Tetrahedron. Vol. 35, pp. 869 to 873. Pergamon Press 1979. Printed in Great Britain

PYRIDINETHIONES—III

SYNTHESIS OF DITHIOCINES BY REACTION OF 3-FORMYL-2(1*H*)-PYRIDINETHIONE WITH AMINES. CRYSTAL STRUCTURE OF THE RESULTING 5,11-IMINO-5*H*-11*H*-DIPYRIDO[2,3-b: 2',3'-f][1,5]DITHIOCINE RING SYSTEM

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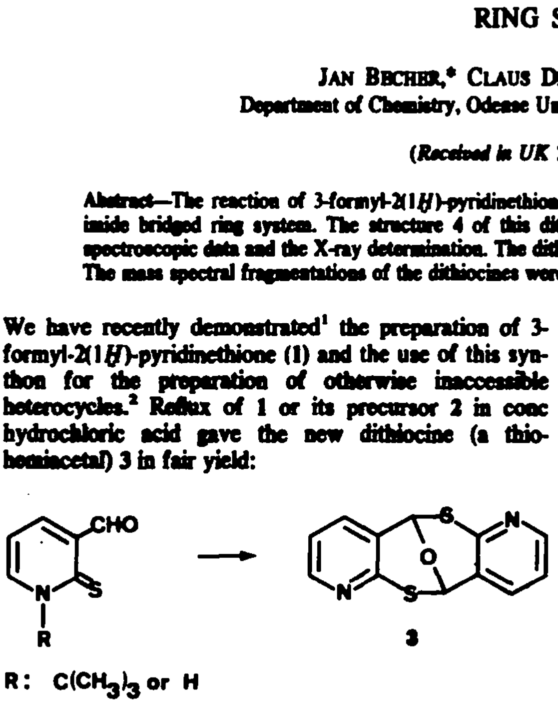
(*Received in UK 25 September 1978*)

Abstract—The reaction of 3-formyl-2(1*H*)-pyridinethione and alkyl or aryl primary amines gives rise to a novel imide bridged ring system. The structure 4 of this dithiocine was assigned by synthesis as well as from the spectroscopic data and the X-ray determination. The dithiocine ring was found to have the "folded" configuration. The mass spectral fragmentations of the dithiocines were investigated in detail.

We have recently demonstrated[1] the preparation of 3-formyl-2(1*H*)-pyridinethione (1) and the use of this synthon for the preparation of otherwise inaccessible heterocycles.[2] Reflux of 1 or its precursor 2 in conc hydrochloric acid gave the new dithiocine (a thiohemiacetal) 3 in fair yield:



1 or 2

3

Scheme 1.

As an extension of this work, we have reacted 2 with primary amines and found this reaction to give rise to the novel imide-bridged ring system 4.

RESULTS AND DISCUSSION

Preparation of 4. Reflux of 2 in ethanol with an equivalent amount of a primary amine followed by addition of an ethanolic solution of hydrogen chloride to eliminate the t-Bu group, yielded upon neutralization and work up the ring system 4:

In the alkyl series with R as an alkyl group, the yields were about 60%, while better yields were found in the aromatic series, probably reflecting the easy formation of the Schiff-base in the first step of the reaction.

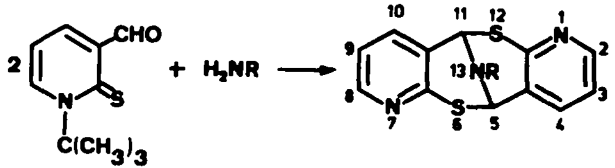
In all cases the products 4 were high melting crystalline bases.

Assignment of structure. The structure of 4a–h were inferred from the synthesis and from the spectra as well as from single crystal X-ray diffraction. The ^{1}H, ^{13}C NMR and UV spectra closely resemble the data of the oxygen analogue 3 previously reported.[1] The ^{1}H and ^{13}C NMR spectra show that 4a–h are symmetric molecules which means that the C atom shift values are identical two and two. The ^{13}C NMR values for 4a and 4e are shown in Scheme 3.

It is seen that the values for C(5) and C(11) are dependent on the substituent on N(13).

Many related systems derived from 1,2-substituted aromatics have been reported, the well known Tröger's base[3] is a good example. Recently Eichler *et al.*[4] obtained a dimer (5) of a pyridine aldehyde (Scheme 4).

