Protonation of 2,7-Di-t-butylthiepines. The First Observation of Homothiopyrylium Ions

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The protonated species, generated from 2,7-di-t-butylthiepine and its 4-methyl and 4,5-dimethyl derivatives with fluorosulphuric acid–SO_2 and /or concentrated sulphuric acid, have been shown by ^1H n.m.r. examination to possess homothiopyrylium ion structures.

The concept of homoaromaticity originally proposed by Winstein is one of the most stimulating guiding principles in organic chemistry.[1] Despite many investigations on the carbocyclic homoaromatic ions, heterocyclic homoaromatic species have not been unequivocally identified.[2] Although some derivatives of the homopyrylium ion isoelectronic with the well documented homotropylium ion[3] have been proposed as reaction intermediates,[4] no direct observation of such heterohomoaromatic ions has been reported. This paper describes the generation and characterisation of the as yet unknown homothiopyrylium ions (**2**).

In view of the precedent that on protonation cyclooctatetraene is easily converted into the homotropylium ion,[5] stable 2,7-di-t-butylthiepine (**1a**),[6] and its 4-methyl (**1b**),[7] and 4,5-dimethyl derivatives (**1c**)[7] were expected to be promising candidates for the formation of the homothiopyrylium ions, (**2a**), (**2b**), and (**2c**), respectively. Such is indeed the case.

Treatment of a CD_2Cl_2 solution (0.2 ml) of (**1a**) (5 mg) with an SO_2 solution (0.2 ml) containing FSO_3H (2—3 drops) in an n.m.r. tube at −78 °C gave the opened 2,7-di-t-butyl-3,5-homothiopyrylium ion (**2a**) (as an orange solution). Evidence for the structure (**2a**) was obtained from its ^1H n.m.r.

Table 1. 100 MHz ^{1}H N.m.r. data for the homothiopyrylium ions (**2a**), (**2b**), and (**2c**).[a]

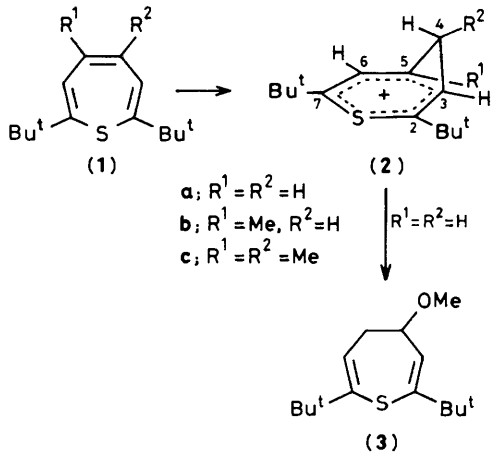
	2-CMe_3	7-CMe_3	3-H	(4o)-H	(4i)-H	5-H	6-H	4-Me	5-Me
(**2a**)[b]	1.26(s)[d]	1.52(s)[d]	6.10(dd)	3.81(ddd)	1.31(m)	7.17(ddd)	7.65(d)		
					2.66(br. s)[c]				
			$J_{3,4o} = J_{3,4i} = 7.5$, $J_{4o,4i} = 11.6$, $J_{5,6} = 9.4$, $J_{5,4i} = 8.6$, $J_{5,4o} = 8.4$						
(**2b**)[b]	1.23(s)	1.49(s)	6.05(dd)	3.75(dd)	1.66(m)		7.61(s)		2.58(s)
				$J_{3,4o} = J_{3,4i} = 7.6$, $J_{4i,4o} = 9.2$					
(**2c**)[c]	1.31(s)	1.57(s)	5.66(d)		1.68(br. s)[e]		7.63(s)	1.68(br. s)[e]	2.57(s)
					$J_{3,4} = ca.\ 6$				

[a] Chemical shifts are in p.p.m. relative to Me_4Si, using $\delta_{CDHCl_2}(Me_4Si) = 5.30$, coupling constants are in Hz. [b] In FSO_3H–SO_2–CD_2Cl_2 at −70 °C. [c] In 97% H_2SO_4 at room temperature. [d] Assignments were made by nuclear Overhauser enhancements of 2- and 7-t-butyl protons (17% and 8.9%) with 3-H and 6-H, respectively. [e] Averaged chemical shift.

Table 2. ^{13}C N.m.r. data for the homothiopyrylium ions (**2a**), (**2b**), and (**2c**).[a]

	2-CMe_3	7-CMe_3	C-2	C-3	C-4	C-5	C-6	C-7	4-Me	5-Me
(**2a**)	28.9 39.8	29.6 46.4	162.5	144.7	31.4	130.1	120.7	216.0		
(**2b**)	30.5 40.4	31.6 48.4	179.0	131.6	29.9	157.4	128.1	218.5		40.3
(**2c**)	29.9 39.7	31.0 46.8[b]	180.6	131.3	24.2	157.2	130.4	212.0	14.3	44.8[b]

[a] Chemical shifts are in p.p.m. relative to Me_4Si, using $\delta_{CH_2Cl_2}(Me_4Si) = 53.8$ p.p.m., in 97% H_2SO_4 at room temperature. [b] Assignment may be reversed.



spectrum measured at −70 °C, as summarized in Table 1, which indicates charge delocalisation [the average shift of protons 3-H, 5-H, and 6-H in (**2a**) was δ 7.01]. The striking features of the spectrum were a fairly large chemical shift difference (Δδ = 2.5 p.p.m.)† between methylene protons, (4o)-H and (4i)-H, and the *geminal* coupling constant of 11.6 Hz for these protons.

