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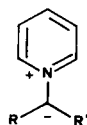
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An improved procedure to prepare dithioester stabilised pyridinium ylides is described. The structure of the products is discussed.

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Disubstituted pyridinium *N*-methylides (Figure 1) have been used in a great variety of cycloaddition reactions with different dipolarophiles [1,2]. Several synthetic approaches have been used successfully. Dicyanomethylides are specifically prepared from tetracyanomethylene oxide [3,4]. Other products have been obtained by carbene attack on the corresponding heterocycle [5], but the more common method seems to be the reaction of monosubstituted ylides with acyl halides [6,7], isocyanates or their thio analogs [6,8].



$R, R' = ArCO, COOEt, CN, CONH_2$

Figure 1

A classical paper from Krohnke [9] described the synthesis in two steps of 1-(methylthiothiocarbonylmethyl)pyridinium iodides **1-5** (Figure 2) as the first example of a pyridinium salt linked to a dithioester group. As the product showed interesting properties from a synthetic point of

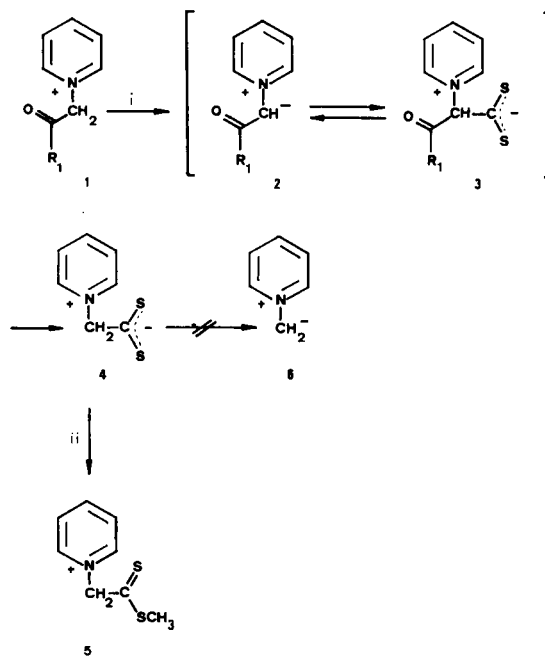


Fig. 2 Reagents: i, aq. NaOH, CS<sub>2</sub>; ii, CH<sub>3</sub>I, MeOH.

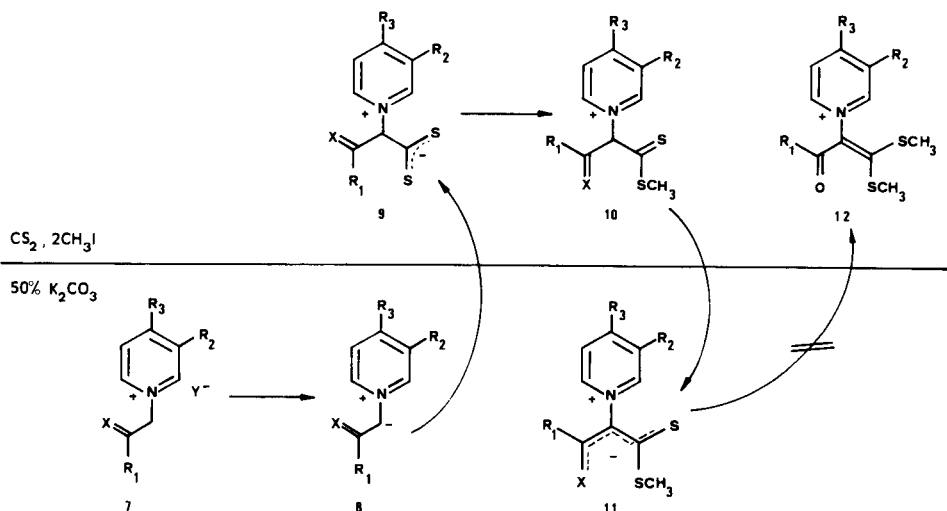
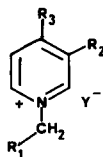


Fig. 3

Table 1  
N-Substituted Cycloimmonium Salts 7



Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X	Y	Procedure [a]	Yield (%)	Mp (°C)	Lit Mp (°C)	Formula	Found (%)		
											(Required)	(%)	(%)
											C	H	N
<b>7a</b>	C <sub>6</sub> H <sub>5</sub> -	H	H	O	I	A	88		215-219 [b]				
<b>7b</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	H	H	O	I	A	71		218-219 [c]				
<b>7c</b>	<i>o,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	H	H	O	I	A	65	202-203		C <sub>13</sub> H <sub>16</sub> INO	50.98 (50.99)	4.89 (4.56)	3.94 (3.96)
<b>7d</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	H	H	O	I	A	73		233-235 [c]				
<b>7e</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	H	H	O	I	A	72		217-218 [c]				
<b>7f</b>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> -	H	H	O	I	A	78		211-212 [c]				
<b>7g</b>	CH <sub>3</sub> O-	H	H	O	Cl	B	85	178-180	191 [d]				
<b>7h</b>	CH <sub>3</sub> S-	H	H	S	I	C	90		158 [e]				
<b>7i</b>	C <sub>6</sub> H <sub>5</sub> -	CONH <sub>2</sub>	H	O	Br	B	95		236-238 [f]				
<b>7j</b>	C <sub>6</sub> H <sub>5</sub> -	H	C <sub>6</sub> H <sub>5</sub> -	O	Br	B	98	242-243	203-205 [g]	C <sub>13</sub> H <sub>16</sub> BrNO	64.35 (64.42)	4.48 (4.55)	3.95 (3.95)
<b>7k</b>	C <sub>6</sub> H <sub>5</sub> -	-(CH=CH) <sub>2</sub> -		O	Br	B	98		204-206 [h]				
<b>7l</b>	CH <sub>3</sub> O-	-(CH=CH) <sub>2</sub> -		O	Cl	B	65	180		C <sub>12</sub> H <sub>12</sub> ClNO <sub>2</sub>	60.52 (60.64)	4.95 (5.08)	5.56 (5.89)

[a] Procedure A is described in Ref [25], B as in Ref [26], C as in Ref [9]. [b] Described in Ref [25]. [c] Described in Ref [27]. [d] Described in Ref [28]. [e] Described in Ref [9]. [f] Described in Ref [29]. [g] Described in Ref [30]. [h] Described in Ref [31].

view [10,11], we tried the synthesis of dithioester derived from **3** (Figure 2) using a non nucleophilic base as potassium carbonate, in the Krohnke process [12]. However **3**, when isolated, yielded back the free ylide **2** and carbon disulfide. As expected, **4** is isolated without quick decomposition as it would produce the highly unstable ylide **6**.