Knoll *et al.*[5] prepared and identified an imide bridged eight-ring 6 from *o*-hydroxybenzaldehyde and amines. For the bridgehead carbons in these bicyclic systems the shift values for the methine protons in the ^{1}H NMR spectra are found within the range 5.43–7.20 ppm, while the corresponding values for these C atoms in the ^{13}C NMR spectra are found at 63.3–81.6 ppm.

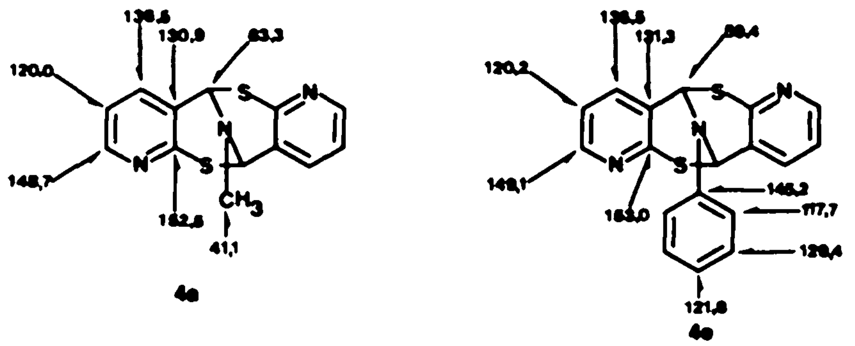


2

4

R	R
4a methyl	**4e** phenyl
4b iso-butyl	**4f** *p*-bromophenyl
4c benzyl	**4g** *p*-cyanophenyl
4d carboxyethyl	**4h** 3,4,5-trimethoxyphenyl

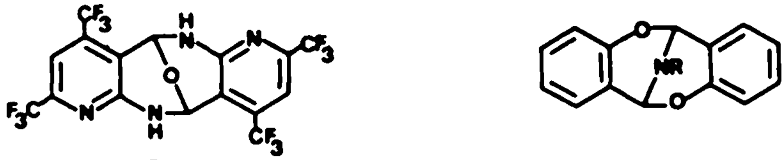
Scheme 2.



4a

4e

Scheme 3.

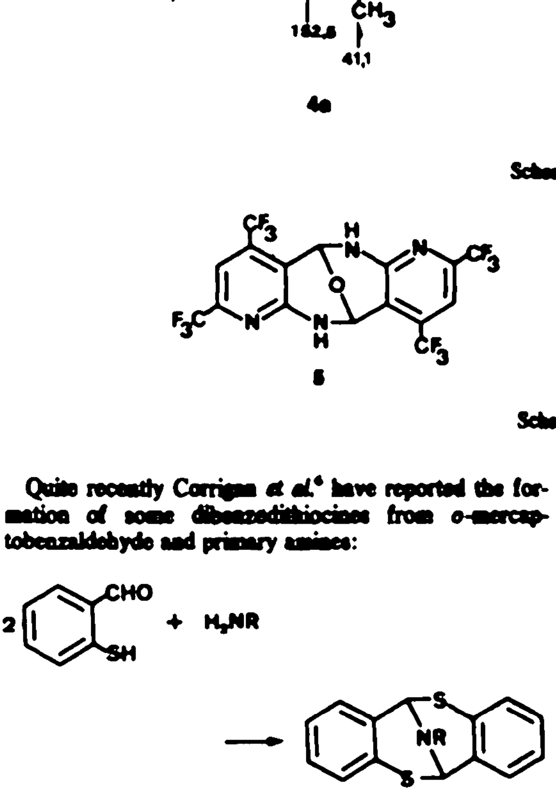


5

6

Scheme 4.

Quite recently Corrigan *et al.*[6] have reported the formation of some dibenzodithiocines from *o*-mercaptobenzaldehyde and primary amines:



