Reaction of 1,4,2-Dithiazolium and 1,3-Dithiolium Salts with Malononitrile

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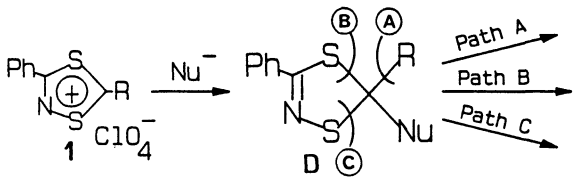
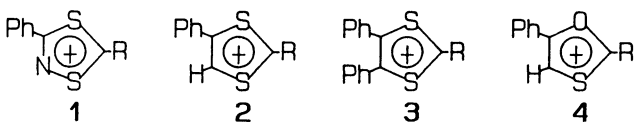
The reaction of 5-substituted 3-phenyl-1,4,2-dithiazolium salts with malononitrile gave not only 5-dicyanomethylene-3-phenyl-1,4,2-dithiazole and an isothiazole derivative, but 4-amino-5-cyano-2-(1-cyano-2-dialkylamino-2-mercaptovinyl)-6-phenylpyrimidines (**6**) and a butadiene derivative, depending on substituents at C-5 and bases used. The structure of **6** was confirmed by X-ray crystallographic analysis of its methylated derivative. These results are well explained by assuming three possible fission modes of the initial adduct: liberation of substituents at C-5 (Path A), ring opening-ring closure reaction (Path B), and fragmentation of dithiazole ring (Path C). On the other hand, 2-dialkylamino-4,5-diphenyl-1,3-dithiolium salts were allowed to react with malononitrile to afford 2-amino-3-cyano-5,6-diphenyl-1,4-dithiin (**13**) and 4-amino-3-cyano-2-dicyanomethylene-5,6-diphenyl-2*H*-thiin (**14**) as well as 2-dicyanomethylene-4,5-diphenyl-1,3-dithiole (**12**). In a separate experiment, both **13** and **14** were formed by the reaction of **12** with malononitrile. This pathway can be interpreted in terms of considerable contribution of polar structure of **12** due to the push-pull effect of sulfur atoms and cyano groups. Furthermore, the reaction of 2-substituted 4-phenyl-1,3-dithiolium salts with malononitrile also gave 2-dicyanomethylene-4-phenyl-1,3-dithiole and thiophene derivatives.

Five-menbered heteroaromatic-cation compounds have attracted much attention on their reactivity to serve as versatile intermediates in organic synthesis.[1-3] In particular, it is well known that the reactions of 1,3-dithiolium cations (**2**)[3a,d] and 1,3-oxathiolium cations (**4**)[1b,3] with various kinds of nucleophiles lead to a wide range of heterocyclic compounds. The preparation of 1,4,2-dithiazolium cations (**1**) was recently established by three independent groups, and the reaction of **1** with a few nucleophiles was also reported.[4] We have shown in a previous paper that the reaction of **1** with various amino compounds can be classified into three types (Paths A, B, and C) depending on three possible fission modes (A, B, and C in Scheme 1) of the initial adduct (**D**), leading to 5-imino-1,4,2-dithiazole, 1,3,4-thiadiazole, and thiourea derivatives, respectively.[5] In our continuing investigation into the chemistry of **1**, we carried out the reaction of **1** with malononitrile, one of highly reactive methylene compounds, in the presence of various bases. For comparison, the behavior of 4-phenyl- and 4,5-diphenyl-1,3-dithiolium cations (**2** and **3**), carba-analogues of **1**, toward malononitrile was also examined, and some interesting information on their reactivity was obtained.



Scheme 1.