By using a biphasic system, (Figure 3) we have been able to trap the dithiocarboxylate intermediate **9** with methyl iodide as soon as it is formed. The method is a new example of phase transfer catalysis of pyridinium ylides [13,14]. In addition to several contributions to the structure of cycloimmonium ylides [15-19], a detailed structural study was undertaken on compounds **11** (Figure 3).

## Results and Discussion.

### Synthesis.

In the process (Figure 3), a monosubstituted ylide **8**, generated in the aqueous phase (50% potassium carbonate) reacts with a mixture of carbon disulfide and methyl iodide, producing the disubstituted ylide **11** in one step. Yields and analysis of **7** and **11** are given in Tables 1 and 2.

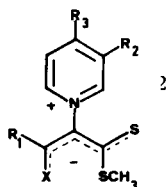
Dipolar species in the process, **8** and **9**, are relatively liposoluble, and cations **7** and **10** are hydrosoluble, hence the reactive species are not simply carried from one layer to another, but they cross the interface several times, producing a multiple phase transfer catalysis mechanism.

Although direct synthesis of dithioacetal derivatives **12** was attempted, compounds **11** were recovered precipitated from the system, as they seem to be too insoluble to appreciably dissolve into the organic layer. However a 1:2 ratio of **1**:methyl iodide was necessary to increase the yields, as a 1:1 ratio produced 70% of **11a**.

As we have shown with other liquid-liquid systems [20], use of ultrasound in the process reduced reaction time, but the yields were always slightly lower [21] because the product suffered partial decomposition.

Previous publications [22,23] described a similar method, performed with isoquinolinium salts, such as **7k** and **7l**, in dioxane/water or pyridine, being the cycloaddition product **13** (Figure 4) obtained instead of the open ylide, as in our procedure. Another paper from Kobayashi and co-workers [24] described better yields for **11h**, but our mp and nmr spectrum, disagree with theirs.

Table 2  
Cycloimmonium Ylides **11**.



Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X	U.S. [a]	Yield [b] (%)	Mp (°C, dec)	Lit Yield (%)	Lit Mp (°C)	Formula	Found (%) (Required) (%)		
											C	H	N
<b>11a</b>	C <sub>6</sub> H <sub>5</sub> -	H	H	O		80	215-216 [d]	22	214 [c]	C <sub>15</sub> H <sub>13</sub> NOS <sub>2</sub>	62.33 (62.68)	4.68 (4.55)	4.89 (4.87)
<b>11b</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	H	H	O	+	90	216-217 [e]			C <sub>16</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	60.53 (60.54)	4.95 (4.76)	4.53 (4.41)
<b>11c</b>	<i>o,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	H	H	O		75	205-206 [d]			C <sub>17</sub> H <sub>17</sub> NOS <sub>2</sub>	64.56 (64.72)	5.61 (5.43)	4.36 (4.44)
<b>11d</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	H	H	O		88	225-226 [e]			C <sub>15</sub> H <sub>12</sub> BrNOS <sub>2</sub>	49.58 (49.18)	3.33 (3.60)	3.67 (3.82)
<b>11e</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	H	H	O		75	222-223 [f]			C <sub>15</sub> H <sub>12</sub> ClNOS <sub>2</sub>	56.02 (55.97)	3.76 (3.75)	4.45 (4.35)
<b>11f</b>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>5</sub> -	H	H	O	+	86	240-241 [e]			C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	53.83 (54.20)	3.93 (3.63)	8.25 (8.42)
<b>11g</b>	CH <sub>3</sub> O-	H	H	O		27	220-221 [d]			C <sub>10</sub> H <sub>11</sub> NO <sub>2</sub> S <sub>2</sub>	49.52 (49.77)	4.80 (4.59)	6.31 (5.80)
<b>11h</b>	CH <sub>3</sub> S-	H	H	S		30	230 [d]	69	221 [g]	C <sub>10</sub> H <sub>11</sub> NS <sub>4</sub>	43.69 (43.92)	4.06 (4.05)	4.98 (5.12)
<b>11i</b>	C <sub>6</sub> H <sub>5</sub> -	CONH <sub>2</sub>	H	O		65	206-207 [e]			C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	57.97 (58.16)	4.31 (4.27)	8.33 (8.47)
<b>11j</b>	C <sub>6</sub> H <sub>5</sub> -	H	C <sub>6</sub> H <sub>5</sub>	O		83	223-224 [h]			C <sub>21</sub> H <sub>17</sub> NOS <sub>2</sub> ·1H <sub>2</sub> O	66.25 (66.11)	5.17 (5.01)	3.75 (3.67)
<b>11k</b>	C <sub>6</sub> H <sub>5</sub> -	-(CH=CH) <sub>2</sub> -		O		73	220-221 [i]			C <sub>19</sub> H <sub>15</sub> NOS <sub>2</sub>	67.97 (67.62)	4.57 (4.48)	4.01 (4.15)
<b>11l</b>	CH <sub>3</sub> O-	-(CH=CH) <sub>2</sub> -		O		82	229 [e]			C <sub>14</sub> H <sub>13</sub> NO <sub>2</sub> S <sub>2</sub>	57.63 (57.71)	4.84 (4.49)	5.11 (4.80)

[a] As described in Ref [22]. After 1 hour at room temperature. [c] From Ref [23]. [d] From ethanol. [e] From ethanol/water.

[b] In isolated pure product, after 20 hours at room temperature except when stated. [f] From methanol. [g] From Ref [25]. [h] From acetone. [i] From dichloromethane/methanol.