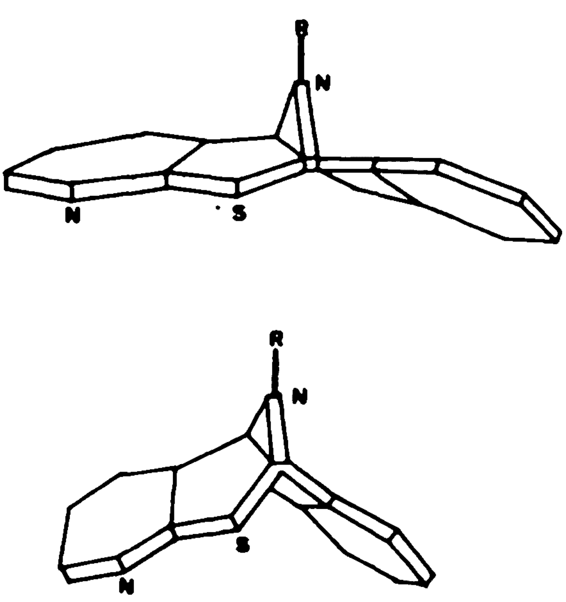
The methine protons in these dithiocines† were found within the range δ 5.98–5.41 ppm. Corrigan *et al.*[6] correctly reject a previous assignment of a 4-membered ring structure suggested to these reaction products by Russian workers.[7] The corresponding dimer of salicylaldehyde has been reported by Fiedler[8] as well as by Droff and Krasse.[9]

From all these reports, and from the present work including the X-ray investigation, the 8-membered ring structure is strongly confirmed, and it may be concluded that imino- or epoxy-bridged 8-membered rings or bicyclic nonanes are quite common reaction products from 1,2-disubstituted aromatics containing the appropriate 1,2-substituents.

Mass spectra of 4. The fragmentation of the dithiocines 4 upon electron impact was studied. The MS are found in the experimental. In all spectra the base peak was the molecular ion or the ion $m/e = 154$ with the elemental composition $C_6H_4NS_2$. In one case however, for R = benzyl the base peak was found as expected to be the $m/e = 258$ ion (M^+–benzyl).

The prominent feature of the fragmentation pattern in this series is that the substituent R has a very small influence on the fragmentation, but a large influence on the intensity. Similar characteristic losses of $HS_2^{\cdot}$ and S_2 from other sulphur heterocycles have been reported.[10a–d]

X-ray diffraction. In order to assign the correct geometry to these compounds (4) an X-ray investigation of the compound 4g was undertaken. From model considerations it is obvious that the configuration around the bridgehead carbons 5,11 is very important for the configuration of the entire molecule. *A priori* there are two reasonable configurations, a "folded" and a "twisted" one (Scheme 5), of which the folded configuration is the most likely as there is a very close sulphur–sulphur contact and higher angle strain in the twisted configuration. The X-ray investigation carried out here supports these considerations, which are also in agreement with the results[11] obtained for "Tröger's base".



Scheme 5. Possible conformations of the dithiocines 4. Top: "twisted conformation"; bottom: "folded conformation".

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†Corrigan *et al.*[6] tentatively described a by-product to which the epoxydithiocine structure is suggested on the basis of a peak at δ 7.33 ppm in the ^1H NMR spectrum. This seems highly probable, as our previous reported epoxydithiocine 3 had the methine protons at δ 7.06 ppm.

Crystal data. Compound **4g** has a formular weight of 360.46. The crystals are yellow prisms. M.p.: 276°. Space group $P2_1/c$ (No. 14) a = 15.450(2) Å, b = 10.315(2) Å, c = 12.029(2) Å, β = 118.616(8)°, Z = 4, D_m = 1.43(1) g cm^{-3}, D_c = 1.42 g cm^{-3}.†

Each of the two molecular fragments N(11), C(12), C(13), C(14), C(15), C(16), C(17), S(1) and N(21), C(22), C(23), C(24), C(25), C(26), C(27), S(2), are nearly planar (plane I and II).

These molecular fragments make a dihedral angle of 99° and therefore the molecule is folded about the line C(17)–C(27) (folded conformation) (Fig. 2). The plane defined by C(17), N(3) and C(27) makes the angles 130.9° and 125.6° with planes I and II respectively. The phenyl ring (plane III) is tilted towards plane II. The position of the phenyl ring is probably determined by steric factors.

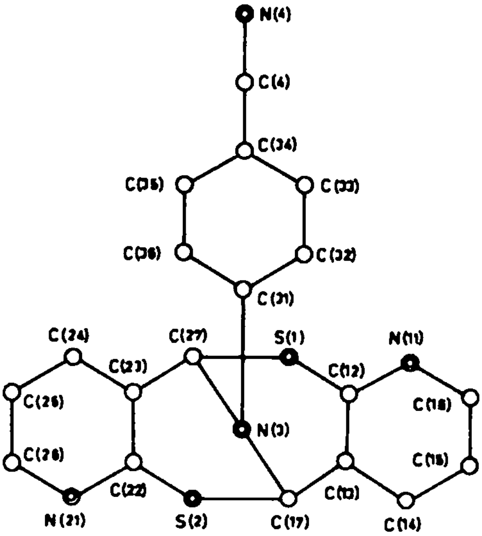

Fig. 1. Numbering of the atoms in the **4g**-molecule. Each hydrogen atom (omitted on the drawing) has the same number as the atom to which it is attached.

