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HETEROCYCLIC SYSTEMS CONTAINING BRIDGEHEAD NITROGEN ATOMS.
PART LXVIII. REACTION OF 5-FLUOROBENZIMIDAZOLYL-2-THIONE WITH
CHLOROACETIC ACID : STUDIES OF ORIENTATION OF CYCLIZATION IN THE
SYNTHESES OF 6-FLUORO- AND 7-FLUOROTHIAZOLO[3,2-a]BENZIMIDAZOL-
3(2H)-ONES

H.K. PUJARI*, B.R. SHARMA, RAJENDER DAHIYA and SUDHIR KUMAR

Department of Chemistry, Kurukshetra University,
Kurukshetra - 132 119 (India)

YASUOKI MURAKAMI* and MASANOBU TANI

School of Pharmaceutical Science, Toho University,
2-2-1, Miyama, Funabashi, Chiba 274 (Japan)

SUMMARY

4-Fluoroaniline on successive acetylation, nitration and hydrolysis affords 4-fluoro-2-nitroaniline which on reduction with Raney nickel and hydrazine hydrate followed by treatment of the resulting diamine with carbon disulphide in situ gives 5-fluorobenzimidazolyl-2-thione. The thione on condensation with chloroacetic acid yields [(5-fluoro-2-benzimidazolyl)-thio]acetic acid which on cyclization in a mixture of acetic anhydride and pyridine furnishes two isomers viz. 6-fluoro- and 7-fluorothiazolo[3,2-a]benzimidazol-3(2H)-ones. The condensation of thione with 1,2-dibromoethane affords sym-bis-(5-fluorobenzimidazo-2-yl-mercapto)ethane. The structural assignments for the 6-fluoro- and 7-fluorothiazolo[3,2-a]benzimidazol-3(2H)-ones have been made by ¹H NMR spectral data using two different methods.

* Authors for correspondence.

INTRODUCTION

In continuation of our work aimed towards the studies of orientation of cyclization by determining the directive influence of fluorine atoms on cyclization, we reported that the cyclization of [(4-fluoro-2-benzimidazolyl)thio]acetic acid yielded 8-fluorothiazolo[3,2-a]benzimidazol-3(2H)-one and not 5-fluorothiazolo[3,2-a]benzimidazol-3(2H)-one [1]. On the other hand, the cyclization of [(5-fluoro-2-benzimidazolyl)thio]acetic acid furnished both 6-fluoro- and 7-fluorothiazolo[3,2-a]benzimidazol-3(2H)-ones which forms the subject matter of the present communication.