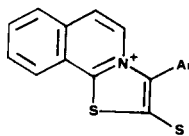


Figure 4

### Molecular Structure.

Figure 5 shows a perspective view of the compounds **11a** and **11j** computed from the final atomic coordinates, given with their ESDs in Table 3, showing the atomic numbering used in the crystallographic study. Bond lengths, and bond and torsion angles are given in Tables 4-6. As it can be seen there the O7, C6, C1, C2, S3 and S4 atoms appear as a fairly planar moiety since their maxi-

mum deviations are 0.028(8) and 0.027(4) Å in **11a** and **11j** respectively; hence, it is possible to consider a conjugated system which is corroborated by the following atomic distances:

a) The C6-O7 bond length (~1.25 Å) is longer than the C=O normal value (1.20 Å).

b) The C6-C1 and C1-C2 distances (~1.4 Å) are intermediate between a C-C (1.54 Å) and a C=C (1.33 Å).

c) The C-S distances (1.7 and 1.8 Å) are intermediate between a C-S and a C=S bond.

The aromatic rings are planar (average torsion angles: 1.67 and 1.42° in A and B rings of **11a**, and 0.94, 1.20 and 0.40° in A, B and C rings of **11j**). As expected, steric repulsion forces the rings A and B to tilt apart, so torsion angles through C6-C8 bond are 98.21(20)° in **11a** and 51.85(15)° in **11j**, all in good agreement with the lengths of C6-C8 bonds; also, the torsion angles through C1-N14 bonds are

Table 3a

Atomic Parameters for Non-hydrogen Atoms of **11a**.  
Coordinates and Thermal Parameters as  $U_{eq} = (1/3)$ ,  
 $\Sigma(U_{ij}A_i^*A_j^*A_iA_j\cos(A_iA_j)) \times 10^4$

Atom	X/A	Y/B	Z/C	$U_{eq}$
C1	0.5439(18)	0.3839(13)	0.1594(15)	37(6)
C2	0.6928(5)	0.4067(12)	0.2042(15)	34(5)
S3	0.7609(5)	0.4768(5)	0.3304(5)	50(2)
S4	0.8065(5)	0.3550(4)	0.1221(4)	47(2)
C5	0.9809(32)	0.4122(18)	0.1967(30)	56(11)
C6	0.4728(20)	0.3222(12)	0.0598(17)	40(6)
O7	0.5427(16)	0.2836(14)	-0.0065(15)	73(7)
C8	0.3102(19)	0.3011(13)	0.0274(17)	42(6)
C9	0.2173(20)	0.3412(20)	-0.0750(20)	58(8)
C10	0.0720(26)	0.3164(19)	-0.1115(19)	72(10)
C11	0.0184(24)	0.2469(17)	-0.0455(23)	57(9)
C12	0.1095(29)	0.2084(18)	0.0578(22)	61(10)
C13	0.2560(26)	0.2336(17)	0.0955(22)	60(9)
N14	0.4494(15)	0.4369(10)	0.2211(13)	35(5)
C15	0.3990(21)	0.5265(19)	0.1778(21)	52(7)
C16	0.3271(24)	0.5840(20)	0.2407(23)	62(9)
C17	0.3019(25)	0.5477(22)	0.3469(26)	67(10)
C18	0.3496(21)	0.4572(19)	0.3868(20)	51(8)
C19	0.4233(21)	0.4009(17)	0.3253(19)	53(8)

Table 3b

Atomic Parameters for Hydrogen Atoms of **11a**.  
Coordinates and Thermal Parameters as  
 $\exp(-8\pi^2U(\sin\theta/\lambda)^2) \times 10^3$

Atom	X/A	Y/B	Z/C	U
H51	1.04(2)	0.42(2)	0.17(2)	11(5)
H52	1.01(3)	0.38(3)	0.27(2)	16(11)
H53	0.96(2)	0.48(2)	0.17(2)	5(6)
H91	0.29(5)	0.39(4)	-0.16(3)	10(20)
H101	0.01(2)	0.32(1)	-0.18(1)	0(4)
H111	-0.07(2)	0.21(1)	-0.06(1)	0(4)
H121	0.09(2)	0.15(2)	0.09(2)	0(6)
H131	0.32(2)	0.20(1)	0.16(1)	0(4)
H151	0.45(2)	0.53(1)	0.14(2)	0(4)
H161	0.30(3)	0.65(3)	0.19(3)	12(10)
H171	0.27(3)	0.61(3)	0.37(3)	12(10)
H181	0.33(3)	0.43(2)	0.47(3)	5(12)
H191	0.46(3)	0.35(3)	0.36(2)	2(8)

90.59(27)° in **11a** and 76.16(15)° in **11j**.

In the pyridine ring, bond lengths are typical for an aromatic system, but the exocyclic C1-N14 bond could be considered long for a link between  $sp^2$  atoms. However, this can be explained by the rotation of ring A around this bond (Figure 5).

Table 3c

Atomic Parameters for Non-hydrogen Atoms of **11j**.  
Coordinates and Thermal Parameters as  $U_{eq} = (1/3)$ ,  
 $\Sigma(U_{ij}A_i^*A_j^*A_iA_j\cos(A_iA_j)) \times 10^4$

Atom	X/A	Y/B	Z/C	$U_{eq}$
C1	0.6072(2)	0.0665(4)	0.1344(2)	41(2)
C2	0.6153(2)	0.2029(4)	0.1156(2)	43(2)
S3	0.6679(1)	0.2403(1)	0.0930(1)	57(1)
S4	0.5665(0)	0.3349(1)	0.1170(1)	48(1)
C5	0.5906(3)	0.4868(5)	0.0895(3)	61(3)
C6	0.5658(2)	0.0250(4)	0.1575(2)	45(2)
O7	0.5267(1)	0.1092(3)	0.1554(2)	56(2)
C8	0.5676(2)	-0.1228(4)	0.1822(2)	46(2)
C9	0.6302(2)	-0.1920(5)	0.2480(3)	57(3)
C10	0.6285(3)	-0.3250(5)	0.2722(4)	73(4)
C11	0.5650(4)	-0.3915(6)	0.2315(4)	85(6)
C12	0.5029(4)	-0.3259(6)	0.1654(4)	83(5)
C13	0.5031(3)	-0.1914(5)	0.1406(3)	64(3)
N14	0.6416(1)	-0.0428(3)	0.1238(2)	42(2)
C15	0.7126(2)	-0.0582(4)	0.1819(2)	52(2)
C16	0.7458(2)	-0.1547(4)	0.1695(2)	49(2)
C17	0.7075(2)	-0.2374(4)	0.0952(2)	41(2)
C18	0.6341(2)	-0.2155(4)	0.0356(2)	45(2)
C19	0.6031(2)	-0.1208(4)	0.0512(2)	45(2)
C20	0.7427(2)	-0.3411(4)	0.0800(2)	45(2)
C21	0.8146(2)	-0.3330(5)	0.1231(3)	55(3)
C22	0.8467(3)	-0.4294(5)	0.1078(3)	66(3)
C23	0.8077(3)	-0.5351(5)	0.0494(3)	69(4)
C24	0.7368(3)	-0.5461(5)	0.0064(3)	72(4)
C25	0.7043(2)	-0.4491(5)	0.0212(3)	61(3)
O26	0.0000(0)	0.7898(9)	0.2500(0)	117(4)

