Restricted Rotation about the Carbon–Nitrogen Single Bond of 1-Aryl-4,6-dimethylpyrimidin-2(1*H*)-ones and the Corresponding Thiones

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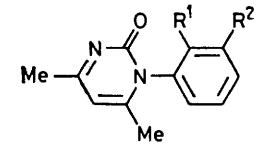
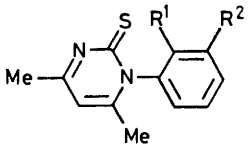
By recrystallizing the salts (3) and (4) with D-camphor-10-sulphonic acid, the rotational isomers due to restricted rotation about the carbon–nitrogen single bond in *ortho*-substituted-1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (1) and the corresponding thiones (2) were separated. The activation energies for the racemization of the pyrimidin-2(1*H*)-ones (1c and f) were found to be 31.8 and 34.0 kcal mol^{-1}, respectively and those of the pyrimidine-2(1*H*)-thiones (2c, d, and g) were 31.5, 30.1, and 31.1 kcal mol^{-1}, respectively.

MANY papers [1-9] have reported on the optical resolution of rotational isomers caused by restricted rotation about the carbon–carbon single bond, ever since the first example, the optical resolution of 6,6'-dinitrophenoic acid, was reported by Christie.[10] On the other hand, few papers [11] concerning restricted rotation about the carbon–nitrogen single bond have been reported. In



(1)



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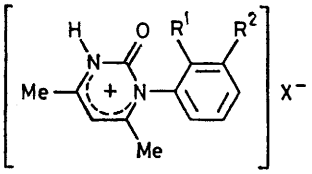

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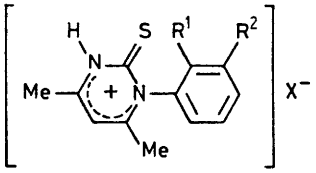

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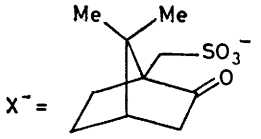


a, R^1 = H, R^2 = Me
b, R^1 = H, R^2 = OMe
c; R^1 = Me, R^2 = H
d; R^1 = Cl, R^2 = H
e; R^1 = OMe, R^2 = H
f, R^1 = Et, R^2 = H
g, R^1 = Me, R^2 = Cl

1931, Bock and Adams succeeded in separating the enantiomers of 1-(2-carboxyphenyl)-2,5-dimethylpyrrole-3-carboxylic acid by the formation of the brucine salt.[12,13] Recently, the barriers to hindered rotation around the *N*-glycosidic single bond were determined [14-16] by dynamic ^{1}H and ^{13}C n.m.r. spectroscopy and found to be 10—17 kcal mol^{-1}.

In the course of our studies on restricted rotation about the carbon–nitrogen single bond in aryl-substituted heterocyclic compounds, we investigated the structure and rotational isomerism around the carbon–nitrogen single bond of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (1) and the corresponding thiones (2). In the previous paper,[17] we reported that the 6-methyl protons of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (1) resonated at higher field due to the anisotropic effect of the aryl ring. This fact suggested that the pyrimidine ring was nearly perpendicular to the aryl ring in the most stable conformation. If the rotational barrier is $>ca.$ 23 kcal mol^{-1} at room temperature,[18] it should be possible to resolve the two rotational isomers, which are the result of restricted rotation about the carbon–nitrogen single bond between the aryl and the pyrimidine rings.

In this paper, we discuss the optical resolution of the enantiomers of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (1) and the corresponding thiones (2), and the magnitude of the rotational barrier.

RESULTS AND DISCUSSION

First we calculated the rotational barrier about the carbon–nitrogen single bond of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (1) by means of the Force-field method. In the case of 1-(*o*-tolyl)-4,6-dimethylpyrimidin-2(1*H*)-one (1c), the relation between dihedral angle (θ) about the carbon–nitrogen single bond and potential energy (*E*) is shown in Figure 1. From this calculation we found that the dihedral angle of the most stable conformation was 41°, and the rotational barrier was 39.5 kcal mol^{-1}. Furthermore, this result indicated that the repulsion between the 6-methyl group and the aryl-methyl group is much greater than that between the aryl-methyl group and the carbonyl oxygen. In the same way, the rotational barriers for the 1-(*o*-substituted)phenyl-4,6-dimethylpyrimidin-2(1*H*)-ones (1e and f) were calculated to be 30.2 and 42.5 kcal mol^{-1}, respectively. On the other hand, rotational barriers for the 1-(*m*-substituted)phenyl-4,6-dimethylpyrimidin-2(1*H*)ones (1a and b) were calculated to be 14.7 and 13.0 kcal mol^{-1}, respectively (see Table 1). From these calculated values, we predicted that the two rotational isomers of 1-(*o*-substituted)phenyl-4,6-dimethylpyrimidin-2(1*H*)-ones (and the corresponding thiones) should be separable, and this we attempted by the optical resolution method.