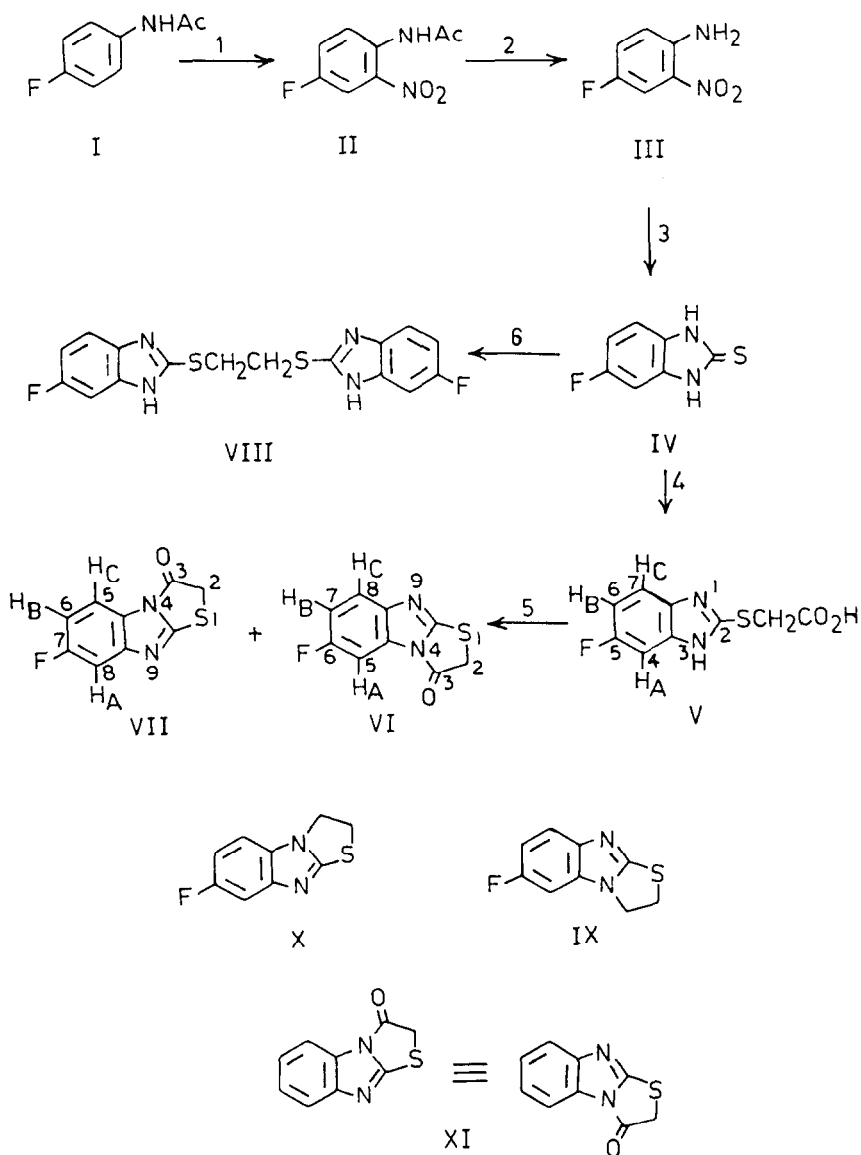
Murakami and co-workers [2,3] obtained the cyclized products (VI and VII; $\text{CH}_3, \text{OCH}_3, \text{NO}_2, \text{Cl}$ or Br in place of F) from the respective acids (V; $\text{CH}_3, \text{OCH}_3, \text{NO}_2, \text{Cl}$ or Br in place of F). Their structural assignment to the individual isomers was based on the downfield shift of $\text{C}_5\text{-H}$ compared to that of the corresponding protons of the acids. The Indian workers, on the other hand, assigned the correct structure (VI; OCH_3 in place of F) [4], (VII; Br in place of F) [5] and (VI and VII; Br in place of F and OCH_3 in place of H_B) [6] to the cyclized products obtained from the corresponding acids on the basis of comparative studies of the observed chemical shift and calculated chemical shifts of the aromatic protons. The calculated chemical shifts of the aromatic protons were derived by taking into consideration the shielding (or deshielding) effect of the substituents on the chemical shifts of the corresponding protons of the parent compound (XI). We report herein that the structural assignment of VI and VII obtained by the cyclization of V has been secured by the application of both the methods, thus indicating that the first method used by the Japanese workers and the second by the Indian workers are complementary to each other.

RESULTS AND DISCUSSION

4-fluoroaniline on successive acetylation, nitration and hydrolysis afforded 4-fluoro-2-nitroaniline (III) via 4-fluoroacetanilide (I) and 4-fluoro-2-nitroacetanilide (II). III on

