Two New Heteroaromatic Cations: Furo[2,3-*c*]thiapyrylium and Furo-[3,2-*c*]thiapyrylium Perchlorates (1).

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Following previous work on cation systems in which the thiapyrylium ring is condensed with heterocyclic rings (2-4), in this note we report the synthesis of the two isomeric furothiapyrylium cations (I) and (II) as the first examples of a new class of heteroaromatic systems having 10 π electrons (Figure 1).

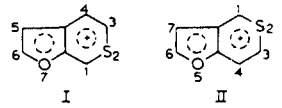
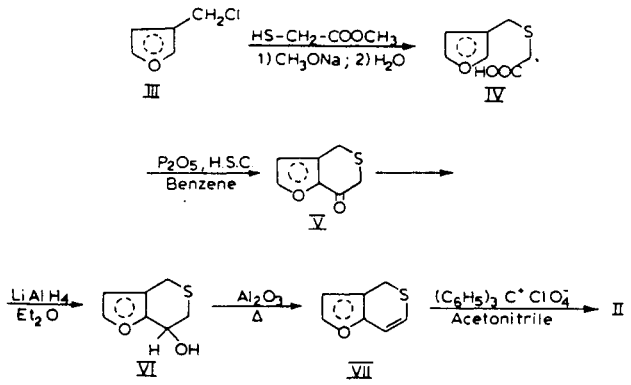


Figure 1. Two New Heteroaromatic Cations: Furo-[2,3-*c*]thiapyrylium and Furo[3,2-*c*]thiapyrylium.

Furo[2,3-*c*]thiapyrylium (I) and furo[3,2-*c*]thiapyrylium (II) were prepared by means of synthesis patterns that differed only in certain details from those reported for the corresponding thienothiapyrylium cations (4). Synthetic sequence leading to cation II is shown in Scheme 1.



Scheme 1. Two New Heteroaromatic Cations: Furo[2,3-*c*]thiapyrylium and Furo[3,2-*c*]thiapyrylium.

In the same way, cation I was obtained *via* the following intermediates: 3,4-dihydro-1*H*-furo[2,3-*c*]thiopyran-4-one (VIII) (5), 3,4-dihydro-1*H*-furo[2,3-*c*]thiopyran-4-ol (IX), 1*H*-furo[2,3-*c*]thiopyran (X), furo-[2,3-*c*]thiapyrylium (I).

All the intermediates are stable, apart from VII and X which readily decompose and should be aromatised to salts as soon as possible. However, these may be kept cold and in absence of air for a few days (VII) or hours (X).

Cations I and II were isolated as perchlorates. They remain stable for months if protected from the atmospheric moisture; their nmr spectra were consistent with the assigned structures. In fact, in the nmr spectra of I and II in deuterotrifluoroacetic acid, all five proton resonances are well separated and integrated for one proton each; these are unambiguously assignable also on the basis of preceding assignments for comparable systems containing the thiapyrylium ring (4,6a-f). The coupling constants also corroborate the assignments reported in Table 1.

In the case of cation I, the lowest field resonance at 10.40 δ assigned to H-1, is split into a doublet with a coupling constant of 3.1 Hz, which must be due to coupling with the H-3 through sulphur, as previously observed for similar systems (4,6). This doublet is further complicated by a small long-range constant with the β-furan proton ($J_{1,5}$ = 1.0 Hz). The H-4 resonance occurs at 9.45 δ as a doublet with a splitting of 9.1 Hz, due to coupling with H-3. Each doublet line in the band of the latter H-3 at 9.72 δ, is split into a doublet with a splitting of 3.1 Hz. Lastly, the furan proton resonances occur as an AB spectrum at 7.95 and 9.17 δ, with a splitting of 2.2 Hz. The doublet at 7.95 δ (assigned to H-5) is further complicated by the long-range coupling constant with H-1. An equally satisfactory interpretation can be found for the nmr spectrum for cation II (see Table 1).

EXPERIMENTAL

3-Furylmethylthioacetic Acid (IV).