The racemic 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones

(1) and the corresponding thiones (2) were synthesized by the condensation of acetylacetone with *N*-arylureas [19] and *N*-arylthioureas,[20] respectively. The optically active pyrimidinones and pyrimidinethiones were obtained by recrystallization of the salts (3) and (4), which were formed from racemic pyrimidinones (1) and pyrimidinethiones (2) with D-camphor-10-sulphonic acid, followed by neutralization. The results are listed in Table 2. In the case of 1-(*o*-tolyl)-4,6-dimethylpyrimidin-2(1*H*)-one (1c) and the corresponding thione (2c), the absolute rotation was determined by means of the ^{1}H n.m.r. spectrum in the presence of the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-D-camphorato]europium(III) [Eu(tfc)$_3$]. These experimental results are in good agreement with our calculations based upon the Force-field method.

To clarify the relation between rotational barrier and the calculated values, the rate of racemization of optically active forms was studied. Arrhenius plots showed a good linear relation and the activation parameters were obtained (see Table 3).

The standard bond length of the C=O double bond is 1.22 Å, and that of the C=S double bond is 1.71 Å. The van der Waals radius of oxygen is 1.4 Å, and that of sulphur is 1.85 Å. From these facts the rotational barrier was expected to increase when a sulphur replaced oxygen; however, the rotational barrier of (2c) was found to be nearly equal that of (1c) (see Table 4).

TABLE 1

Rotational barriers calculated by the Force-field method

Compound	r [a]/Å	θ [b]/°	$E_{t.s.}$ [c] / kcal mol^{-1}	r [a]/Å	θ [b]/°	$E_{m.s.}$ [d] / kcal mol^{-1}	$\Delta H^{\ddagger}$ [e] / kcal mol^{-1}
(1a)	1.51	0	9.6	1.46	49	−5.1	14.7
(1b)	1.51	0	10.1	1.46	59	−2.9	13.0
(1c)	1.54	5.6	34.3	1.46	41	−5.2	39.5
(1e)	1.53	4.3	31.4	1.49	53	1.2	30.2
(1f)	1.56	7.3	37.6	1.47	42	−4.9	42.5

[a] C^7–N^1 Single-bond length. [b] Dihedral angle between C^2–N^1 and C^7–C^8 bond. [c] Potential energy in transition state. [d] Potential energy in the most stable conformation. [e] $\Delta H^{\ddagger} = E_{t.s.} - E_{m.s.}$

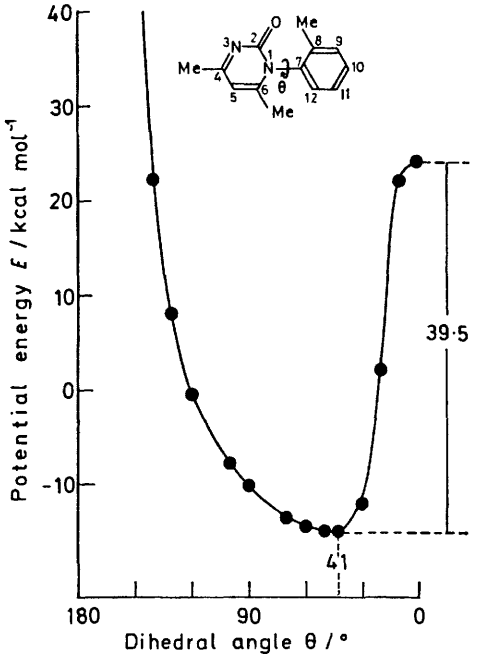


FIGURE 1 Potential energy of 4,6-dimethyl-1-*o*-tolyl-pyrimidin-2(1*H*)-one as a function of the dihedral angle θ

Stewart reported [21] that the rotational barrier about carbon–nitrogen single bonds for thioamides was 3—5 kcal mol^{-1} higher than for the corresponding amides, and this difference can be attributed to more single-bond character in the carbon–sulphur double bond in thioamides. Evidence for greater single-bond character in the carbon–sulphur double bond was observed in both the ^{1}H and ^{13}C n.m.r. spectrum of (2c), as shown in Table 4. The lower-field shifts of the signals of (2c) may be attributed to a larger anisotropic effect from the pyrimidine ring, which is caused by the contribution of the polarized form in Table 4. Furthermore, the greater single-bond character would probably promote bond bending, which will cause a decrease in the inter-atomic repulsion between the sulphur atom and the *ortho*-methyl group on the aryl ring.