reduction with Raney nickel and hydrazine hydrate followed by treatment of the resulting diamine with carbon disulphide in situ gave 5-fluorobenzimidazolyl-2-thione (IV). The thione (IV) when condensed with chloroacetic acid yielded [(5-fluoro-2-benzimidazolyl)thio]acetic acid (V). The acid (V) being unsymmetrical on cyclization was expected to give 6-fluorothiazolo[3,2-a]benzimidazol-3(2H)-one (VI) or 7-fluorothiazolo[3,2-a]benzimidazol-3(2H)-one (VII) or both depending upon the direction of cyclization (Scheme). The acid (V), whose structure was characterized by IR, ^1H NMR and ^{19}F NMR (see Experimental), in the presence of a mixture of acetic anhydride and pyridine underwent cyclization to furnish both the isomers (VI and VII). The products were purified to a mixture by short column chromatography and ^1H NMR spectroscopy used for estimation of their ratios. The signals arising from each aromatic proton of each component have almost the same intensity, showing that the ratio of VI:VII is 1:1. The mixture was impossible to separate into the two compounds, the 6-fluoro- (VI) and 7-fluorothiazolo[3,2-a]benzimidazol-3(2H)-ones (VII) by column chromatography as shown by their proximity on TLC. A part of them was, however, separated by repeated flash column chromatography on silica gel for characterization of VI and VII as colourless prisms - one melts at $176-178^\circ$ and the other at $180-182^\circ$. The observation of a band at 1735 cm^{-1} ($>\text{N}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}=\text{O}$) in the IR spectrum and a molecular ion peak $[\text{M}]^+$ at m/z 208 (100%) in the mass spectrum of the compound of m.p. $176-178^\circ$ suggested that cyclization had indeed occurred. Similarly, the band at 1730 cm^{-1} ($>\text{N}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}=\text{O}$) and a molecular ion peak $[\text{M}]^+$ at m/z 208 (100%) observed in the IR and mass spectra respectively of the second compound of m.p. $180-182^\circ$ corroborated the cyclic nature of the compound. The structure (direction of cyclization) of thiazolidinones (VI and VII) thus obtained was finally determined as follows by ^1H NMR according to our previous papers[2-6].

All the aromatic protons of the acid (V) and the thiazolidinones (VI and VII) were assigned easily on the basis of coupling patterns of each protons as shown in Table 1. As fluorine also couples with protons, all protons have coupling constants, $J_{\text{H-H}}$ and $J_{\text{H-F}}$. As the reported $J_{\text{H-F}}$ (ortho) and $J_{\text{H-F}}$



1. Conc. HNO₃, conc. H₂SO₄; 2. 35% H₂SO₄; 3. i. Raney nickel, H₂NNH₂·H₂O; ii. CS₂, KOH; 4. ClCH₂CO₂H; 5. Ac₂O, pyridine; 6. BrCH₂CH₂Br

Scheme

TABLE 1

^1H NMR spectral data of aromatic protons of V, VI and VII in DMSO- d_6 (δ , ppm) (400 MHz)

Structure	Chemical shifts (J, Hz)				
	$\text{C}_4\text{-H}$	$\text{C}_5\text{-H}$	$\text{C}_6\text{-H}$	$\text{C}_7\text{-H}$	$\text{C}_8\text{-H}$
V	H_A , 7.26 (dd , $J=3$ and 10Hz)	-	H_B , 6.97 (ddd , $J=3, 9$ and 10Hz)	H_C , 7.42 (dd , $J=5$ and 9Hz)	-
VI	-	H_A , 7.65 (dd , $J=3$ and 8Hz)	-	H_B , 7.25 (ddd , $J=3, 9$ and 10Hz)	H_C , 7.62 (dd , $J=5$ and 9Hz)
VII	-	H_C , 7.85 (dd , $J=5$ and 9Hz)	H_B , 7.18 (ddd , $J=3, 9$ and 10Hz)	-	H_A , 7.49 (dd , $J=3$ and 10Hz)

(meta) coupling constants are 6-10 and 5-6 Hz respectively [7], the values in Table 1 are reasonable. Tables 2 and 3 show the difference in the values of aromatic protons between the thiazolidinones (VI and VII) and the corresponding protons of the acid (V). The most downfield shifted proton of each thiazolidinones (VI and VII) must be due to $\text{C}_5\text{-H}$. From this result we assigned their structures as illustrated in the scheme. The shift values of $\text{C}_5\text{-H}$ δ 0.39 and δ 0.43 found in case of VI and VII respectively (vide Tables 2 and 3) tally well with the shift value, ca δ 0.40 reported earlier [2] in similar systems.