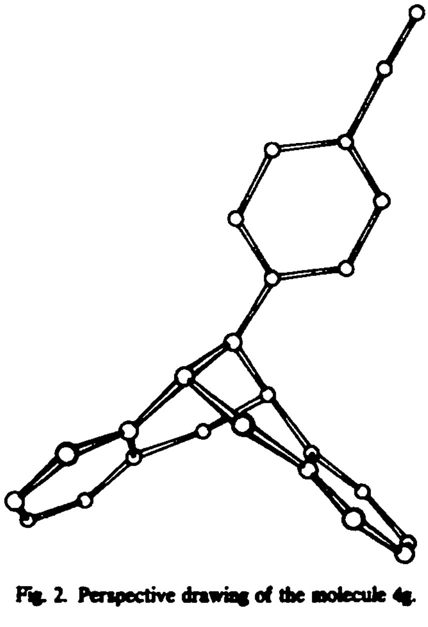

Fig. 2. Perspective drawing of the molecule **4g**.

The interatomic distances are all normal,† as can be seen from the comparison with the corresponding distances in other heterocyclic compounds (C–S. distances,[12,13] pyridine ring distances,[14,15] C–N distances[16–18]). Corresponding bond distances in the two molecular fragments separated by plane IV are of nearly the same length, except for the pair N(11)–C(16), N(21)–C(26). This is in agreement with the symmetry results obtained from the ^{13}C NMR spectra of the compounds **4a** and **4e** (Scheme 3).

Table 1. Final atomic coordinates with estimated standard deviations in parentheses

Atom	x	y	z
S(1)	0.6846(1)	0.3598(2)	0.2821(1)
S(2)	0.8774(1)	0.4916(2)	0.6722(1)
N(3)	0.6874(3)	0.4764(4)	0.4842(4)
N(4)	0.4435(5)	0.9223(6)	0.6430(6)
N(11)	0.7728(4)	0.1372(5)	0.3596(5)
N(21)	0.9669(4)	0.6308(5)	0.5811(5)
C(4)	0.4854(5)	0.8461(6)	0.6182(6)
C(12)	0.7551(4)	0.2479(6)	0.4028(5)
C(13)	0.7855(4)	0.2731(5)	0.5307(5)
C(14)	0.8381(4)	0.1747(6)	0.6155(5)
C(15)	0.8571(5)	0.0600(6)	0.5715(6)
C(16)	0.8220(5)	0.0464(7)	0.4437(6)
C(17)	0.7629(4)	0.3964(6)	0.5805(5)
C(22)	0.8825(4)	0.5681(6)	0.5435(6)
C(23)	0.8053(4)	0.5653(6)	0.4191(5)
C(24)	0.8217(5)	0.6296(7)	0.3285(6)
C(25)	0.9101(5)	0.6924(7)	0.3638(7)
C(26)	0.9783(5)	0.6946(7)	0.4897(8)
C(27)	0.7057(4)	0.5047(6)	0.3793(5)
C(31)	0.6438(4)	0.5724(6)	0.5237(5)
C(32)	0.6256(5)	0.6972(6)	0.4719(6)
C(33)	0.5733(5)	0.7862(6)	0.5025(6)
C(34)	0.5406(4)	0.7535(5)	0.5882(5)
C(35)	0.5613(4)	0.6313(6)	0.6440(5)
C(36)	0.6124(4)	0.5421(6)	0.6120(5)

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Department of the University of Copenhagen. *Instrumentation*: IR in KBr: Perkin Elmer 457, UV in abs. ethanol: Beckman Acta III, ^{1}H NMR: Jeol C-60 HL, ^{13}C NMR: Jeol FX 60 (in DMSO-d_6, δ ppm from TMS, *J* in Hz). MS: Varian Mat 311A (Grant No. 511-3809 from the Danish Science Research Council). M.p. Büchi apparatus uncorrected.

