) of the 1-styrylpyridinium salts (**14**–**19**)

				Pyriridinium ring (A)				Benzene ring (C)		Other		
Compound	Medium	ν C=O	Benzene ring (C)	**8a**	**8b**	**19a**	**19b**	+ ν C=C		ν C≡N	δ CH_3	ν C=S
14	KBr			1620 s		1490 w	1475 m	1584 vs 1570 sh	1538 s	2208 m	1386 s	
	$(CH_3)_2SO$			1612 s		1488 sh	1475 m	1580 vs 1570 sh	1530 s	2205 w	1375 s	
15	KBr			1621 m 1612 m		1481 w	1468 m	1562 vs 1556 vs	1538 m 1522 vs		1384 s	1181 vs
	Solid (Raman)				1605 w			1555 s	1520 m			1178 s
	$(CH_3)_2SO$			1623 w 1613 m		1485 sh	1468 w	1563 vs	1526 vs		1383 s	1189 vs 1178 sh
	$CDCl_3$			1626 w 1617 m		1484 w	1472 m	1563 vs	1528 vs		1383 s	1189 vs 1178 sh
16	KBr	1630 m	1600 vw 1581 s 1575 s	1620 m	1610 sh	1490 w	1480 m	1563 vs	1545 sh 1533 s		1390 m	
	Solid (Raman)	1628 w	1580 w	1623 sh	1610 w			1563 s	1533 w			
	$(CH_3)_2SO$	1638 w	1576 sh	1626 m		1486 w	1473 w	1583 vs	1533 s		1380 m	
	$CDCl_3$	1636 w	1598 sh 1574 sh	1624 m				1581 vs	1531 s		1381 m	
17	KBr	1640 m	1608 m	1624 m		1485 w	1465 s	1582 vs	1532 s		1384 s	
	Solid (Raman)	1633 w	1603 vw 1585 sh	1619 w				1568 vs 1564 vs	1536 w			
	$(CH_3)_2SO$	1635 sh	1605 m 1570 sh	1625 m		1485 sh	1473 w	1582 vs	1532 s		1382 m	
	$CDCl_3$	1635 w	1606 m 1570 sh	1624 m		1480 sh	1469 w	1579 vs	1530 s		1380 m	
18	KBr	1635 w	1615 sh	1626 m		1484 w	1471 m	1579 vs 1567 sh	1542 w 1524 s		1374 m	
	Solid (Raman)	1632 w		1620 w				1574 vs 1565 m	1544 w			
	$(CH_3)_2SO$	1635 sh	1615 sh	1626 m		1486 sh	1473 w	1578 vs 1567 sh	1532 s		1382 m	
19	KBr	1633 w	1605 sh	1623 m		1480 w	1466 m	1575 vs 1560 sh	1538 sh 1524 s		1372 m	
	Solid (Raman)	1633 w	1600 sh	1621 w				1575 vs 1565 sh	1545 w 1520 vw			
	$(CH_3)_2SO$	1636 w		1627 m			1472 m	1580 vs	1531 s		1382 m	

Abbreviations as in Table 7.

Table 9. ${}^{1}H$-NMR of compounds **14**–**19**[a]



Compound	R	X	H2,6	H3,5	H4	Hβ	H2′,6′	H3′,5′	NCH_3	Others
14	CN	BF_4	9.30 dd ${}^{3}J = 6.6$ ${}^{4}J = 1.5$	8.23 t†	8.70 t ${}^{3}J = 7.8$	8.06 s	6.86 d ${}^{3}J = 9$	7.80 d	3.10 s	
15	CH_3SCS	Br	9.20 dd ${}^{3}J = 6.6$ ${}^{4}J = 1.4$	8.43 t†	8.95 tt ${}^{3}J = 7.8$ ${}^{4}J = 1.4$	8.36 s	6.65 s	6.65 s	3.03 s	2.75 (s, 3H)
16	C_6H_5CO	I	9.30 dd ${}^{3}J = 6.6$ ${}^{4}J = 1.5$	8.46 t†	8.96 tt ${}^{3}J = 7.8$ ${}^{4}J = 1.5$	7.75 s	6.65 s	6.65 s	3.00 s	7.84 (dd, 2H, ${}^{3}J = 6.8$, ${}^{4}J = 1.8$), 7.80[b] (m, 1H), 7.76 (t†, 2H)
17	p-$CH_3C_6H_4CO$	I	9.30 dd ${}^{3}J = 6.8$ ${}^{4}J = 1.3$	8.45 t†	8.96 tt ${}^{3}J = 7.8$ ${}^{4}J = 1.3$	7.76 s	6.63 s	6.63 s	3.00 s	7.80 (d, 2H, ${}^{3}J = 8.1$), 7.42 (d, 2H), 2.45 (s, 3H)
18	p-ClC_6H_4CO	I	9.25 d† ${}^{3}J \simeq 6$	8.43 t†	8.83 t† ${}^{3}J \simeq 7$	7.76 s	6.63 s	6.63 s	2.98 s	7.86 (d, 2H, ${}^{3}J = 8.7$), 7.66 (d, 2H)
19	p-BrC_6H_4CO	I	9.23 dd ${}^{3}J = 6.6$ ${}^{4}J = 1.5$	8.43 t†	8.93 t ${}^{3}J = 7.8$	7.80 s	6.63 s	6.63 s	3.00 s	7.83 (s, 4H)