The same conclusion was also arrived at from the comparison of observed and calculated chemical shifts of the cyclized products. The calculated chemical shifts of the aromatic protons in VI and VII were derived by taking into consideration the shielding effect of the fluorine atom (fluorine shields ortho and meta-protons by δ 0.30 and 0.02 respectively) [8] on the values of the corresponding protons of the parent compound (XI). In the ^1H NMR spectrum (DMSO- d_6 , 400 MHz) of XI, the signals at δ 7.87,

TABLE 2

Proton shifts* (δ values) of 6-fluorothiazolo[3,2-a]benzimidazol-3(2H)-one (VI) from the corresponding protons of the acid (V), ^1H NMR, 400 MHz, in DMSO-d_6

Structures		Chemical shifts of protons		
VI	7.65($\text{C}_5\text{-H}$) (H_A)	7.25($\text{C}_7\text{-H}$) (H_B)	7.62($\text{C}_8\text{-H}$) (H_C)	
V	7.26($\text{C}_4\text{-H}$) (H_A)	6.97($\text{C}_6\text{-H}$) (H_B)	7.42($\text{C}_7\text{-H}$) (H_C)	
Shift value		0.39	0.28	0.20

* Protons at C_4^- , C_6^- and C_7^- positions in V correspond to the C_5^- , C_7^- and C_8^- protons in VI respectively.

TABLE 3

Protons shifts* (δ values) of 7-fluorothiazolo[3,2-a]benzimidazol-3-(2H)-one (VII) from the corresponding protons of the acid (V), ^1H NMR, 400 MHz, in DMSO-d_6

Structures		Chemical shifts of protons		
VII	7.85($\text{C}_5\text{-H}$) (H_C)	7.18($\text{C}_6\text{-H}$) (H_B)	7.49($\text{C}_8\text{-H}$) (H_A)	
V	7.42($\text{C}_7\text{-H}$) (H_C)	6.97($\text{C}_6\text{-H}$) (H_B)	7.26($\text{C}_4\text{-H}$) (H_A)	
Shift value		0.43	0.21	0.23

* Protons at C_4^- , C_6^- and C_7^- positions in V correspond to the C_8^- , C_6^- and C_5^- protons in VII respectively.

7.38, 7.32 and 7.60 were assigned to $\text{C}_5\text{-H}$, $\text{C}_6\text{-H}$ (or $\text{C}_7\text{-H}$), $\text{C}_7\text{-H}$ (or $\text{C}_6\text{-H}$) and $\text{C}_8\text{-H}$ protons respectively. The most downfield resonance of $\text{C}_5\text{-H}$ was due to the deshielding effect on this proton by the carbonyl group of the thiazolidinone ring. This deshielding effect has its origin in the magnetic anisotropy of the carbonyl group with little contribution from rest of the ring. In our scheme of calculation only $\text{C}_5\text{-H}$ and $\text{C}_8\text{-H}$ protons of the

cyclized products are involved. If the structure VI is correct, then the calculated chemical shifts for C_5-H (H_A) and C_8-H (H_C) would be δ 7.57 (7.87 - 0.30) and 7.58 (7.60 - 0.02) respectively (Set-A). On the other hand, if the structure VII is correct the calculated values for C_5-H (H_C) and C_8-H (H_A) would be 7.85 (7.87 - 0.02) and 7.30 (7.60 - 0.30) respectively (Set-B). The observed 1H NMR signals of the cyclized product of m.p. 176-178° at δ 7.65 and 7.62 may be due to C_5-H (H_A) and C_8-H (H_C) protons respectively (Set-C) if the structure VI is correct. On the other hand, the observed 1H NMR signals at δ 7.65 and 7.62 may be due to C_8-H (H_A) and C_5-H (H_C) protons respectively (Set-D), if the structure VII is correct. Since the Set-A is very close to Set-C and Set-B does not tally with Set-D (Table 4), the structure VI is assigned to the compound having m.p. 176-178°.