TABLE 2

Specific rotation of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones and the corresponding thiones

Compound	Concentration [a]	$[\alpha]_D^{25}$/°
(1a)	0.6	0
(1b)	0.8	0
(1c)	0.6	−6.2 (−120) [b]
(1d)	0.8	−1.4
(1e)	0.8	+0.4
(1f)	0.5	+4.5
(2c)	1.0	−23.4 (−200) [b]
(2d)	1.9	+3.3
(2e)	2.2	+0.6
(2f)	1.1	−0.4
(2g)	1.0	+6.5

[a] Grams per 100 ml. [b] Absolute rotation.

TABLE 3

Activation parameters of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones and the corresponding thiones

Compound	E_a / kcal mol^{-1}	$\Delta G^{\ddagger}$ / kcal mol^{-1}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
(1c)	31.8	30.3	31.2 (39.5 *)	2.9
(1f)	34.0	30.2	33.3 (42.5 *)	8.0
(2c)	31.5	27.7	30.8	8.8
(2d)	30.1	26.6	29.4	7.9
(2g)	31.1	27.0	30.4	9.5

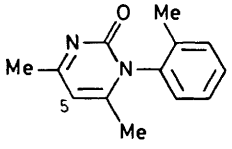
* Calculated value by means of the Force-field method.

EXPERIMENTAL

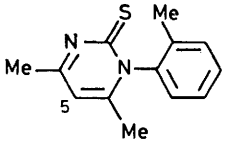
I.r. spectra were recorded on a Jasco ITA-1 i.r. spectrophotometer. Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on a Hitachi R-20 and a JEOL-100 n.m.r. spectrometer, respectively, using tetramethylsilane as an internal standard. Optical rotations were measured on a Union

TABLE 4

Spectroscopic data for (1c) and (2c)

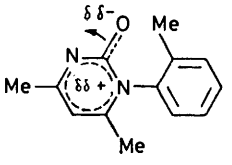


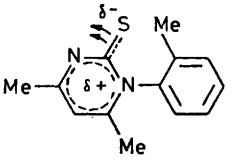
(1c)



(2c)

	(1c)	(2c)
δ_H(5-H)	6·22	6·56
δ_C(5-C)	105·3	111·2
$\Delta H^{\ddagger}$ kcal mol^{-1}	31·2 ± 0·7	30·8 ± 0·2





Polarized forms

OR-50 digital polarimeter. Absolute rotations were determined from the ^1H n.m.r. spectrum in the presence of the chiral shift reagent [Eu(tfc)$_3$], in deuteriochloroform containing dichloromethane as an internal standard.