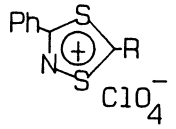
Results and Discussion

When 5-dimethylamino-3-phenyl-1,4,2-dithiazolium perchlorate (**1a**) was treated with malononitrile in the presence of Et_3N at room temperature, the reaction gave a yellow compound as the sole product (Entry 1 in Table 1). On the grounds of its elemental analysis and spectral data, i.e., mercapto, amino, and two cyano bands in IR spectrum, the signals attributable to dimethylamino and phenyl groups in ^1H NMR spectrum, and the molecular ion peak in mass spectrum, the pyrimidine derivative (**6a**) was proposed as the structure of this compound. The reaction of **1b** with malononitrile in the presence of Et_3N and γ-picoline also afforded this type of compound **6b** (Entries 2 and 3). Since the structure of the above products cannot be unequivocally determined from the present data, it was examined by X-ray crystallographic analysis of **7** which was obtained by methylation of **6b**. It proved the proposed pyrimidine structure; an ORTEP illustration of **7** is given in Fig. 1. It shows that the ring skeleton of starting material **1** is divided into sections

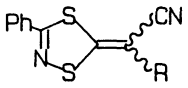
Table 1. The Reaction of 1,4,2-Dithiazolium Perchlorates **1** with Malononitrile

Entry	NR_2	Base (pK_a)	Solvent	Product (Yield/%)[a]
1	NMe_2	Et_3N (10.9)	CH_2Cl_2	**6a** (49)
2	NEt_2	Et_3N	THF	**6b** (83)
3	NEt_2	γ-Picoline (6.02)	CH_2Cl_2	**6b** (36)
4	NEt_2	NaH	EtOH	**8** (32)[b]
5	NEt_2	NaH	THF	**8** (67)[b]
6	NMe_2	Pyridine (5.19)	MeCN	**5a** (54)
7	Morpholino	γ-Picoline	MeCN	**5a** (27)
8	SMe	γ-Picoline	MeCN	**5a** (10)
9	Ph	Et_3N	MeCN	**9** (58)

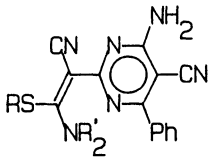
a) Isolated yield. b) Combined yield of *Z*- and *E*-forms.



1a: R=NMe_2
1b: R=NEt_2
1c: R=morpholino
1d: R=SMe
1e: R=Ph



5a: R=CN
5b: R=SO_2Ph
5c: R=COPh



6a: R=H ; R'=Me
6b: R=H ; R'=Et
7 : R=Me; R'=Et

with elimination of one sulfur atom, into which two malononitrile molecules are consequently incorporated.

Detailed mechanism of the present reaction is not clear, but the formation of **6** is most likely rationalized by the pathway shown in Scheme 2. The initial adduct **D** formed by reaction of **1** with malononitrile undergoes ring opening (Path B) and subsequent ring closure leading to the intermediate **E**, which then brings about ring expansion with sulfur extrusion to give six-membered intermediate **F**; another malononitrile molecule attacks on C-2 position of **F** to afford intermediate adduct **G**, which then undergoes ring opening and ring closure to lead to the final products **6**.

The reaction of **1b** with malononitrile was carried out in NaH/THF or NaH/EtOH, i.e., EtONa/EtOH. In both cases, 2-amino-4-diethylamino-4-mercapto-1,1,3-tricyano-1,3-butadiene (**8**) was formed (Entries 4 and 5). On the other hand, in the case of using the combinations of **1** with relatively weak bases such as pyridine and γ-picoline (Entries 6—8), the reaction of **1** with malononitrile in MeCN at room temperature gave 5-dicyanomethylene-3-phenyl-1,4,2-dithiazole (**5a**). The formation of **8** and **5a** can be explained as follows. The initial adduct **D** (in Scheme 2) undergoes ring cleavage leading to intermediate **H** together with benzonitrile and sulfur (via Path C), which then reacts with another malononitrile to give **8**; **D** is alternatively converted into **5a** with liberation of dialkylamino or methylthio groups (via Path A).