TABLE 4

Observed and calculated chemical shifts (in δ , ppm) for the aromatic protons in XI and the cyclized products VI and VII (for compound m.p. 176-178°), 1H NMR, 400 MHz, in DMSO- d_6

Structure	C_5-H		C_8-H	
	Calc.	Obs.	Calc.	Obs.
XI	-	7.87	-	7.60
VI	7.57	7.65	7.58	7.62
VII	7.85	7.62	7.30	7.65

Similarly the observed 1H NMR signals of the cyclized product of m.p. 180-182° at δ 7.85 and 7.49 may be due to C_5-H (H_C) and C_8-H (H_A) protons respectively (Set E) if the structure VII is correct. On the other hand, the observed 1H NMR signals at 7.85 and 7.49 may be due to C_8-H (H_C) and C_5-H (H_A) protons respectively (Set-F), if the structure VI is correct. Since Set-B is closer to Set-E than Set-A to Set-F (Table 5), the cyclized compound of m.p. 180-182° must be represented by structure VII.

TABLE 5

Observed and calculated chemical shifts (in δ , ppm) for the aromatic protons in XI and the cyclized products VI and VII (for compound m.p.180-182°), ^1H NMR, 400 MHz, in DMSO-d_6

Structure	$\text{C}_5\text{-H}$		$\text{C}_8\text{-H}$	
	Calc.	Obs.	Calc.	Obs.
XI	-	7.87	-	7.60
VI	7.57	7.49	7.58	7.85
VII	7.85	7.85	7.30	7.49

[(4-Fluoro-2-benzimidazolyl)thio]acetic acid on cyclization gives only one isomer [1] whereas [(5-Fluoro-2-benzimidazolyl)thio]acetic acid on cyclization yields two isomers. A rational explanation for the apparent anomaly is given as follows. In the former case the preferred cyclization takes place at the nitrogen meta with respect to fluorine and not at the nitrogen ortho to fluorine in order to avoid the steric hindrance exerted by the substituent. On the other hand, in the latter case in which there is a lack of such steric hindrance the cyclization can take place at both the nitrogen atoms of the benzimidazole ring and it is indeed found resulting in the synthesis of both isomers in a 1:1 ratio.

The reaction of thione (IV) with 1,2-dibromoethane yielded a product whose elemental analysis showed the participation of 1 mole of 1,2-dibromoethane and 2 moles of IV. The appearance of a band at 3040 cm^{-1} (NH) in the IR spectrum and one singlet at δ 3.68 integrated for four methylene protons, one multiplet at δ 6.98 and two doublets of doublet at 7.26 and 7.43 each integrated for two aromatic protons in the ^1H NMR spectrum and the molecular ion peak $[\text{M}]^+$ at m/z 362 in the mass spectrum was consistent with the bis-structure (VIII) and not with the cyclized structures (IX or X). The ^{19}F NMR showed two singlets at -122.7 and -124.0 ppm, which may be due to two conformers although its ^1H NMR showed a normal pattern as a single compound.

At the present moment, this phenomenon in the ^{19}F NMR of compound VIII is not properly explainable.