General procedure for the preparation of 13-*substituted*-5,11-*imino*-5H,11H-*dipyrido*[2,3-b: 2′,3′-f][1,5]*dithiocines* (**4a** to **4h**). To a soln of **2**[13] (5×10^{-3} mole) in ethanol (25 ml) was added 5×10^{-3} mole of the required amine. This mixture was refluxed for 10 min followed by stirring at room temp. for 18 hr. EtOH saturated with HCl (5 ml) was then added followed by reflux for 30 min. After cooling the mixture was neutralized with 2 M NaOH and further cooled to 5°. Isolation of the ppt and recrystallization from 2-methoxyethanol/water yielded pale yellow crystals of **4**.

Compound **4a**: 0.91 g ~ 67%, m.p. 201–202°. IR: 1580, 1568, 1420. UV: (λ, log ϵ), (207, 4.36), (245, 4.28), (303, 3.85). ^{1}H NMR:

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† Lists of atomic coordinates, interatomic distances, bond angles and distances from some last square planes are deposited in the Cambridge Crystallographic Data Bank. Copies may be obtained on request from the authors.

8.32 (d. of d., J = 5 Hz and J = 1.5 Hz, 2H), 7.52 (d. of d., J = 8 Hz and J = 1.5 Hz), 7.03 (d. of d., J = 8 Hz and J = 5 Hz, 2H), 5.43 (s, 2H), 2.83 (s, 3H). MS (m/z, %): (275, 12.0), (274, 18.5), (273 = $M^{+\cdot}$, 100.0), (258, 9.3), (243, 10.8), (241, 8.0), (240, 42.5), (225, 9.8), (209, 23.0), (208, 33.5), (156, 9.0), (155, 8.7), (154, 83.5), (151, 12.1), (132, 8.5), (122, 11.4), (110, 8.6), (92, 9.5), (91, 7.0), (79, 5.0), (78, 25.0), (69, 7.9), (65, 6.5), (63, 8.2), (51, 9.8), (45, 10.9), (42, 12.0), (39, 10.5). Anal: Found: C, 57.35; H, 4.09; N, 15.15. $C_{13}H_{11}N_3S_2$ requires: C, 57.11; H, 4.06; N, 15.37%.

Compound **4b**. 0.50 g ~ 31.6%, m.p. 192–194°. IR: 1580, 1560, 1412. UV: (λ, log ε), (206, 4.39), (244, 4.32), (302, 3.93). ^{1}H NMR: 8.06 (d. of d., J = 5 Hz and J = 1.5 Hz, 2H), 7.30 (d. of d., J = 8 Hz and J = 1.5 Hz, 2H), 7.10 (d. of d., J = 8 Hz and J = 5 Hz, 2H), 5.98 (s, 2H), 3.00–1.70 (m, 3H), 0.93 (d. of d., J = 6 Hz and J = 2 Hz, 6H). MS (m/z, %): 317, 11.5), (316, 21.0), (315 = $M^{+\cdot}$, 100.0), (283, 12.0), (282, 58.0), (272, 5.9), (260, 6.9), (259, 19.5), (258, 52.0), (245, 10.0), (244, 12.0), (243, 24.0), (227, 8.4), (226, 35.0), (225, 44.5), (211, 6.4), (195, 12.5), (194, 9.2), (193, 8.6), (191, 7.9), (156, 6.6), (155, 6.2), (154, 63.5), (149, 5.9), (137, 12.0), (124, 11.0), (123, 7.4), (122, 28.0), (79, 6.4), (78, 24.0), (63, 5.4), (51, 5.0), (45, 8.4), (41, 13.0), (39, 7.8). Anal.: Found: C, 60.80; H, 5.18; N, 13.05. $C_{16}H_{17}N_3S_2$ requires: C, 60.92; H, 5.43; N, 13.32%.