A mixture of 10.60 g. (0.1 mole) of methyl mercaptoacetate and 11.65 g. (0.1 mole) of 3-furylmethyl chloride (7) was refluxed for 6 hours in a solution of sodium methoxide prepared from 2.76 g. (0.12 g.-atoms) of sodium and 150 ml. of methanol. Part of the solvent was evaporated *in vacuo*, the residue was diluted with 150 ml. of 3% sodium hydroxide and refluxing was continued for an additional hour. After extraction with ether, the solution was acidified and extracted again with ether, which was then dried and evaporated. The residue was 13.93 g. (yield 81%) of IV, m.p. 43-44° from hexane; nmr (carbon tetrachloride): 11.16 δ (s, 1, COOH); 7.31 and 6.31 (two m, 1:2, H furo); 3.63 and 3.05 (two s, 2:2, 2 CH_2).

Table 1

Nmr Data for I and II (a)

Compound	Chemical Shifts (δ) (b)						Coupling Constants (Hz)					
	H-1	H-3	H-4	H-5	H-6	H-7	J_{13}	J_{15}	J_{34}	J_{47}	J_{56}	J_{67}
I	10.40 d (c)	9.72 dd	9.45 d	7.95 d (c)	9.17 d		3.1	1.0	9.1		2.2	
II	10.41 d	9.70 dd	9.01 d (d)		8.41 d	7.55 d (d)	3.3		9.5	0.9		2.4

(a) The nmr spectra were recorded on a "Jeol" INM-MN-60 II spectrometer in deuterotrifluoroacetic acid with tetramethylsilane as internal reference. (b) Multiplicity as d, dd, for doublet and doublet of doublets, respectively. (c) Further complicated by the long-range J_{15}. (d) Further complicated by the long-range J_{47}.

Anal. Calcd. for $C_7H_8O_3S$: C, 48.83; H, 4.68; S. 18.62. Found: C, 48.93; H, 4.78; S, 18.75.

3,4-Dihydro-1*H*-furo[3,2-*c*]thiopyran-4-one (V).

A stirred mixture of 5.0 g. of 3-furylmethylthioacetic acid, 10 g. of phosphorus pentoxide and 5.0 g. of Hyflo Super Cell was refluxed for 4 hours in 150 ml. of dry benzene. Then an additional 10 g. of phosphorus pentoxide was added and the mixture was refluxed and stirred for a further 4 hours. The benzene solution was separated and the residue was extracted several times with boiling benzene. The benzene extracts were washed with a solution of 5% sodium hydroxide and then with water. The solvent was evaporated and the residue was chromatographed through silica gel with benzene-ether (97:3) as eluant, to give 2.28 g. (yield 51%) of V, m.p. 45-46° from hexane; nmr (carbon tetrachloride): 7.58 and 6.45 δ, AB system (2 H furo; J = 2.2 Hz); 3.77 and 3.40 (two s, 2:2, 2 CH_2).

Anal. Calcd. for $C_7H_6O_2S$: C, 54.53; H, 3.92; S, 20.80. Found: C, 54.45; H, 4.01; S, 20.73.

3,4-Dihydro-1*H*-furo[3,2-*c*]thiopyran-4-ol (VI).

To a stirred soluiton of 3.08 g. (20 mmoles) of V in 300 ml. of dry ether, 0.38 g. (10 mmoles) of lithium aluminum hydride was added over a period of 10 minutes. The mixture was stirred for an additional 20 minutes and then cautiously decomposed with water. The ether solution was evaporated to dryness to give 2.90 g. (yield 93%) of VI, m.p. 53-54° from hexane; nmr (carbon tetrahcloride + deuterium oxide): 7.30 and 6.20 δ, AB system (2H furo; J = 2.2 Hz); 4.65 (t, 1, CHOH; J = 4.5); two m centered at 3.53 and 2.98 (2:2, 2 CH_2).

Anal. Calcd. for $C_7H_8O_2S$: C, 53.83; H, 5.16; S, 20.53. Found: C, 53.93; H, 5.21; S, 20.41.