EXPERIMENTAL

Melting points were determined in conc. sulphuric acid bath and on a Yanagimoto micro melting hot stage apparatus and are uncorrected. IR spectra (ν_{max} in cm^{-1}) were recorded in Nujol mulls on a Shimadzu IR-400 and Beckmann IR-20 spectrophotometers. ^1H NMR spectra were recorded on Perkin-Elmer R-32 (90 MHz) and JEOL GX-400 (400 MHz) spectrometer with tetramethylsilane as an internal reference (chemical shifts in δ , ppm). ^{19}F NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer with C_6F_6 as an external reference at room temperature. Mass spectra were scanned with a JEOL JMS D-300 spectrometer using a direct inlet system at 70 eV. For column chromatography, Merck Silica gel 60 (70-230 mesh for short column, and 230-400 mesh for flash column chromatography) were used, while for TLC, Merck Silica Gel 60 F_{254} was used. For the check of separation of the two products (VI and VII), TLC and Hitachi 635A liquid chromatographs [Column: Waters Radial Pack Silica ($5\ \mu\text{m}$) ($8\times 100\ \text{mm}$), wavelength; 295 nm, solvent; n -hexane : AcOEt = 2:1] were used.

4-Fluoroacetanilide (I)

I was prepared in 73% yield by acetylation of 4-fluoroaniline with a mixture of glacial acetic acid and acetic anhydride following the method of Milos [9], m.p. 150° (Lit. [9], m.p. $150.5\text{--}151.5^\circ$).

4-Fluoro-2-nitroacetanilide (II)

A mixture of conc. HNO_3 (18 ml) and conc. H_2SO_4 (15 ml) was added slowly to a solution of 4-fluoroacetanilide (I; 20.0 g) in conc. H_2SO_4 (40 ml) at $0\text{--}3^\circ$. The reaction mixture was then poured into ice-cold water (250 ml). The yellow slurry, thus obtained, was filtered, washed well with water and air dried, m.p. 71° (Lit. [10] m.p. 71.5°).

Hydrolysis of 4-fluoro-2-nitroacetanilide (II) : Preparation of 4-fluoro-2-nitroaniline (III)

4-Fluoro-2-nitroaniline (III) was prepared by heating 4-fluoro-2-nitroacetanilide (II; 25 g) with 35% H_2SO_4 (125 ml) at 100° for about one h. The reaction mixture was diluted with 400 ml of water and heated till the solution became clear. Neutralization with dilute ammonia gave III as orange prisms, which was filtered, washed well with water and dried, m.p. 92° (Lit. [9] m.p. $90-92^\circ$).

5-Fluorobenzimidazolyl-2-thione (IV)

IV was prepared by the reduction of III with Raney nickel and hydrazine hydrate followed by the reaction of the resulting diamine with carbon disulphide in situ following the method of Van Allan and Deacon [11] for the synthesis of benzimidazolyl-2-thione, m.p. 280° (EtOH), IR: 1632 (C=N), 3050-3160 (NH); ^1H NMR (90 MHz) (TFA): 7.36 (m, 2H, $\text{C}_4\text{-H}$ and $\text{C}_6\text{-H}$), 7.70 (dd, 1H, $\text{C}_7\text{-H}$, $J^{1\text{H}-^{19}\text{F}}(\text{meta}) = 5 \text{ Hz}$, $J^{1\text{H}-^{19}\text{F}}(\text{ortho}) = 9 \text{ Hz}$); Analysis: Found: S, 19.1. $\text{C}_7\text{H}_5\text{FN}_2\text{S}$ requires S, 19.04%.

[(5-Fluoro-2-benzimidazolyl)thio]acetic acid (V)