Table 3d

Atomic Parameters for Hydrogen Atoms of **11j**.  
Coordinates and Thermal Parameters as  
 $\exp(-8\pi^2U(\sin\theta/\lambda)^2) \times 10^3$

Atom	X/A	Y/B	Z/C	$U_{eq}$
H51	0.577(2)	0.482(5)	0.029(3)	46(14)
H52	0.637(3)	0.510(6)	0.129(4)	60(17)
H53	0.564(2)	0.558(5)	0.085(3)	23(11)
H91	0.674(3)	-0.145(5)	0.282(3)	36(13)
H101	0.673(3)	-0.373(6)	0.315(4)	64(18)
H111	0.565(3)	-0.477(6)	0.249(4)	68(18)
H121	0.458(3)	-0.361(5)	0.135(3)	52(15)
H131	0.460(3)	-0.134(6)	0.095(4)	62(18)
H151	0.738(2)	0.004(4)	0.235(3)	28(10)
H161	0.796(2)	-0.167(4)	0.213(2)	18(10)
H181	0.608(2)	-0.270(4)	-0.015(3)	25(10)
H191	0.554(2)	-0.098(4)	0.010(3)	23(10)
H211	0.842(2)	-0.256(4)	0.162(2)	14(9)
H221	0.898(3)	-0.425(5)	0.138(3)	49(15)
H231	0.829(2)	-0.612(5)	0.037(3)	41(13)
H241	0.708(3)	-0.620(5)	-0.035(3)	53(14)
H251	0.656(2)	-0.453(4)	-0.008(3)	31(11)
H261	0.540(2)	0.281(4)	0.298(3)	0(8)

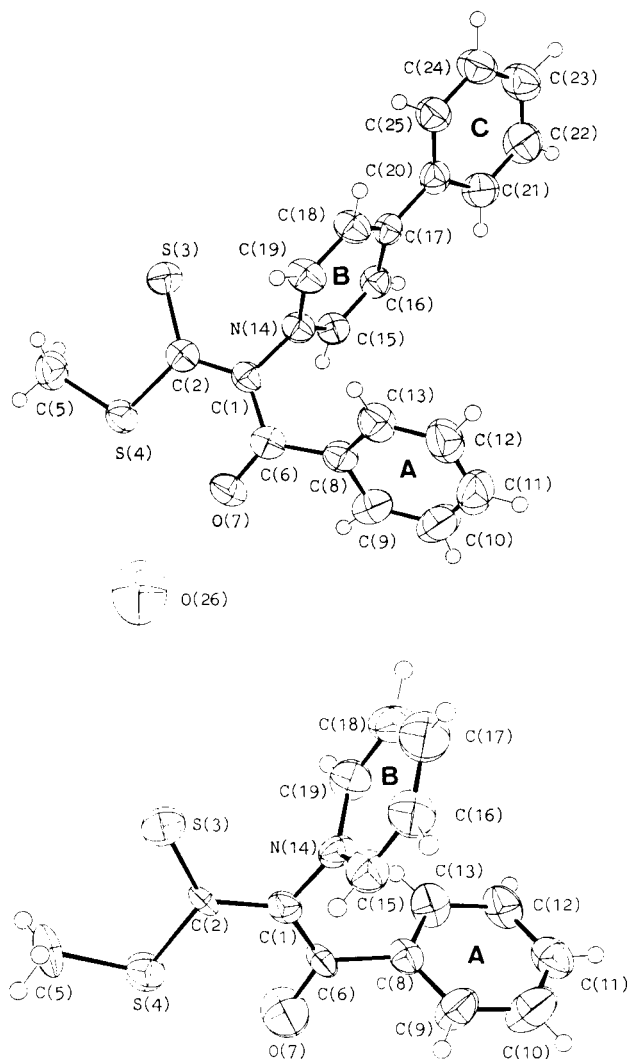


Figure 5

Table 4

Bond Distances (Å)

	11a	11j
C1 - C2	1.397(8)	1.414(5)
C1 - C6	1.413(9)	1.436(8)
C1 - N14	1.475(9)	1.455(6)
C2 - S3	1.684(7)	1.680(6)
C2 - S4	1.760(8)	1.766(5)
S4 - C5	1.810(6)	1.795(6)
C6 - O7	1.251(9)	1.244(6)
C6 - C8	1.512(8)	1.494(6)
C8 - C9	1.353(8)	1.394(5)
C8 - C13	1.391(10)	1.400(7)
C9 - C10	1.368(8)	1.378(8)
C10 - C11	1.392(11)	1.372(11)
C11 - C12	1.344(9)	1.373(8)

C12 - C13	1.380(8)	1.385(9)
N14 - C15	1.356(9)	1.350(4)
N14 - C19	1.361(9)	1.344(5)
C15 - C16	1.368(10)	1.366(7)
C16 - C17	1.379(10)	1.392(5)
C17 - C18	1.351(10)	1.402(5)
C18 - C19	1.359(10)	1.355(7)
C17 - C20		1.483(7)
C20 - C21		1.391(7)
C20 - C25		1.387(5)
C21 - C22		1.381(9)
C22 - C23		1.369(7)
C23 - C24		1.372(9)
C24 - C25		1.388(10)

Table 5

Bond Angles (°)