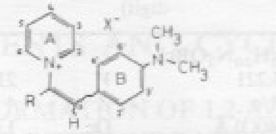
[a] Spectra recorded at 90 MHz in DMSO, TMS as internal reference, chemical shifts in δ and coupling constants in Hz.

[b] Overlapped signal.

Approximate region is given.

Abbreviations: d, doublet; s, singlet; t, triplet; dd, doublet of doublets; tt, triplet of triplets; †, unresolved.

Table 10. ^{13}C-NMR of compounds 14–19[a]



Comp.	R	X	C2,6	C3,5	C4	C=O	Cα	Cβ	C1′
14	CN	BF_4	144.26 d $^1J = 195$	128.34 d $^1J = 173$	146.87 d $^1J = 167$	—	—[b]	132.53 d $^1J = 158$	—[b]
15	CH_3SCS	Br	147.84 d $^1J = 196$	129.97 d $^1J = 177$	149.04 d $^1J = 174$	—	115.99 s	135.29 d $^1J = 155$	137.13 s
16	C_6H_5CO	I	147.16	128.57	148.00	188.89	115.53	143.48	132.61
17	p-$CH_3C_6H_4CO$	I	146.99	129.08	148.12	191.07	115.47	143.12	132.54
18	p-ClC_6H_4CO	I	147.00 d $^1J = 195$	129.27 d $^1J = 177$	148.15 d $^1J = 173$	193.00 s	115.57 s	143.69 d $^1J = 156$	132.25 s
19	p-BrC_6H_4CO[c]	I	146.99	129.34	148.13	187.95	115.44	143.62	132.18

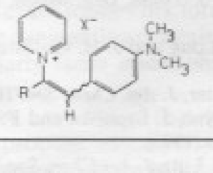
Comp.	C2′,6′	C3′,5′	C4′	C1″	C2″,6″	C3″,5″	C4″	$NHCH_3$	Others
14	132.53 d $^1J = 158$	111.84 d $^1J = 163$	153.5 s	—	—	—	—	39.42 q	105.24 (s, CN)
15	134.35 d $^1J = 155$	112.96 d $^1J = 162$	153.39 s	—	—	—		40.19[d]	19.71 (q, SCH_3, $^1J = 142$)
16	133.24	112.06	152.85	136.44	129.44[e]	129.23[e]	132.26	39.50	
17	133.08	112.00	152.71	133.56	129.32	129.32	142.57	39.40	21.38 (CH_3)
18	133.43 d $^1J = 159$	112.10 d $^1J = 161$	152.23 s	137.09 s	131.04 d $^1J = 166$	128.75 d $^1J = 169$	134.08 s	39.50 q $^1J = 136$	
19	133.30	111.93	152.84	135.46	131.57[e]	131.13[e]	126.02	39.33	

[a] Spectra recorded at 20 MHz unless otherwise stated.
[b] Insufficient signal-to-noise ratio.
[c] Spectra recorded at 90 MHz.
[d] Overlapped signal.
[e] Signals may be interchanged.

EXPERIMENTAL

General. IR spectra were recorded on a Perkin–Elmer 599B spectrophotometer. Indene and polystyrene were used for instrument calibration. Samples were compressed into KBr pellets and spectra in $CDCl_3$ and DMSO solns were also recorded. Raman spectra were measured with a powdered sample on a Jobin-Yvon 4-1000 double monochromator, using either an argon ion laser (5145 Å) or a krypton laser (6471 Å) according to the fluorescence of the sample. A photon counting detector was employed. The powdered sample was packed inside a glass capillary tube, or in some cases, when the overheating caused by the laser beam could damage the sample, a KBr pellet in a rotating cell was used.