A mixture of IV (1.68 g, 0.01 mol), chloroacetic acid (0.94 g, 0.01 mol) and anhyd. sodium acetate (0.82 g, 0.01 mol) in anhyd. ethanol (60 ml) was heated, under reflux, on a steam bath for 3h. The reaction mixture was concentrated and allowed to cool to room temperature. The solid, thus separated, was filtered, washed well with water and crystallized from ethanol to give V as light yellow crystals, m.p. 180° , IR: 1590 (C=N), 1700 (C=O), 2340-2700 (COOH), 3400 (NH); ^1H NMR (400 MHz) (DMSO-d_6): 4.12 (s, 2H, SCH_2), 6.97 (ddd, 1H, $\text{C}_6\text{-H}$, $J^{1\text{H}-^{19}\text{F}}(\text{ortho}) = 9 \text{ Hz}$, $J^{1\text{H}-^{19}\text{F}}(\text{ortho}) = 10 \text{ Hz}$, $J^{1\text{H}-^{19}\text{F}}(\text{meta}) = 3 \text{ Hz}$), 7.26 (dd, 1H, $\text{C}_4\text{-H}$, $J^{1\text{H}-^{19}\text{F}}(\text{meta}) = 3 \text{ Hz}$, $J^{1\text{H}-^{19}\text{F}}(\text{ortho}) = 10 \text{ Hz}$), 7.42 (dd, 1H, $\text{C}_7\text{-H}$, $J^{1\text{H}-^{19}\text{F}}(\text{meta}) = 5 \text{ Hz}$, $J^{1\text{H}-^{19}\text{F}}(\text{ortho}) = 9 \text{ Hz}$), 12.79 (bs, 1H, NH); ^{19}F NMR (DMSO-d_6): -123.5 ppm (s, 1F, $\text{C}_5\text{-F}$); Analysis: Found: S, 14.2. $\text{C}_9\text{H}_7\text{FN}_2\text{O}_2\text{S}$ requires S, 14.15%.

Cyclization of [(5-Fluoro-2-benzimidazolyl)thio]acetic acid (V):
Formation of 6-Fluorothiazolo[3,2-a]benzimidazol-3(2H)-one (VI)
and 7-Fluorothiazolo[3,2-a]benzimidazol-3(2H)-one (VII)

To a solution of the carboxylic acid (V; 50.8 mg, 0.225 mmol) in pyridine (1 ml) was added acetic anhydride (0.5 ml, 5.3 mmol) and the whole was stirred at 0° for 2.5 h. The reaction mixture was poured into water and extracted with AcOEt. The organic layer was washed with 10% HCl, saturated NaHCO₃ and saturated NaCl successively, dried over MgSO₄, and evaporated to dryness in vacuo. The residue was purified by short column chromatography on silica gel with *n*-hexane-AcOEt (4:1, v/v) to obtain a pure mixture of two cyclized products (VI and VII). The ¹H NMR spectrum of the pure mixture showed that the ratio of VI: VII was 1:1. The pure mixture was then subjected to flash column chromatography on silica gel with *n*-hexane-AcOEt (2:1, v/v) under pressure (1.5 atm.) to give VII and VI in order of elution. Fractions of the mixture were chromatographed again in the same way.

VII: The first eluent (16.0 mg, 34.2%) was recrystallized from AcOEt-*n*-hexane to give VII as colourless prisms (10.0 mg, 21.4%), m.p. 180-182°, IR: 1730 (C=O); ¹H NMR (400 MHz) (DMSO-d₆): 4.61 (s, SH, C₂-H), 7.18 (ddd, 1H, C₆-H, J¹H-¹H(*meta*) = 3 Hz, J¹H-¹H(*ortho*) = 9 Hz, J¹H-¹⁹F(*ortho*) = 10 Hz), 7.49 (dd, 1H, C₈-H, J¹H-¹H(*meta*) = 3 Hz, J¹H-¹⁹F(*ortho*) = 10 Hz), 7.85 (dd, 1H, C₅-H, J¹H-¹⁹F(*meta*) = 5 Hz, J¹H-¹H(*ortho*) = 9 Hz); ¹⁹F NMR (DMSO-d₆): -117.8 ppm (s, 1F C₇-F); MS: m/z 208 (M⁺, 100%); Analysis: Found: C, 52.22; H, 2.41; N, 13.37. C₉H₅FN₂OS requires C, 51.92; H, 2.42; N, 13.45%.