Preparation of 1-*Aryl*-4,6-*dimethylpyrimidin*-2(1H)-*ones* (1) *and the Corresponding Thiones* (2).—*Method A*. To a solution of acetylacetone (40 mmol) and urea (34 mmol) in 95% ethanol (50 ml) was added concentrated hydrochloric acid (8.5 ml). The mixture was refluxed with stirring for 3 h. The reaction mixture was then neutralized with aqueous sodium hydroxide and extracted with dichloromethane. In this way were prepared 4,6-*dimethyl*-1-(m-*tolyl*)*pyrimidin*-2(1H)-*one* (1a) (from benzene–hexane); $\nu_{max.}$ (KBr) 1 660 cm^{-1}; δ ($CDCl_3$) 1.98 (3 H, d, *J* 0.7 Hz), 2.30 (6 H, s), 6.12 (1 H, q, *J* 0.7 Hz), and 6.9—7.4 (4 H, m): 1-(m-*methoxyphenyl*)-4,6-*dimethylpyrimidin*-2(1H)-*one* (1b) (from benzene); $\nu_{max.}$ (KBr) 1 655 cm^{-1}; δ ($CDCl_3$) 1.95 (3 H, d, *J* 0.7 Hz), 2.34 (3 H, s), 3.73 (3 H, s), 6.15 (1 H, q, *J* 0.7 Hz), and 6.6—7.4 (4 H, m): 4,6-*dimethyl*-1-(o-*tolyl*)*pyrimidine*-2(1H)-*thione* (2c) (from ethanol); δ ($CDCl_3$) 1.92 (3 H, d, *J* 0.7 Hz), 2.10 (3 H, s), 2.40 (3 H, s), 6.56 (1 H, q, *J* 0.7 Hz), and 7.1—7.4 (4 H, m): 1-(o-*chlorophenyl*)-4,6-*dimethylpyrimidine*-2(1H)-*thione* (2d) (from ethanol); δ ($CDCl_3$) 1.98 (3 H, d, *J* 0.7 Hz), 2.40 (3 H, s), 6.55 (1 H, q, *J* 0.7 Hz), and 7.2—7.6 (4 H, m): 1-(o-*methoxyphenyl*)4,6-*dimethylpyrimidine*-2(1H)-*thione* (2e) (from ethyl acetate); δ($CDCl_3$) 2.00 (3 H, d, *J* 0.7 Hz), 2.40 (3 H, s), 3.73 (3 H, s), 6.22 (1 H, q, *J* 0.7 Hz), and 7.1—7.4 (4 H, m): 1-(o-*ethylphenyl*)-4,6-*dimethylpyrimidine*-2(1H)-*thione* (2f) (from ethyl acetate); δ ($CDCl_3$) 1.19 (3 H, t, *J* 7.0 Hz), 1.94 (3 H, d, *J* 0.7 Hz), 2.40 (3 H, s), 2.42 (2 H, q, *J* 7.0 Hz), 6.22 (1 H, q, *J* 0.7 Hz), and 7.1—7.5 (4 H, m): and 1-(2-*methyl*-3-*chlorophenyl*)-4,6-*dimethylpyrimidine*-2(1H)-*thione* (2g) (from ethanol); δ ($CDCl_3$) 1.95 (3 H, d, *J* 0.7 Hz), 2.10 (3 H, s), 2.40 (3 H, s), 6.58 (1 H, q, *J* 0.7 Hz), and 7.1—7.4 (3 H, m).

Method B. The solution of acetylacetone (0.14 mol) and urea (0.12 mol) in distilled benzene (100 ml) was heated to reflux. After reflux, concentrated sulphuric acid (13 ml) was added dropwise to the solution cautiously. After another 5 h refluxing, the reaction mixture was neutralized with aqueous sodium hydroxide, extracted with dichloromethane, and dried over magnesium sulphate. The resulting viscous oil was chromatographed on silica gel with chloroform–acetone–ethanol (100 : 20 : 4). In this way were prepared 4,6-*dimethyl*-1-(o-*tolyl*)*pyrimidin*-2(1H)-*one* (1c) (from benzene–hexane); $\nu_{max.}$ (KBr) 1 650 cm^{-1}; δ ($CDCl_3$) 1.95 (3 H, d, *J* 0.7 Hz), 2.16 (3 H, s), 2.48 (3 H, s), 6.22 (1 H, q, *J* 0.7 Hz), and 7.1—7.3 (4 H, m): 1-(o-*chlorophenyl*)-4,6-*dimethylpyrimidin*-2(1H)-*one* (1d) (from benzene–hexane); $\nu_{max.}$ (KBr) 1 660 cm^{-1}; δ ($CDCl_3$) 2.03 (3 H, d, *J* 0.7 Hz), 2.48 (3 H, s), 6.28 (1 H, q, *J* 0.7 Hz), and 7.2—7.5 (4 H, m): 1-(o-*methoxyphenyl*)-4,6-*dimethylpyrimidin*-2(1H)-*one* (1e) (from benzene–hexane); $\nu_{max.}$ 1 660 cm^{-1}; δ ($CDCl_3$) 1.98 (3 H, d, *J* 0.7 Hz), 2.38 (3 H, s), 3.72 (3 H, s), 6.17 (1 H, q, *J* 0.7 Hz), and 6.7—7.4 (4 H, m): 1-(o-*ethylphenyl*)-4,6-*dimethylpyrimidin*-2(1H)-*one* (1f) (from benzene–hexane); $\nu_{max.}$ (KBr) 1 645 cm^{-1}; δ ($CDCl_3$) 1.18 (3 H, t, *J* 6.0 Hz), 1.89 (3 H, d, *J* 0.7 Hz), 2.40 (3 H, s), 2.43 (2 H, q, *J* 6.0 Hz), 6.12 (1 H, q, *J* 0.7 Hz), and 7.0—7.4 (4 H, m). Analytical data are presented in Table 5.