	11a	11j
C6 - C1 - N14	116.8(5)	117.6(3)
C2 - C1 - N14	114.4(6)	115.3(4)
C2 - C1 - C6	128.7(6)	127.0(4)
C1 - C2 - S4	115.7(5)	116.1(3)
C1 - C2 - S3	122.5(5)	122.9(3)
S3 - C2 - S4	121.8(4)	121.0(3)
C2 - S4 - C5	101.7(3)	101.9(3)
C1 - C6 - C8	122.0(6)	120.0(4)
C1 - C6 - O7	120.7(6)	121.3(4)
O7 - C6 - C8	117.3(6)	118.7(4)
C6 - C8 - C13	120.7(5)	118.1(4)
C6 - C8 - C9	120.1(6)	122.9(4)
C9 - C8 - C13	119.0(5)	118.9(4)
C8 - C9 - C10	120.9(6)	120.4(5)
C9 - C10 - C11	120.2(6)	120.4(5)
C10 - C11 - C12	119.2(6)	119.9(8)
C11 - C12 - C13	120.8(7)	120.8(7)
C8 - C13 - C12	119.9(6)	119.5(5)
C1 - N14 - C19	120.9(5)	119.5(3)
C1 - N14 - C15	118.5(5)	120.8(3)
C15 - N14 - C19	120.4(6)	119.4(4)
N14 - C15 - C16	120.9(6)	121.2(4)
C15 - C16 - C17	118.6(7)	120.9(4)
C16 - C17 - C18	119.6(7)	116.0(4)
C17 - C18 - C19	121.7(6)	121.3(4)
N14 - C19 - C18	118.8(6)	121.3(4)
C16 - C17 - C20		122.3(3)
C18 - C17 - C20		122.3(3)
C17 - C20 - C25		120.5(5)
C17 - C20 - C21		121.6(3)
C21 - C20 - C25		117.9(5)
C20 - C21 - C22		121.1(4)
C21 - C22 - C23		120.1(6)
C22 - C23 - C24		120.0(5)
C23 - C24 - C25		120.1(5)
C20 - C25 - C24		120.8(5)

Table 6  
Some Torsion Angles (°)

	<b>11a</b>	<b>11j</b>
C6 - C1 - N14 - C15	-90.0(7)	-109.8(5)
C2 - C1 - N14 - C15	86.3(7)	73.8(5)
C2 - C1 - C6 - O7	-4.2(11)	6.5(7)
C2 - C1 - C6 - C8	176.7(6)	-175.2(4)
C6 - C1 - C2 - S4	2.4(10)	-2.4(6)
C6 - C1 - C2 - S3	-176.2(6)	177.6(3)
C1 - C2 - S4 - C5	173.8(5)	-179.5(3)
S3 - C2 - S4 - C5	-7.6(5)	0.5(3)
C1 - C6 - C8 - C9	107.1(7)	54.5(6)
O7 - C6 - C8 - C9	-72.0(8)	-127.1(5)
C16 - C17 - C20 - C21		-19.8(7)
C16 - C17 - C20 - C25		160.7(5)

In compound **11j**, rings B and C are twisted with respect to each other by an angle of 19.6(1)°, so the conjugation should be diminished.

In all, both products show roughly similar bond lengths and angles, only C16-C17-C18 angle is smaller in **11j**, as a consequence of the phenyl group attached to C17 atom.

#### IR Spectra.

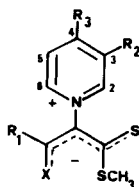
Data for the more characteristic ir bands of compounds **7** and **11** are given in Table 7 for comparison (ir data of compounds **7a**, **7d**, **7e**, **7h** have been previously described [31]). As it was revealed by X-ray diffraction all compounds **11** showed a delocalised  $\delta^- \text{O}^- \text{C}^- \text{C}^- \text{C}^- \text{S}^- \delta^-$  moiety which produce absorption bands, in potassium bromide disks, in around 1550 and 1365  $\text{cm}^{-1}$ .

Table 7  
IR Frequencies ( $\text{cm}^{-1}$ ) of the Compounds **7** and **11** [a]

Compound	Pyridinium/Isoquinolinium ring	C=O	Compound	Pyridinium/Isoquinolinium ring	C=C ylide band	C=O	C=S
<b>7a</b>	1635 s 1482 s	1695 vs	<b>11a</b>	1620 s 1460 s	1375 vs	1550 s	1020 m
<b>7b</b>	1610 vs 1485 s	1675 vs	<b>11b</b>	1600 vs 1460 s	1350 vs	1545 s	1027 m
<b>7c</b>	1635 vs 1488 s	1685 vs	<b>11c</b>	1620 s 1465 s	1350 vs	1550 s	1004 m
<b>7d</b>	1638 m 1574 s 1490 s	1697	<b>11d</b>	1625 s 1468 m	1360 vs	1554 s	1005 m
<b>7e</b>	1635 m 1485 s	1700 vs	<b>11e</b>	1625 s 1470 m	1360 vs	1550 s	1000 m 1013 m
<b>7f</b>	1630 s 1485 s	1700 vs	<b>11f</b>	1625 s 1468 s	1365 vs	1565 s	1007 m 1019 m
<b>7g</b>	1640 s 1635 s 1583 m 1495 vs	1750 vs	<b>11g</b>	1620 s 1465 m	1400 vs	1650 s	1002 m 1038 m
<b>7h</b>	1645 s 1502 s		<b>11h</b>	1616 s 1464 s	1320 vs		1005 m
<b>7i</b>	1615 s 1480 m	1700 vs 1690 vs	<b>11i</b>	1650 s	1375 vs	1700 s 1520 s	1021 m 1039 m
<b>7j</b>	1640 vs 1482 s	1692 vs	<b>11j</b>	1624 vs 1482 s	1350 vs	1545 s	1027 m
<b>7k</b>	1645 s 1460 m	1700 vs	<b>11k</b>		1635 s	1370 vs	1540 s 1019 m
<b>7l</b>	1645 s 1465 m	1735 vs	<b>11l</b>		1640 s 1445 s	1410 vs	1655 s 1054 m

[a] Determined in potassium bromide disk. Abbreviations: s, strong; m, medium; w, weak; v, very.