Compound **4c**. 0.50 g ~ 57%, m.p. 172.5–174.0°. IR: 1580, 1560, 1412. UV: (λ, log ε), (207, 4.51), (244, 4.28), (302, 3.88). ^{1}H NMR: 8.25 (d. of d., J = 4.5 Hz and J = 1.5 Hz, 2H), 7.72 (d. of d., J = 7 Hz and J = 1.5 Hz, 2H), 7.38 (s, 5H), 7.08 (d. of d., J = 7 Hz and J = 4.5 Hz, 2H), 5.88 (s, 2H), 4.23 (J = 14 Hz, 1H), 3.88 (J = 14 Hz, 1H). MS (m/z, %): (350, 6.5), (349 = $M^{+\cdot}$, 30.0), (269, 5.2), (260, 10.5), (259, 16.0), (258 = $M^{+\cdot}$–C_7H_7, 100.0), (243, 6.0), (240, 6.4), (227, 6.3), (225, 15.5), (195, 6.1), (194, 9.2), (193, 25.5), (184, 11.0), (168, 18.5), (154, 21.5), (140, 7.7), (139, 5.7), (138, 23.0), (137, 49.0), (122, 16.0), (111, 7.5), (92, 7.6), (91, 73.0), (78, 12.0), (67, 5.0), (65, 13.0), (57, 15.5), (40, 14.0), (38, 8.2). Anal.: Found: C, 65.15; H, 4.21; N, 11.97. $C_{19}H_{15}N_3S_2$ requires: C, 65.30; H, 4.33; N, 12.02%.

Compound **4d**. 0.59 g ~ 71%, m.p. 234–236°. IR: 1580, 1560, 1410. UV: (λ, log ε), (210, 4.22), (242, 4.17), (298, 3.81). ^{1}H NMR: 8.33 (d. of d., J = 5 Hz and J = 1.5 Hz, 2H), 8.03 (d. of d., J = 8 Hz and J = 1.5 Hz, 2H), 7.23 (d. of d., J = 8 Hz and J = 5 Hz, 2H), 7.18 (s, 2H), 4.30 (q, J = 7 Hz, 2H), 1.30 (t, J = 7 Hz, 3H). MS (m/z, %): (333, 9.6), (332, 16.5), (331 = $M^{+\cdot}$, 86.0), (260, 8.7), (259, 17.5), (258, 80.0), (243, 6.6), (242, 30.0), (226, 8.3), (225, 17.5), (156, 8.9), (155, 8.5), (154, 100.0), (122, 24.5), (78, 18.5), (45, 9.0). Anal.: Found: C, 54.25; H, 4.09; N, 12.47. $C_{15}H_{13}N_3O_2S_2$ requires: C, 54.36; H, 3.95; N, 12.68%.

Compound **4e**. 0.75 g ~ 90%, m.p. 269–270°. IR: 1606, 1584, 1568, 1505, 1418. UV: (λ, log ε), (210, 4.46), (244, 4.46), (299, 3.89). ^{1}H NMR: 8.30 (d. of d., J = 5 Hz and J = 1.5 Hz, 2H), 7.93 (d. of d., J = 8 Hz and J = 1.5 Hz, 2H), 7.30 (s, 5H), 7.20 (d. of d., J = 8 Hz and J = 5 Hz, 2H), 7.03 (s, 2H). MS (m/z, %): (337, 9.8), (336, 17.0), (335 = $M^{+\cdot}$, 74.0), (303, 12.0), (302, 47.0), (301, 6.0), (271, 11.0), (270, 35.0), (244, 6.9), (243, 31.5), (242, 7.7), (213, 11.7), (199, 5.1), (198, 8.1), (181, 5.4), (156, 10.8), (155, 10.3), (154, 100.0), (110, 7.0), (93, 5.2), (78, 27.0), (77, 26.0), (51, 17.0), (45, 5.7). Anal: Found: C, 64.45; H, 4.01; N, 12.66. $C_{18}H_{13}N_3S_2$ requires: C, 64.45; H, 3.91; N, 12.53%.

Compound **4f**. 0.89 g ~ 86%, m.p. 233–235°. IR: 1595, 1585, 1570, 1500, 1420. UV: (λ, log ε), (212, 4.42), (247, 4.45), (296, 3.96). ^{1}H NMR: 8.33 (d. of d., J = 5 Hz and J = 1.5 Hz, 2H), 7.93 (d. of d., J = 8 Hz and J = 5 Hz, 2H), 7.42 (AB, 4H), 7.23 (d. of d., J = 8 Hz and J = 1.5 Hz, 2H), 7.02 (s, 2H). MS (m/z, %): (417, 5.1), (416, 10.7), (415 = $M^{+\cdot}$, 41.0), (414, 11.0), (413, 38.0), (382, 16.5), (381, 6.7), (380, 15.5), (350, 11.8), (348, 12.1), (293, 5.4), (291, 5.2), (244, 6.8), (243, 35.5), (242, 6.0), (156, 11.5), (155, 12.8), (154, 100.0), (78, 13.5), (76, 8.2), (75, 6.9), (51, 5.1), (41, 7.6), (39, 6.6). Anal.: Found: C, 52.10; H, 3.13; N, 10.02. $C_{18}H_{12}BrN_3S_2$ requires: C, 52.18; H, 2.92; N, 10.14%.