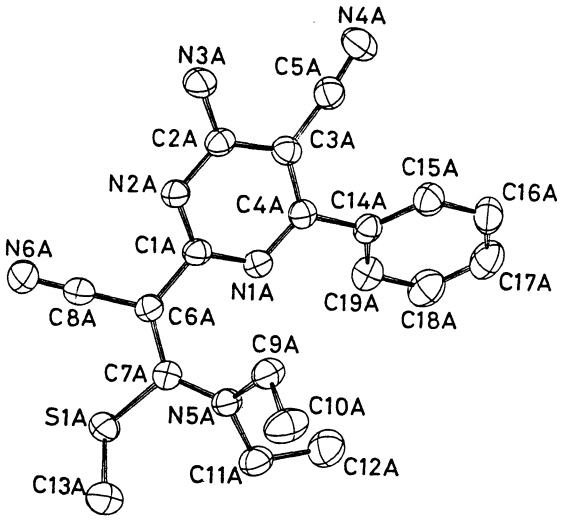
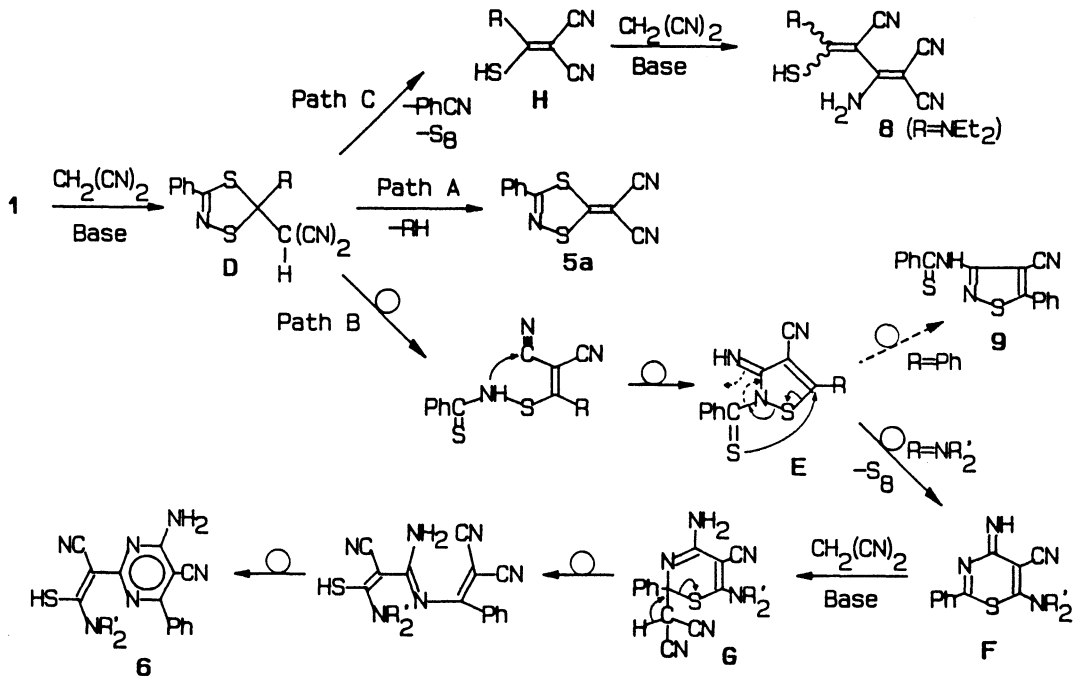


Fig. 1. Molecular structure[15] of **7** with the numbering system for the non-hydrogen atoms. Thermal ellipsoids are drawn at 40% probability.



Scheme 2.

5-Phenyl form **1e** was allowed to react with malononitrile in the presence of Et_3N to give only 4-cyano-5-phenyl-3-(thiobenzoylamino)isothiazole (**9**) in 58% yield (Entry 9). The result was well explained in terms of [1,3]-shift of thiobenzoyl group in the intermediate **E** (in Path B).

From the above results, except the case of Entry 3, **5a** is preferentially formed (via Path A) in the presence of weaker bases such as pyridine and γ-picoline, whereas, in the presence of stronger bases such as Et_3N, NaH, and EtONa, the reaction undergoes ring opening (via Path B) or ring fragmentation (via Path C) resulting in the preferential formation of **6**, **8**, or **9**. In our previous work, a similar trend has been shown in the reaction of **1** with *p*-substituted aniline derivatives in the presence of various bases.[5]

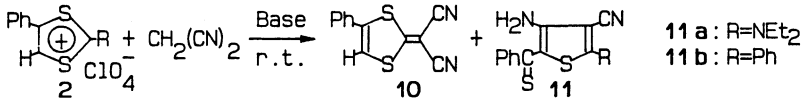
On the other hand, the reactions of **1** with dimethyl malonate and Meldrum's acid in the presence of Et_3N have been reported, which lead to only 5-alkylidene-1,4,2-dithiazole derivatives (via Path A in Scheme 1).[4b,d] In order to examine generality of reaction courses corresponding to Path B (ring opening) or Path C (ring fragmentation), the reaction of **1a** with other active methylene compounds such as phenylsulfonylacetonitrile and benzoylacetonitrile in the presence of Et_3N was attempted; but the products other than 5-alkylidene-1,4,2-dithiazole derivatives **5b** and **5c** were not obtained.