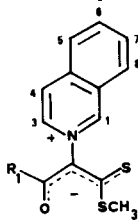
Table 8  
<sup>1</sup>H NMR of Compounds **11a-j** [a]



Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X	H <sub>2,6</sub>	H <sub>3,5</sub>	H <sub>4</sub>	SCH <sub>3</sub>	Others
<b>11a</b>	C <sub>6</sub> H <sub>5</sub> -	H	H	O	8.86 d <sup>3</sup> J = 5.8	7.83 t	8.34 t <sup>3</sup> J = 7.3	2.41 s	7.13 (bs, 5H, C <sub>6</sub> H <sub>5</sub> )
<b>11b</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	H	H	O	8.86 d <sup>3</sup> J = 5.5	7.86 t	8.37 t <sup>3</sup> J = 7.8	2.40 s	7.07 (d, 2H, <sup>3</sup> J = 8.6), 6.66 (d, 2H), 3.65 (s, 3H, CH <sub>3</sub> O)
<b>11c</b>	<i>o,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	H	H	O	8.76 d <sup>3</sup> J = 5.4	7.84 t	8.34 t <sup>3</sup> J = 7.4	2.38 s	6.89 (d, 1H, <sup>3</sup> J = 7.2), 6.86 (s, 1H), 6.68 (d, 1H), 2.22 (s, 3H), 2.14 (s, 3H)
<b>11d</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	H	H	O	8.87 d <sup>3</sup> J = 5.4	7.87 t	8.38 t <sup>3</sup> J = 7.8	2.41 s	7.34 (d, 2H, J = 8.5), 7.10 (d, 2H)
<b>11e</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	H	H	O	8.87 d <sup>3</sup> J = 5.7	7.87 t	8.37 t <sup>3</sup> J = 7.7	2.41 s	7.19 (s, 4H, C <sub>6</sub> H <sub>4</sub> )
<b>11f</b>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	H	H	O	8.93 d <sup>3</sup> J = 5.4	7.89 t	8.39 t <sup>3</sup> J = 7.8	2.43 s	8.01 (d, 2H, <sup>3</sup> J = 8.7), 7.45 (d, 2H)
<b>11g</b>	CH <sub>3</sub> O-	H	H	O	8.76 d <sup>3</sup> J = 5.5	8.01 t	8.51 t <sup>3</sup> J = 7.7	2.39 s	3.45 (s, 3H, CH <sub>3</sub> O)
<b>11h</b>	CH <sub>3</sub> S-	H	H	S	8.81 d <sup>3</sup> J = 5.3	8.10 t	8.63 t <sup>3</sup> J = 7.0	2.39 s [b]	
<b>11i</b>	C <sub>6</sub> H <sub>5</sub> -	CONH <sub>2</sub>	H	O	9.29 s 8.72 d <sup>3</sup> J = 8.19	7.98 t	9.03 t <sup>3</sup> J = 5.9	2.43 s	8.31 (s, 1H, NH), 7.95 (s, 1H, NH), 7.14 (bs, 5H, C <sub>6</sub> H <sub>5</sub> )
<b>11j</b>	C <sub>6</sub> H <sub>5</sub> -	H	C <sub>6</sub> H <sub>5</sub>	O	8.90 d	8.22 d		2.43 s	7.60-7.73 (m, 5H, C <sub>6</sub> H <sub>5</sub> ), 7.29 (bs, 5H, C <sub>6</sub> H <sub>5</sub> )

[a] Spectra recorded at 80 MHz in DMSO, TMS as internal reference, chemical shifts in  $\delta$  and coupling constants in Hz [b] Six protons from two equivalent methyl groups. [c] Abbreviations: d, doublet; s, singlet; t, triplet; b, broad.

Table 9  
<sup>1</sup>H NMR of Compounds **11k,l** [a]



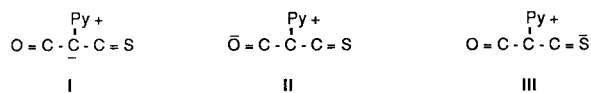
Compound	R <sub>1</sub>	H <sub>1</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5,6,7</sub>	H <sub>8</sub>	SCH <sub>3</sub>	Others
<b>11k</b>	C <sub>6</sub> H <sub>5</sub> -	10.00 s		8.23-8.45 m			2.44 s	7.04-7.13 (m, 5H, C <sub>6</sub> H <sub>5</sub> )
<b>11l</b> [b]	CH <sub>3</sub> O-	9.96 s	8.22 d <sup>3</sup> J = 7.5	7.87-7.92 m	8.08-8.10 m	8.16 d <sup>3</sup> J = 1.5	2.46 s	3.50 (s, 3H, OCH <sub>3</sub> )

[a] Notes and Abbreviations as in Table 8. [b] Spectra recorded at 360 MHz.

### <sup>1</sup>H and <sup>13</sup>C-NMR Spectra.

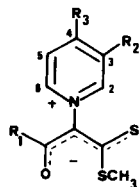
The <sup>1</sup>H-nmr data for compounds **11a-l** are presented in Tables 8 and 9. <sup>13</sup>C-nmr of **11a,e,g** and **j** are in Table 10. From both groups of data some considerations can be drawn:

a) As observed in the crystalline state, there is in solution a  $\pi$ -system which can be represented as **I-II-III** resonance hybrid, with a high contribution of **II**. The



chemical shift of carbonyl carbons (from about 191 to 196 ppm) are very much in the range of the chemical shifts found in planar  $\alpha,\beta$ -unsaturated ketones [33,32]. Similar effects can be observed in the carbons.