The same ion (**2a**) was also formed when (**1a**) was dissolved in concentrated H_2SO_4. The ^{1}H n.m.r. spectrum of this solution at room temperature showed essentially the same signals except that the resonance for the methylene protons appeared at δ 2.66 as a broad singlet. Apparently, the ^{1}H n.m.r. spectrum of (**2a**) is temperature dependent and at −20 °C in FSO_3H–SO_2–CD_2Cl_2 the methylene proton signals at δ 1.31 and 3.81 became broad and at 0 °C in the same solvent these signals almost disappeared. The process is reversible, since lowering the temperature of the solution to −70 °C regenerated the original signals. The coalescence temperature was found to be *ca.* 7 °C in H_2SO_4. The analysis of these spectra afforded a value of $\Delta G^{\ddagger}$ for the ring flipping process of 13.0 kcal/mol‡ (1 kcal = 4.18 kJ).

Quenching of the H_2SO_4 solution of (**2a**) with a mixture of MeOH and $NaHCO_3$ at −30 °C gave 2,7-di-t-butyl-4-methoxy-4,5-dihydrothiepine (**3**), a pale yellow oil: *m/z* 254 (M^+), 223 (M^+ − OMe), calc. for $C_{15}H_{26}OS$ *m/z* 254.1702, found *m/z* 254.1675; δ (^{1}H, 100 MHz, $CDCl_3$) 1.15 (9H, s), 1.19 (9H, s), 2.55—2.70 (2H, m), 3.38 (3H, s), 4.29 (1H, ddd, *J* 8.3, 6.0, 3.9 Hz), 5.84 (1H, t, *J* 6.3 Hz), 5.88 (1H, d, *J* 3.9 Hz), indicating the retention of the seven-membered ring skeleton during the protonation of (**1a**). These findings together with the ^{13}C n.m.r. data (see Table 2)§ are well in accord with a homothiopyrylium ion formulation such as (**2a**).

On protonation either in FSO_3H–SO_2–CD_2Cl_2 or concentrated H_2SO_4, methyl substituted thiepines (**1b**) and (**1c**) were also converted into the corresponding homothiopyrylium

† The chemical shift difference between the outer and the inner protons [Δδ = δ(4o)-H − δ(4i)-H] for the 'frozen-out' ion (**2a**) was about one half of the corresponding value for the homotropylium ion (Δδ = 5.77 p.p.m.).[1a] The possible explanations for this difference are that (i) the bent angle of C-4 in (**2a**) is smaller than that of C-8 in the homotropylium ion, as a result (4i)-H is located in a weaker shielding region of the homothiopyrylium ring current, (ii) the area of the ring of (**2a**) is smaller than that of the homotropylium ion, (iii) the effectiveness of 6π electron delocalisation in (**2a**) is smaller than that in the homotropylium ion because the unfavourable 2p–3p overlap is involved in the former molecule.

‡ This value is intermediate between 22.3 and 8.4 kcal/mol (1 kcal = 4.18 kJ) for those of the homotropylium ion (S. Winstein, *J. Am. Chem. Soc.*, 1959, **81**, 6524) and the homocyclopropenium ion (G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *J. Am. Chem. Soc.*, 1975, **97**, 5489), respectively.

§ Substantially large downfield chemical shifts observed for C-2 and C-7 in (**2a**), (**2b**), and (**2c**) are attributed to the t-butyl substitution (D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 499) and can be compared to the difference in chemical shift between 2,6-di-t-butylthiopyrylium ion (δ 186.7 for C-2 and C-6) and the parent thiopyrylium ion (δ 159.6 for C-2 and C-6). K. Yamamoto, S. Yamazaki, H. Ohsedo, and I. Murata, unpublished result.

ions, (**2b**) and (**2c**), respectively, as evidenced by their ^{1}H and ^{13}C n.m.r. spectra (see Tables 1 and 2). It should be noted that the protonation of (**1a**), (**1b**), and (**1c**) occurred regiospecifically at the 5-positions.¶ To our knowledge this is the first observation of six-membered heterohomoaromatic cations.

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¶ Owing to the different numbering system of (**1**) and (**2**), protonation at C-5 in (**1**) is shown to give the 4*H* ions (**2**). Although in (**1a**) and (**1c**) positions 4 and 5 are equivalent, (**1b**) does protonate at C-5 and not C-4.