In order to obtain additional information on the reactivity of five-membered heteroaromatic cations toward malononitrile, the reaction of 4-phenyl- and 4,5-diphenyl-1,3-dithiolium salts (**2** and **3**) bearing different substituents at C-2 position was carried out in the presence of different bases.[6] The results are presented in Tables 2 and 3, respectively.

The reaction of 2-diethylamino-4-phenyl-1,3-dithiolium perchlorate (**2a**) with malononitrile in the presence of γ-picoline (weak base) gave only 2-dicyanomethylene-4-phenyl-1,3-dithiole (**10**)[3d] (Entry 10), whereas, in the presence of Et_3N (strong base), **2a** afforded 3-amino-4-cyano-5-diethylamino-2-thiobenzoylthiophene (**11a**) (Entry 11). However, 2-dimethylamino form **2b** afforded only **10** (Entry 12) even under the same conditions as used in Entry 11. On the other hand, the sole formation of thiophene derivative **11b** by reaction of **2d** (Entry 14) is associated with the fact that phenyl group at C-2 has no leaving ability. Thus the reactivity of **2** seems to depend delicately on both substituents at C-2 position and bases used. The similar effects of base strength on reactivity have been observed in the reaction of 1,3-oxathiolium salts **4** with active methylene compounds; the reaction leads to 2-alkylidene-1,3-oxathioles (1,4-oxathiafulvenes) and open chain compounds which often undergo ring closure reaction to afford thiophene derivatives.[3b]

2-Morpholino- and 2-diethylamino-4,5-diphenyl-

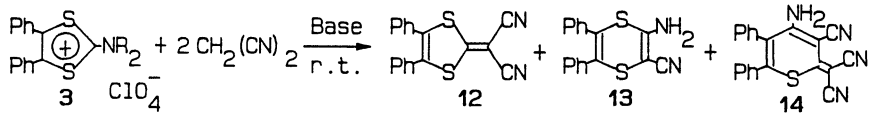
Table 2. The Reaction of 4-Phenyl-1,3-dithiolium Perchlorates **2** with Malononitrile



Entry	Dithiolium cation		Conditons	Product yield/%[a]	
	No.	R		**10**	**11**
10	**2a**	NEt_2	γ-Picoline/CH_2Cl_2/5h	62	—
11	**2a**	NEt_2	Et_3N/CH_2Cl_2/1h	Trace[b]	50
12	**2b**	NMe_2	Et_3N/CH_2Cl_2/1h	42	—
13	**2c**	Morpholino	γ-Picoline/MeCN/2h	88	—
14	**2d**	Ph	Et_3N/MeCN/0.5h	—	78

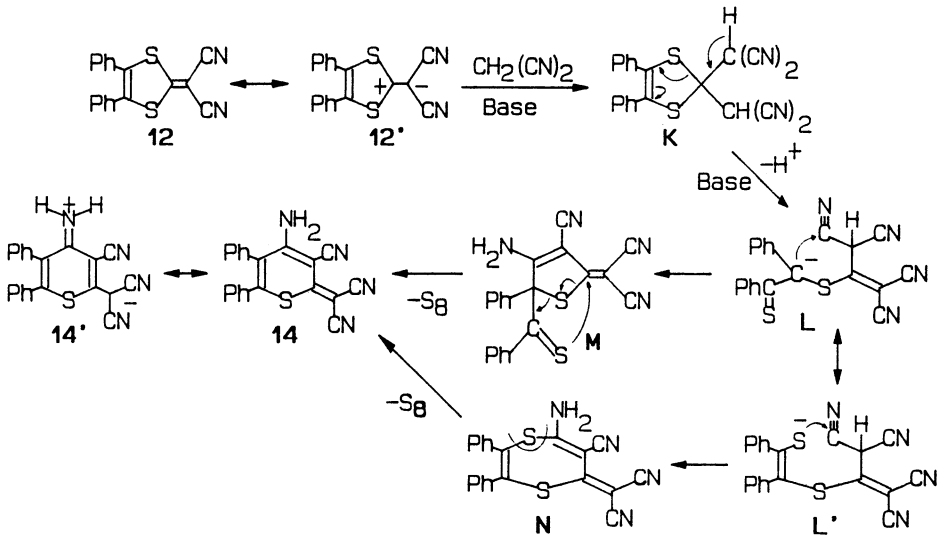
a) Isolated yield. b) Product **10** was detected only on TLC.