3,4-Dihydro-1*H*-furo[2,3-*c*]thiopyran-4-ol (IX).

This was prepared as described above from 3.08 g. of 3,4-dihydro-1*H*-furo[2,3-*c*]thiopyran-4-one (5) and 0.38 g. of lithium aluminum hydride. The yield was 2.86 g. (92%), b.p. 103-104°/0.5 mm Hg; nmr (carbon tetrachloride + deuterium oxide): 7.22 and 6.38 δ: AB system (2H furo; J = 2.2 Hz); 4.65 (t, 1, CHOH, J = 4.5); two m centered at 3.42 and 2.72 (2:2, 2 CH_2).

Anal. Calcd. for $C_7H_8O_2S$: C, 53.83; H, 5.16; S, 20.53. Found: C, 53.95; H, 5.26; S, 20.48.

1*H*-Furo[3,2-*c*]thiopyran (VII).

A mixture of 2.0 g. of VI and 3.0 g. of aluminum oxide was heated in a Claisen flask *in vacuo* (60 mm), by gradually raising the bath temperature to 200-210° during an hour, and left at this temperature for 20 minutes. Then, cautiously, the pressure was lowered to 30 mm. 1*H*-Furo[3,2-*c*]thiopyran (0.90 g., yield 51%) distilled quickly, b.p. 119-120°/30 mm Hg; nmr (carbon tetrachloride): 7.30 and 6.30 δ, AB system (2H furo; J = 2.2), 6.35 and 5.92, AB system (2H ethylenic; J = 9.7), 4.15 (s, 2H methylenic).

Anal. Calcd. for C_7H_6OS: C, 60.87; H, 4.35; S, 23.19. Found: C, 60.95; H, 4.29; S, 23.29.

1*H*-Furo[2,3-*c*]thiopyran (X).

A mixture of 2.0 g. of IX and 2.0 g. of aluminum oxide was heated, as described above, in a Claisen flask *in vacuo* (40 mm), by gradually raising the bath temperature to 165-170°, and left at this temperature for 10 minutes. Then, cautiously, the pressure was lowered to 4 mm. 1*H*Furo[2,3-*c*]thiopyran (1.01 g., yield 57%) distilled quickly, b.p. 95-96°/0.4 mm Hg; nmr (carbon tetrachloride): 7.30 and 6.30 δ, AB system (2H furo; J = 2.2 Hz), 6.62 and 6.18, AB system (2H ethylenic; J = 9.7), 4.19 (s, 2H methylenic).

Anal. Calcd. for C_7H_6OS: C, 60.87; H, 4.35; S, 23.19. Found: C, 60.75; H, 4.43; S, 23.10.

Furo[3,2-*c*]thiapyrylium Perchlorate (II).

A solution of 0.28 g. (2 mmoles) of VII in 2 ml. of acetonitrile was added dropwise to an ice-cold solution of 0.68 g. (2 mmoles) of trityl perchlorate in the same solvent. The reaction was immediate and the salt was at once precipitated by dry ether. The yield was 74%. The perchlorate was recrystallized from acetonitrile-ether, and decomposed at 222°; uv (96% sulfuric acid): 235 nm (log ε = 4.53), 270 (3.44), 319 (3.30).

Anal. Calcd. for $C_7H_5ClO_5S$: C, 35.52; H, 2.11; S, 13.53. Found: C, 35.63; H, 2.06; S, 13.60.

Furo[2,3-*c*]thiapyrylium Perchlorate (I).

This was prepared in the same way from 0.28 g. of X and 0.68 g. of trityl perchlorate in acetonitrile. The yield was 80%. The perchlorate obtained was recrystallized from acetonitrile-ether and decomposed at 210°; uv (96% sulfuric acid): 241 nm (log ε = 3.88), 289 (3.93), 338 (4.10).

Anal. Calcd. for $C_7H_5ClO_5S$: C, 35.52; H, 2.11; S, 13.53. Found: C, 35.45; H, 2.17; S, 13.61.

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(1) This work has been supported by the National Research Council (CNR).

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