Table 10

<sup>13</sup>C-NMR of Compounds II [a]

Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	C <sub>2,6</sub>	C <sub>3,5</sub>	C <sub>4</sub>	C-S	SCH <sub>3</sub>	C	CO	C1'	Phenyl ring on R <sub>1</sub>			Others
												C2',6'	C3',5'	C4'	
<b>IIa</b>	C <sub>6</sub> H <sub>5</sub> -	H	H	150.19 d 'J = 195	126.98 d 'J = 171	146.17 d 'J = 173	179.56 s	18.47 q 'J = 139.4	134.67 d 'J = 2.3	195.8 s	141.38 s	126.06 d 'J = 159	127.79 'J = 160	128.54 'J = 161	
<b>IIe</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	H	H	150.07 d	127.06 d	145.26 d	178.16 s	18.33	133.17 s	196.45 s	140.23	128.11	127.79	134.44	
<b>IIg</b>	CH <sub>3</sub> O-	H	H	149.91 d	127.33 d	145.04 d	160.44 s	17.67 q		191.26					50.22 (CH <sub>3</sub> O-)
<b>IIj [b]</b>	C <sub>6</sub> H <sub>5</sub> -	H	C <sub>6</sub> H <sub>5</sub> -	150.10	123.11	153.98	179.60	18.38	133.93	195.94	141.46	126.21	127.86	128.50	133.27, 129.5, 127.72, 131.91 (C <sub>6</sub> H <sub>5</sub> in R <sub>3</sub> )

[a] Spectra recorded at 20 MHz unless otherwise stated, in DMSO, TMS as internal reference, chemical shifts in ppm (signals separated by less than 0.3 ppm could not be assigned with certainty). The coupling constants, in Hz, correspond to first order analysis of the spectrum. [b] Spectra recorded at 90 MHz.

Table 11

## Mass Spectra of Compounds II

Compound	m/e (relative intensity %)
<b>IIa</b>	287 (M <sup>+</sup> , 29), 240 (64), 161 (8), 133 (18), 105 (100), 89 (8), 80 (10), 79 (29), 78 (12), 77 (98), 53 (22), 52 (34), 51 (8)
<b>IIb</b>	317 (M <sup>+</sup> , 52), 271 (15), 270 (100), 191 (8), 163 (18), 153 (64), 92 (9), 77 (12)
<b>IIc</b>	315 (M <sup>+</sup> , 68), 300 (21), 269 (62), 268 (100), 189 (26), 188 (62), 161 (21), 133 (81), 105 (53), 80 (25), 79 (36), 77 (28)
<b>II d</b>	366 (M <sup>+</sup> , 29), 320 (65), 318 (59), 185 (94), 183 (100), 157 (71), 155 (75), 91 (55), 80 (61), 79 (65), 76 (82), 75 (63), 53 (65), 52 (45), 51 (57)
<b>IIe</b>	323 (25), 321 (M <sup>+</sup> , 61), 276 (50), 275 (21), 274 (100), 195 (18), 167 (31), 139 (67), 111 (44), 80 (17), 75 (18)
<b>II f</b>	332 (M <sup>+</sup> , 20), 285 (38), 150 (58), 104 (31), 95 (20), 81 (15), 80 (100), 79 (19), 77 (25), 53 (84), 52 (38), 51 (31)
<b>II g</b>	241 (M <sup>+</sup> , 47), 195 (35), 194 (100), 164 (35), 115 (29), 103 (52), 91 (41), 88 (41), 87 (33), 80 (33), 79 (43), 60 (33), 52 (26)
<b>II h</b>	273 (M <sup>+</sup> , 50), 260 (18), 258 (100), 147 (28), 115 (38), 103 (19), 102 (26), 100 (85), 91 (18), 88 (18), 79 (19), 52 (17)
<b>II j</b>	363 (M <sup>+</sup> , 31), 318 (10), 317 (25), 316 (100), 156 (12), 155 (16), 138 (18), 105 (39), 89 (10), 77 (49), 51 (16)
<b>II k</b>	337 (M <sup>+</sup> , 34), 292 (16), 291 (22), 290 (100), 133 (29), 130 (14), 129 (37), 128 (17), 195 (55), 102 (12), 77 (62), 52 (18), 41 (11)
<b>II l</b>	291 (M <sup>+</sup> , 10), 244 (100), 141 (23), 130 (21), 129 (69), 128 (36), 114 (18), 103 (26), 102 (31), 88 (36), 59 (23)

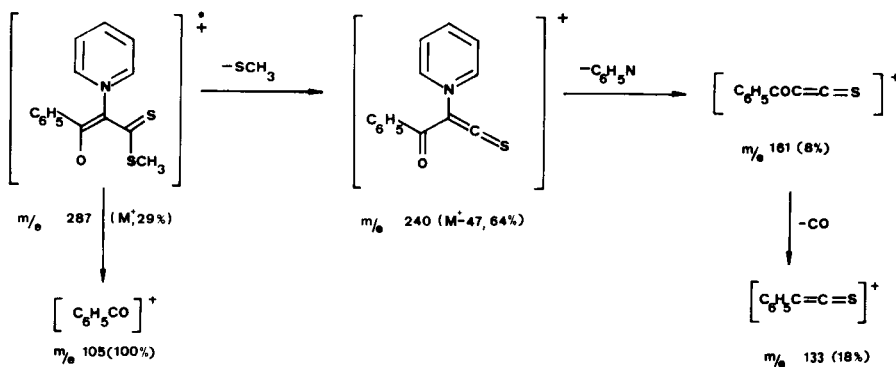


Fig. 6



b) From the  $\pi$ -system, a releasing  $\delta$ -electronic effect towards the pyridine and benzene rings is observed, as  $^{13}\text{C}$  chemical shifts of the pyridinium ring are intermediate between a typical pyridinium cation [32] and a pyridine system [34]. A similar effect is observed for  $^1\text{H}$ -nmr data. It seems doubtful that a conjugation effect could operate between the ylide moiety and the pyridinium ring as steric hindrance should prevent coplanarity, like in the crystalline state.

### Mass Spectra.

The mean features of the mass spectra of compounds **11a-h**,  $j-l$  are described in Table 11. The usual fragmentation pattern is shown, for compound **11a** in Figure 6, with a ( $\text{M}^+$ ) peak of medium intensity, and a ( $\text{M}^+ - 47$ ) which is one of the three most intense peaks of the spectrum. Loss of the heterocycle produces a small peak at  $m/e$  161 and CO extrusion produces another at  $m/e$  133. A similar sequence, together with the formation of the corresponding acylium cation can be observed in every example.

### Conclusions.

Several dithioester stabilized pyridinium ylides were obtained by the use of a biphasic system. The procedure is a superior, simple and mild alternative to classical homogeneous methods, with no traces of cycloadduct formation, even when isoquinolinium substrates are used.

From the structural study, all products show a delocalised  $\pi$ -excessive ylide moiety, approximately orthogonal (in the crystalline state and in solution) with the cycloimmonium ring. From nmr data, it seems that some electron density is transmitted through a  $\sigma$  bond, between both systems, diminishing the pyridinium  $\pi$ -deficient character.