Compound **4g**. 0.84 g ~ 93%, m.p. 276–276.5°. IR: 1610, 1585, 1570, 1520, 1420. UV: (λ, log ε), (206, 4.58), (242, 4.31), (281, 4.49). ^{1}H NMR: 8.33 (d. of d., J = 5 Hz and J = 1.5 Hz, 2H), 7.95 (d. of d., J = 8 Hz and J = 1.5 Hz, 2H), 7.69 (AB, 4H), 7.27 (s, 2H), 7.23 (d. of d., J = 8 Hz and J = 5 Hz, 2H). MS (m/z, %): (362, 6.9), (361, 12.0), (360 = $M^{+\cdot}$, 51.5), (328, 5.1), (327, 18.0), (295, 12.5), (243, 21.5), (238, 7.1), (156, 10.6), (155, 9.8), (154, 100.0), (102, 8.6), (78, 12.5), (51, 6.1). Anal.: Found: C, 63.30; H, 3.47; N, 15.55. $C_{19}H_{12}N_4S_2$ requires: C, 63.31; H, 3.36; N, 15.54%.

Compound **4h**. 0.82 g ~ 77%, m.p. 233.0–234.0°. IR: 1600, 1585, 1570, 1518, 1420. UV: (λ, log ε), (212, 4.66), (246, 4.43), (298, 3.90). ^{1}H NMR: 8.28 (d. of d., J = 4 Hz and J = 2 Hz, 2H), 7.93 (d. of d., J = 7 Hz and J = 2 Hz, 2H), 7.20 (d. of d., J = 7 Hz and J = 4 Hz, 2H), 7.08 (s, 2H), 6.57 (s, 2H), 3.80 (s, 6H), 3.63 (s, 3H). MS (m/z, %): (427, 13.5), (426, 26.5), (425 = $M^{+\cdot}$, 100.0), (410, 12.0), (394, 5.3), (393, 9.2), (392, 36.5), (376, 6.4), (303, 6.2), (259, 7.8), (258, 18.0), (257, 64.0), (256, 7.9), (245, 5.7), (244, 9.1), (243, 50.0), (242, 5.6), (230, 7.2), (226, 7.4), (225, 5.7), (183, 25.0), (168, 43.5), (156, 8.3), (155, 8.0), (154, 89.0), (78, 10.0), (45, 9.2). Anal.: Found: C, 59.15; H, 4.65; N, 9.68. $C_{21}H_{19}N_3O_3S_2$ requires: C, 59.27; H, 4.50; N, 9.87%.

X-ray diffraction. Suitable single crystals of **4g** used in the X-ray investigation were obtained from a 2-methoxyethanol soln by voluntary evaporation. The three dimensional X-ray data were obtained using a three-circle Enraf–Nonius diffractometer and Zr filtered MoKα radiation. A reflection was designated not observed if $I \leqslant 2.2\,\sigma\,(I)$. With this criterion 2063 out of 2943 (independent measured) reflections were regarded as observed, Lorentz and polarization corrections were applied, but no extinction of absorption corrections were made. The crystal size was $(0.7 \times 0.3 \times 0.3)\ \mathrm{mm}^3$, ω-scan was used. The maximum value of sin Θ/λ was 0.617.

Accurate unit cell dimensions were determined by a least-squares refinement of data measured from a Guinier powder photograph taken with CuKα_1 radiation and calibrated with silicon as an internal standard.

All calculations were performed on an IBM 370/165 computer using the X-ray system.[20]

The structure was solved by direct methods and the structural parameters were refined by full-matrix least squares. The positional H-parameters were calculated and then refined separately ($\sin \Theta/\lambda < 0.4\ \text{Å}^{-1}$). Unobserved reflections were not included in the calculations. The quantity minimized was $\Sigma(|F_o| - |F_c|)^2$. The final R index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 6.3%. Atomic scattering factors were taken from International Tables.[21]

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