TABLE 5

Analytical data of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones and the corresponding thiones

			Analysis (%)					
			Found			Required		
Compound	Yield (%)	M.p. (°C)	C	H	N	C	H	N
(1a)	74	215—216	73.1	6.50	13.15	72.87	6.58	13.07
(1b)	42	195	68.0	6.0	12.25	67.80	6.12	12.16
(2c)	89	197 (decomp.)	67.8	6.15	12.2	67.79	6.12	12.16
(2d)	83	139 (decomp.)	57.5	4.3	10.9	57.48	4.42	11.17
(2e)	86	163 (decomp.)	63.35	5.7	11.6	63.38	5.72	11.37
(2f)	85	196 (decomp.)	68.85	6.6	11.45	68.81	6.60	11.46
(2g)	55	191 (decomp.)	59.05	4.8	10.9	58.97	4.94	10.58
(1c)	21	132—133	72.6	6.4	13.1	72.87	6.58	13.07
(1d)	12	103—105	61.6	4.65	12.05	61.41	4.72	11.93
(1e)	14	186—187	67.85	6.15	12.2	67.81	6.12	12.17
(1f)	21	133	73.45	7.0	12.15	73.65	7.06	12.27

Formation of Pyrimidinium Salts with D-*Camphor*-10-*sulphonic Acid*.—*General procedure*. The mixture of 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-one (8.2 mmol) with D-camphor-10-sulphonic acid (8.2 mmol) in ethanol (20 ml) was refluxed for 1 h with vigorous stirring. The solvent