Table 3. The Reaction of 4,5-Diphenyl-1,3-dithiolium Perchlorates **3** with Malononitrile



Entry	Dithiolium cation		Conditions	Product yield/%[a]		
	No.	NR_2		**12**	**13**	**14**
15	**3a**	Morpholino	Et_3N/MeCN/1.5h	42	17	6
16	**3b**	NEt_2	Et_3N/MeCN/1.5h	70	19	8
17	**3b**	NEt_2	Et_3N/MeCN/1d	—	45	19
18	**3b**	NEt_2	γ-Picoline/MeCN/1d	85	—	—
19	**3b**	NEt_2	NaH/THF/1h	50	Trace	Trace[b]

a) Isolated yield. b) Products **13** and **14** were detected only on TLC.



Scheme 3.

1,3-dithiolium perchlorates (**3a** and **3b**) were subjected to react with 2 equiv of malononitrile in the presence of Et_3N in MeCN at room temperature for 1.5 h to give three products (Entries 15 and 16). Their spectral data (IR, ^1H NMR, and MS) and elemental analyses suggested that the main product is the expected 2-dicyanomethylene-4,5-diphenyl-1,3-dithiole (**12**), and that the others are 2-amino-3-cyano-5,6-diphenyl-1,4-dithiin (**13**) and 4-amino-3-cyano-2-dicyanomethylene-5,6-diphenyl-2*H*-thiin (**14**). Characteristically, the ^1H NMR signals of two amino protons of **14** were magnetically unequivalent and broad, indicating large contribution of the polar structure **14′** as shown in Scheme 3.

The same reaction as in Entry 16, except prolonged standing (1 day), resulted in disappearance of **12** and improvement of yields of both **13** and **14**, the ratio of which was almost unchanged (Entry 17). In the case of using γ-picoline (weaker base) instead of Et_3N, neither **13** nor **14** was formed (Entry 18). Under the forced conditions, i.e., NaH/THF system (Entry 19), **12** was preferentially obtained in a short reaction time. Therefore, the formation of **13** and **14** is speculated to go via initially-formed **12**. In fact, the reaction of **12** with malononitrile under the same conditions as those used in Entry 17 gave **13** (42%) and **14** (26%) with no recovery of **12**.

These results are well explained by assuming considerable contribution of the polar structure **12′**, which takes the push-pull effect of two electron-donating sulfur atoms in hetero-ring and two electron-withdrawing cyano groups as shown in Scheme 3. Nucleophilic attack of malononitrile on C-2 position of **12′** leads to intermediate adduct **K** which then undergoes ring opening-ring closure reaction and subsequent rearrengement with sulfur extrusion to give **14** (via intermediates **L** and **M**). This pathway is similar to Path B in Scheme 2 and product **14** corresponds to intermediate **F**. Thus, the isolation of **14** seems to be an evidence for the transient existence of **F** in the proposed reaction pathway. On the other hand, we cannot exclude the possibility that intermediate **L′**, a tautomer of **L**, undergoes ring closure and sulfur extrusion via seven-membered intermediate **N** to give **14**. However, in the case of the reaction of **1**, the pathway similar to that via **L′** and **N** cannot be probable for Path B, because the corresponding seven-membered intermediate 1,4,2-dithiazepine derivative, aza-analogue of **N**, could not afford 1,3-thiazines **F** but 1,2-thiazines. A mechanism of the formation of **13** still remains uncertain.