Table 11. UV spectra of N-styrylpyridinium salts[a]



Comp.	R	X⁻	λ_{max} (nm)	log ε
14	NC—	BF_4	441.9	4.47
			261.5	4.18
15	CH_3SCS—	I	491.5	4.63
			269.1	4.61
16	C_6H_5CO—	Br	427.3	4.58
			260.9	4.30
17	p-$CH_3C_6H_4CO$—	I	424.7	4.63
			265.5	4.41
18	p-ClC_6H_4CO—	I	431.1	4.64
			266.9	4.44
19	p-BrC_6H_4CO—	I	424.9	4.60
			264.3	4.37

[a] Spectra were run in a Spectronic-2000 (Bausch & Lomb) UV–vis spectrophotometer, using 10^{-5} M MeOH solutions.

^{1}H-NMR spectra were recorded on a Varian EM390 (90 MHz) instrument using DMSO solns, and TMS as internal reference. ^{13}C-NMR spectra were recorded on two spectrometers, a Varian FT80A (20 MHz) and a Brüker WM360 (90 MHz), in DMSO solns with TMS. With all compounds broad band decoupled and SFORD spectra were obtained. For **14**, **15** and **18**, proton coupled spectra were obtained. Assignments were based on multiplicity of the signals, coupling constants and literature data.

UV–vis spectra were recorded with a Bausch & Lomb Spectronic-2000 spectrophotometer, using 10^{-5} M MeOH solns. All m.ps were determined on a Buchi–Tottoli apparatus using open capillary tubes, and are uncorrected.

General procedures for preparation of cycloimmonium salts **1–13**

(a) To the heterocycle (0.2 mol) dissolved in acetone (50 ml), the α-halocarbonyl compound XCH_2COR (0.2 mol) was added. The mixture was heated under reflux for 20 hr when X = Cl or 90 min when X = Br. The cycloimmonium salt was filtered off and crystallized from EtOH/ether. When the product was hygroscopic, as in **3**, it was dissolved (0.2 mol) in water (25 ml) and sodium tetrafluoroborate (0.2 mol) was added. On cooling, the pyridinium tetrafluoroborate precipitated in 90–95% yield, and was crystallized from 70% EtOH.

Table 12. Crystal data (ESDs in parentheses refer to the last significant digit)

Formule	$C_{22}H_{20}N_2OBrI$		
Mw	535.221	*V*	2145.4 (1.0) Å^3
Space group	P21/c	Z	4
a	8.440(3) Å	Dc	1.657 Mg m^{-3}
b	11.254(1) Å	*F* (000)	1048
c	23.097(5) Å	$\lambda_{MoK\alpha}$	0.7107 Å
β	102.06(5)°	*μ*	33.333 cm^{-1}

(b) Compound **4** was obtained from 1-phenacylpyridinium bromide as described by Kröhnke and Gerlach.[7]

(c) To the corresponding acetophenone (0.2 mol) dissolved in pyridine (0.4 mol), I_2 (0.2 mol) was added. The mixture was heated on a steam bath for 12 hr. On cooling, the mixture was filtered, and the ppt washed with diethyl ether (10 ml). The product was crystallized from 70% EtOH.

General procedure for preparation of 1-*styrylpyridinium salts* **14–19**

To a suspension of the cycloimmonium salt (5 mmol) in Ac_2O (15 ml), *p*-dimethylaminobenzaldehyde (5.5 mmol) was added. The mixture was stirred at 130°, for 15 min. It was then cooled and diethyl ether was added (30 ml) until a ppt of highly coloured prisms appeared. The solid was filtered and crystallized from MeOH.

Crystallographic studies

Symmetry independent reflections of a single crystal were collected on an Enraf–Nonius CAD4 computer-controlled, four-circle diffractometer with graphite-monochromated MoKα = 0.7170 Å radiation. Cell constants were determined from a least-squares calculation of the setting angles of 25 reflections (Table 12). The data were corrected for Lorentz and polarization factors and for absorption with ORABS. The position of the I^- anion was determined from Patterson maps. From successive Fourier syntheses the positions of all the non-H atoms were determined. Full-matrix least-squares refinement of the positional and anisotropic vibrational parameters of non-H atoms resulted in a conventional *R* = 0.08. The H positions were located in difference Fourier syntheses and they were included in the refinement but their isotropic thermal parameters were kept fixed. Scattering factors were taken from *International Tables for X-ray Crystallography*.[31] All calculations were performed on a 1108 Univac Computer with X-ray System programs.[32] Final *R* = 0.058. The refinement was terminated when the shift/error in all the parameters was less than one-half of the estimated standard deviation. Final difference Fourier maps showed only very small peaks of no physical significance (< 0.02). The final thermal parameters and observed and calculated structure factors are available as supplementary material.

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