was evaporated off and the crude product was recrystallized from an appropriate solvent. In this way were prepared 4,6-*dimethyl*-2-*oxo*-1-(m-*tolyl*)-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (3a) (from ethyl acetate–hexane); $\nu_{max.}$ (KBr) 3 440, 1 730, and 1 625 cm^{-1}; δ ($CDCl_3$) 0.82 (3 H, s), 1.10 (3 H, s), 2.28 (3 H, s), 2.33 (3 H, s), 2.77 (3 H, s), 6.83 (1 H, s), and 7.1—7.3 (4 H, m): 1-(m-*methoxyphenyl*)-4,6-*dimethyl*-2-*oxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (3b) (from ethanol–hexane); $\nu_{max.}$ (KBr) 3 450, 1 735, and 1 620 cm^{-1}; δ ($CDCl_3$) 0.82 (3 H, s), 1.10 (3 H, s), 2.30 (3 H, s), 2.77 (3 H, s), 3.80 (3 H, s), 6.80 (1 H, s), and 7.2—7.3 (4 H, m): 4,6-*dimethyl*-2-*oxo*-1-(o-*tolyl*)-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (3c) (from ethyl acetate–hexane); $\nu_{max.}$ (KBr) 3 470, 1 740, and 1 620 cm^{-1}; δ ($CDCl_3$) 0.80 (3 H, s), 1.08 (3 H, s), 2.08 (3 H, s), 2.22 (3 H, s), 2.78 (3 H, s), 6.58 (1 H, s), and 7.2—7.4 (4 H, m): 1-(o-*chlorophenyl*)-4,6-*dimethyl*-2-*oxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (3d) (from ethanol–ethyl acetate); $\nu_{max.}$ (KBr) 3 450, 1 735, and 1 620 cm^{-1}; δ ($CDCl_3$) 0.79 (3 H, s), 1.05 (3 H, s), 2.25 (3 H, s), 2.77 (3 H, s), 6.78 (3 H, s), and 7.3—7.5 (4 H, m): 1-(o-*methoxyphenyl*)-4,6-*dimethyl*-2-*oxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (3e) (from ethyl acetate–hexane); $\nu_{max.}$ (KBr) 3 450, 1 735, and 1 610 cm^{-1}; δ ($CDCl_3$) 0.80 (3 H, s), 1.10 (3 H, s), 2.25 (3 H, s), 2.76 (3 H, s), 3.80 (3 H, s), 6.78 (1 H, s), and 7.0—7.4 (4 H, s): 1-(o-*ethylphenyl*)-4,6-*dimethyl*-2-*oxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (3f) (from ethyl acetate–hexane); $\nu_{max.}$ (KBr) 3 450, 1 730, and 1 615 cm^{-1}; δ ($CDCl_3$) 0.80 (3 H, s), 1.07 (3 H, s), 1.13 (3 H, t, *J* 7.0 Hz), 2.18 (3 H, s), 2.75 (3 H, s), 6.87 (1 H, s), 7.2—7.5 (4 H, m), and 10.97 (1 H, br s): 4,6-*dimethyl*-2-*thioxo*-1-(o-*tolyl*)-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (4c) (from ethyl acetate—hexane); $\nu_{max.}$ (KBr) 3 460 and 1 735 cm^{-1}; δ ($CDCl_3$) 0.82 (3 H, s), 1.10 (3 H, s), 2.13 (3 H, s), 2.28 (3 H, s), 2.90 (3 H, s), 7.2—7.6 (5 H, m), and 12.80 (1 H, br s): 1-(o-*chlorophenyl*)-4,6-*dimethyl*-2-*thioxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (4d) (from ethanol–hexane); $\nu_{max.}$ (KBr) 3 440, and 1 740 cm^{-1}; δ ($CDCl_3$) 0.80 (3 H, s), 1.07 (3 H, s), 2.27 (3 H, s), 2.83 (3 H, s), 6.97 (1 H, s), 7.3—7.8 (4 H, m), and 12.72 (1 H, br s): 1-(o-*methoxyphenyl*)-4,6-*dimethyl*-2-*thioxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (4e) (from ethyl acetate—hexane); $\nu_{max.}$ (KBr) 3 430 and 1 740 cm^{-1}; δ ($CDCl_3$) 0.82 (3 H, s), 1.10 (3 H, s), 2.30 (3 H, s), 2.85 (3 H, s), 3.83 (3 H, s), 7.1—7.6 (5 H, m), and 12.72 (1 H, br s): 1-(o-*ethylphenyl*)-4,6-*dimethyl*-2-*thioxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (4f) (from ethyl acetate–hexane); $\nu_{max.}$ (KBr) 3 450 and 1 740 cm^{-1}; δ ($CDCl_3$) 0.82 (3 H, s), 1.08 (3 H, s), 1.20 (3 H, t, *J* 7.0 Hz), 2.27 (3 H, s), 2.88 (3 H, s), 7.26 (1 H, s), 7.3—7.5 (4 H, m), and 12.25 (1 H, br s): and 1-(2-*methyl*-3-*chlorophenyl*)-4,6-*dimethyl*-2-*thioxo*-1,2-*dihydropyrimidinium* D-*camphor*-10-*sulphonate* (4g) (from ethanol–ethyl acetate); $\nu_{max.}$ (KBr) 3 440 and 1 735 cm^{-1}; δ ($CDCl_3$) 0.82 (3 H, s), 1.08 (3 H, s), 2.15 (3 H, s), 2.28 (3 H, s), 2.88 (3 H, s), 7.28 (1 H, s), 7.3—7.6 (3 H, s), and 12.17 (1 H, br s). Analytical data for these compounds are presented in Table 6.

TABLE 6

Analytical data of pyrimidinium salts

			Analysis (%)					
			Found			Required		
Compound	Yield (%)	M.p. (°C)	C	H	N	C	H	N
(3a)	98	206 (decomp.)	61.85	6.8	6.05	61.86	6.77	6.27
(3b)	97	179 (decomp.)	59.8	6.3	5.8	59.72	6.53	6.05
(3c)	90	217 (decomp.)	52.2	6.8	5.9	61.86	6.77	6.27
(3d)	92	213 (decomp.)	56.5	5.85	5.9	56.58	5.82	6.00
(3e)	95	200 (decomp.)	59.5	6.35	6.1	59.72	6.53	6.05
(3f)	98	182—183	62.45	6.85	5.85	62.58	7.00	6.08
(4c)	90	227 (decomp.)	60.05	6.55	6.15	59.71	6.53	6.05
(4d)	94	225 (decomp.)	54.7	5.5	5.85	54.70	5.63	5.79
(4e)	88	202 (decomp.)	57.8	6.25	5.9	57.71	6.31	5.85
(4f)	96	206 (decomp.)	60.6	6.65	5.9	60.47	6.76	5.87
(4g)	89	218 (decomp.)	55.5	5.8	5.70	55.07	5.88	5.63

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