In summary, the reaction of 1,4,2-dithiazolium salts **1** with malononitrile gave **5a** and **9** in similar manners to the reactions of 1,3-dithiolium salts **2** and **3** leading to **10**, **11**, and **12**,[3] whereas, via novel courses, **1** gave **6** and **8**, depending on substituents at C-5 position and bases used. It is known that the reaction manner of malononitrile to heteroaromatic cations is often different from that of other active methylene compounds.[2a,7] In this study, this tendency was shown again. Detailed studies on the behavior of fulvene-type compounds such as **5a**, **10**, and **12** toward various kinds of nucleophiles are currently under way.

Experimental

All the melting points were uncorrected. The ^1H NMR spectra were recorded on a HITACHI R-40 or a JEOL FX-90A spectrometer using TMS as an internal standard. The IR spectra were measured on a JASCO A-302 spectrometer using KBr disks. The low-resolution mass spectra were taken on a HEWLETT PACKARD 5995A spectrometer by electron impact ionizing technique at 70 eV.

1,4,2-Dithiazolium salts **1a—c**[4a] and **1b**,[4b] and 4-phenyl-1,3-dithiolium salts **2a—d**[8] were prepared according to the procedures in the literatures. The salt **1e** was prepared from dithiobenzoate in three steps utilizing the similar procedure

Table 4. Fractional Atomic Coordinates($\times 10^4$) and Equivalent Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2
S1A	2267(1)	1141(1)	2940(1)	4.18(3)
N1A	4130(2)	3402(2)	3438(2)	3.50(8)
N2A	3094(2)	4327(2)	3908(2)	3.40(8)
N3A	3361(3)	5823(2)	4219(2)	4.50(10)
N4A	5325(2)	6399(3)	3941(3)	6.15(13)
N5A	3786(2)	1525(2)	3872(2)	3.56(8)
N6A	1217(2)	3149(3)	3347(3)	6.14(13)
C1A	3376(2)	3541(2)	3652(2)	3.23(9)
C2A	3629(2)	5028(2)	3990(2)	3.41(9)
C3A	4454(2)	4936(2)	3808(2)	3.50(9)
C4A	4672(2)	4095(2)	3524(2)	3.26(9)
C5A	4966(2)	5729(3)	3875(2)	4.21(11)
C6A	2796(2)	2771(2)	3555(2)	3.44(9)
C7A	3039(2)	1864(2)	3507(2)	3.33(9)
C8A	1916(3)	2972(2)	3447(3)	4.25(11)
C9A	4290(3)	1935(3)	4631(2)	4.19(11)
C10A	4530(4)	1251(4)	5321(3)	6.18(17)
C11A	4160(3)	741(3)	3523(3)	4.39(12)
C12A	5029(3)	930(4)	3363(4)	5.89(16)
C13A	2292(4)	184(3)	3639(4)	5.52(16)
C14A	5489(2)	3915(2)	3258(2)	3.55(9)
C15A	6238(2)	4335(3)	3637(3)	4.39(11)
C16A	6977(3)	4138(3)	3364(3)	5.44(14)
C17A	6976(3)	3532(4)	2723(3)	5.74(15)
C18A	6235(3)	3122(4)	2343(3)	5.45(15)
C19A	5500(3)	3300(3)	2618(3)	4.38(11)
S1B	−2457(1)	4370(1)	−876(1)	4.63(3)
N1B	−461(2)	2362(2)	305(2)	3.72(8)
N2B	−1572(2)	1342(2)	463(2)	3.49(8)
N3B	−1263(2)	−10(2)	1155(2)	4.57(10)
N4B	884(2)	−276(3)	1716(3)	6.18(12)
N5B	−1167(2)	3414(2)	−1245(2)	4.13(9)
N6B	−3359(3)	2680(3)	206(3)	6.23(13)
C1B	−1272(2)	2115(2)	197(2)	3.45(9)
C2B	−993(2)	747(2)	846(2)	3.42(9)
C3B	−122(2)	929(2)	938(2)	3.40(9)
C4B	120(2)	1765(2)	662(2)	3.36(9)
C5B	463(2)	279(3)	1367(3)	4.16(11)
C6B	−1908(2)	2767(2)	−219(2)	3.61(9)
C7B	−1759(2)	3433(2)	−770(2)	3.69(10)
C8B	−2722(3)	2724(3)	3(3)	4.37(11)
C9B	−735(3)	4235(4)	−1447(4)	5.95(16)
C10B	171(5)	4253(6)	−991(8)	10.09(35)
C11B	−845(3)	2553(3)	−1515(3)	4.58(12)
C12B	−852(4)	2537(5)	−2452(3)	6.13(17)
C13B	−2768(4)	4467(4)	−2002(3)	6.27(17)
C14B	1015(2)	2043(3)	794(2)	3.76(10)
C15B	1240(3)	2889(3)	1131(3)	5.86(15)
C16B	2091(4)	3132(4)	1302(4)	7.49(20)
C17B	2690(3)	2556(4)	1119(4)	6.92(18)
C18B	2467(3)	1735(4)	770(3)	5.89(16)
C19B	1637(3)	1471(3)	615(3)	4.87(13)