VI: The second eluent (18.9 mg, 40.4%) was recrystallized from AcOEt-*n*-hexane to give VI as colourless prisms (10.1 mg, 21.6%), m.p. 176-178°, IR: 1735 (C=O); ¹H NMR (400 MHz) (DMSO-d₆): 4.61 (s, 2H, C₂-H), 7.25 (ddd, 1H, C₇-H, J¹H-¹H(*meta*) = 3 Hz, J¹H-¹H(*ortho*) = 9 Hz, J¹H-¹⁹F(*ortho*) = 10 Hz), 7.62 (dd, 1H, C₈-H, J¹H-¹⁹F(*meta*) = 5 Hz, J¹H-¹H(*ortho*) = 9 Hz), 7.65 (dd, 1H, C₅-H, J¹H-¹H(*meta*) = 3 Hz, J¹H-¹⁹F(*ortho*) = 8 Hz); ¹⁹F NMR (DMSO-d₆): -119.7 ppm (s, 1F, C₆-F); MS: m/z 208 (M⁺, 100%); Analysis:

Found: C, 51.95; H, 2.38; N, 13.38. $C_9H_5FNO_2S$ requires C, 51.92; H, 2.42; N, 13.45%.

Reaction of IV with 1,2-dibromoethane : Synthesis of sym-bis(5-fluorobenzimidazol-2-yl-mercapto)ethane (VIII)

A mixture of 5-fluorobenzimidazolyl-2-thione (IV; 1.68 g, 0.01 mol) and 1,2-dibromoethane (1.88 g, 0.01 mol) in anhyd. ethanol (25 ml) was heated, under reflux, for 3 h. The reaction mixture was cooled and poured into cold water. The hydrobromide thus obtained was neutralized with $NaHCO_3$ to yield free base (VIII) as colourless flakes, m.p. 265° (EtOH), yield 0.88 g (49%); IR: 1600, 1630 (C=C, C=N), 3040 (NH); 1H NMR (400 MHz) (DMSO- d_6): 3.68 (s, 4H, $-CH_2CH_2-$), 6.98 (ddd, 2H, C_6-H and C_6-H , $J^{1H-1H(meta)} = 3$ Hz, $J^{1H-1H(ortho)} = 9$ Hz, $J^{1H-19F(ortho)} = 10$ Hz), 7.26 (dd, 2H, C_4-H and C_4-H , $J^{1H-1H(meta)} = 3$ Hz, $J^{1H-19F(ortho)} = 10$ Hz), 7.43 (dd, 2H, C_7-H and C_7-H , $J^{1H-19F(meta)} = 5$ Hz, $J^{1H-1H(ortho)} = 9$ Hz); ^{19}F NMR (DMSO- d_6): -122.7 ppm (s, 1F, C_5-F or C_5-F), -124.0 ppm (s, 1F, C_5-F or C_5-F); MS: m/z 362 (M^+ , 4.2%), 195 ($M^+ - 167$, 100%); Analysis: Found: C, 52.8; H, 3.2; N, 15.42; S, 17.58. $C_{16}H_{12}F_2N_4S_2$ requires C, 53.03; H, 3.31; N, 15.47; S, 17.68%.

Thiazolo[3,2-a]benzimidazol-3(2H)-one (XI)

(XI) was synthesized according to the method of Duffin and Kendall [12] as colourless needles, m.p. $180-183^\circ$ (AcOEt-n-hexane), (Lit. [12] m.p. 181°); IR: 1735 (C=O); 1H NMR (400 MHz) (DMSO- d_6): 4.62 (s, 2H, C_2-H), 7.32 (dt, 1H, C_6-H or C_7-H , $J = 1$ and 8 Hz), 7.38 (dt, 1H, C_7-H or C_6-H , $J = 1$ and 8 Hz), 7.60 (dif.d, 1H, C_8-H , $J = 8$ Hz), 7.87 (dif.d, 1H, C_5-H , $J = 8$ Hz); MS: m/z 190 (M^+ , 100%).

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