## EXPERIMENTAL

### General.

The ir spectra were recorded on a Perkin-Elmer 599 spectrophotometer. Samples were compressed into potassium bromide pellets.

The  $^1\text{H}$ -nmr spectra were recorded on a Varian FT-80A (80 MHz) instrument. The  $^{13}\text{C}$ -nmr spectra were recorded on two spectrometers, a Varian FT-80A (20 MHz) and a Bruker WM360 (90 MHz). In all examples DMSO solutions were used, with TMS as internal reference. In  $^{13}\text{C}$  nmr measurements, broad band decoupled and SFORD spectra were obtained. For **11j**, proton coupled spectra were obtained.

Mass spectra were measured at 70 eV on a Hitachi Perkin-Elmer RM4-64. Spectra of solid samples were obtained by direct injection into the source at 250° with the probe at a temperature 20° below the melting points. All melting points were determined on a Buchi-Tottoli apparatus using open capillary tubes, and are uncorrected.

### General Procedure for Preparation of Cycloimmonium Salts 7.

a) Compounds **7a,b,d,e,f,g,h,i**, and **k** were obtained as described in the literature (see Table 1).

b) Compounds **7c** was obtained through an Ortoleva-King procedure [25].

c) Compounds **7j**, **7l** were obtained as follows: To a solution of pyridine or isoquinoline (0.2 mole) in acetone (50 ml) the  $\alpha$ -halocarbonyl compound  $\text{XCH}_2\text{COR}$  (0.2 mole) was added. The reaction mixture was heated

under reflux for 2 hours when  $\text{X} = \text{Br}$  or 20 hours when  $\text{X} = \text{Cl}$ . The cycloimmonium salt thus formed was filtered off and crystallized from ethanol (**7j**) or ethanol/ether (**7l**).

### Synthesis of Disubstituted Ylides 11.

To a suspension of 2 mmoles of starting pyridinium salts **7**, in 20 ml of aqueous 50% potassium carbonate, 20 ml of carbon disulfide and 0.25 ml of methyl iodide (4 mmoles) were added under vigorous stirring. The reaction mixture was stirred at room temperature for 20 hours. During the process a change in colour and formation of solid was observed. Finally, the precipitate was filtered, washed with water until alkalinity disappeared, dried and crystallized as described in Table 2.

### Crystallographic Studies.

Symmetry independent reflections of a single crystal were collected on an Enraf-Nonius CAD4 computer-controlled, four circle diffractometer with graphite-monochromated  $\text{MoK}\alpha = 0.7170 \text{ \AA}$  radiation.

The cell parameters of the two molecules **11a** and **11j** were obtained in each case from least-squares calculations of the setting angles of 25 reflections (Table 12).

Table 12

Crystal Data (ESDs in Parentheses Refer to the Last Significant Digit)

	<b>11a</b>	<b>11j</b>
Formula	$\text{C}_{15}\text{H}_{13}\text{S}_2\text{NO}$	$[\text{C}_{21}\text{H}_{17}\text{S}_2\text{NO}]_{1/2} \cdot \text{H}_2\text{O}$
Mw	287.394	380.499
Space Group	P21/c	C2/c
Z	4	8
Dc	1.357(4)	1.378(4)Mg/m <sup>3</sup>
F(000)	600	1592
$\lambda$	0.7107	0.7107 $\text{ \AA}$
$\mu$	0.3531	0.2922 mm <sup>-1</sup>
a	9.518(2)	24.867(5) $\text{ \AA}$
b	13.695(5)	9.591(2) $\text{ \AA}$
c	11.266(6)	20.237(4) $\text{ \AA}$
$\beta$	106.65(3)	130.54(2)°
V	1406.9(10)	3667.9(17) $\text{ \AA}^3$

The dimensions of the crystals used for X-ray structure analysis were 0.15 × 0.20 × 0.20 mm (**11a**) and 0.20 × 0.25 × 0.25 mm (**11j**). Intensity data were collected from the same diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation for  $2 < \theta < 30^\circ$ . W-20 scan technique was used. Two reflections were used as standard and remeasured after every 100 reflections; no decomposition was observed. Reflections measured were 4257 (**11a**) and 3222 (**11j**); 1578 (**11a**) and 2948 (**11j**) were considered as observed with  $I = 2\sigma(I)$ , being determined from counting statistics. Lorentz and polarization corrections were applied, but no correction was made for absorption.

The structures were solved by direct methods with MULTAN 80 [35]. In **11j** an E map generated from the phase set of 350 reflections with the highest combined figure of merit located 23 of the 25 molecular atoms; further Fourier synthesis revealed the two remaining atoms and one oxygen atom of a water molecule in special position on a twofold rotation axis. In **11j** the E map was generated from the phase set with 300 reflections, which located all molecular atoms. Further Fourier synthesis revealed that there are not other significant peaks.

After full-matrix least-squares refinements with isotropic and anisotropic temperature factor, the H atoms were located in a difference map. Further refinement with anisotropic temperature factor for non-hydrogen atoms and isotropic temperature factors for the H-atoms, reduced R to  $R = 0.062$  and  $R_w = 0.082$  for **11j**. The function minimized was  $\Sigma w(|F_o| - |F_c|)^2$  with  $W = K/\sigma^2$ ,  $\sigma = a + b(F_o)$  and  $K = 0.412$  (**11a**) (with  $a = 1.161$ ,  $b = -0.200$  when  $0.5 \leq F_o \leq 7.02$  and  $a = 5.58$ ,  $b = -0.396$

when  $F_o \geq 7.02$ , and  $K = 0.537$  (11j) (with  $a = 1.928$ ,  $b = 0.042$  when  $0.5 \leq F_o \leq 28.59$  and  $a = 0.997$ ,  $b = 0.019$  when  $F_o \geq 28.59$ ) [36].

A difference Fourier final map had all residual peaks less than  $0.23 \text{ eA}^{-3}$  in both structures. The scattering factors were taken from International Table for X-ray Crystallography (1974). The computations were made with programs of X-RAY 76 Systems [37], PARST [38] and on a VAX 11/750 computer.

#### Acknowledgements.

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