for **1a**—**c**.[9] 4,5-Diphenyl-1,3-dithiolium salts **3** were prepared from the reaction of dithiocarbamate and 2-bromo-2-phenylacetophenone in a similar manner to that described in Ref. 8. Other commercially available reagents and bases were used without any purification.

Reaction of 1,4,2-Dithiazolium Salts 1 with Malononitrile. 1,4,2-Dithiazolium perchlorates **1** (1 mmol) were added with stirring to the solution (6 ml) of malononitrile (2 mmol) and bases (2 mmol): the combinations of bases and solvents are listed in Table 1. The reaction mixture was stirred for 6 h at room temperature. In some cases, the products were recrystallized out and filtered off. The crude product was extracted with dichloromethane after addition of dil HCl. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel and recrystallized from appropriate solvents. The yields of products are presented in Table 1.

5-Dicyanomethylene-3-phenyl-1,4,2-dithiazole (5a): Pale yellow powder. Mp 160.0—162.0 °C (CH_2Cl_2-hexane). ^{1}H NMR ($CDCl_3$) δ=7.5—7.7 (3H, m), 7.8—8.0 (2H, m). IR ν 2208, 1535, 1469, 1239 cm^{-1}. MS m/z (rel intensity) 243 (M^+, 29), 103(100). Found: C, 53.99; H, 2.10; N, 17.14; S, 26.25%. Calcd for $C_{11}H_5N_3S_2$: C, 54.30; H, 2.07; N, 17.27; S, 26.35%.

4-Amino-5-cyano-2-(1-cyano-2-dimethylamino-2-mercaptovinyl)-6-phenylpyrimidine (6a): Yellow powder. Mp 270.5—271.5 °C (DMF-water). ^{1}H NMR (DMF-d_7) δ=3.35 (6H, s), 7.5—7.7 (3H, m), 7.9—8.1 (2H, m). IR ν 3416, 3308, 3180, 2600(br), 2224, 2204, 1644, 1558 cm^{-1}. MS m/z (rel intensity) 322 (M^+, 63), 289 (21), 88 (100). Found: C, 59.39; H, 4.35; N, 25.68; S, 9.94%. Calcd for $C_{16}H_{14}N_6S$: C, 59.61; H, 4.38; N, 26.07; S, 9.94%.

4-Amino-5-cyano-2-(1-cyano-2-diethylamino-2-mercaptovinyl)-6-phenylpyrimidine (6b): Yellow powder. Mp 266.0—268.0 °C (DMF-water). ^{1}H NMR (DMSO-d_6) δ=1.25 (6H, t, J=7.2 Hz), 3.87 (4H, q, J=7.2 Hz), 7.6—7.8 (3H, m), 7.8—8.0 (2H, m). IR ν 3372, 3176, 2600, 2216, 2188, 1658, 1558 cm^{-1}. MS m/z (rel intensity) 350 (M^+, 26), 317 (8), 253 (86), 116 (31). Found: C, 61.58; H, 5.39; N, 24.16; S, 8.87%. Calcd for $C_{18}H_{18}N_6S$: C, 61.69; H, 5.18; N, 23.98; S, 9.15%.

(*Z*)- and (*E*)-2-Amino-4-diethylamino-4-mercapto-1,1,3-tricyano-1,3-butadiene (8): It is difficult to distingush between *Z*- and *E*-forms: a 3:2 isomeric mixture from comparison of the relative areas of ^{1}H NMR signals (diethylamino group). Yellow powder. Mp 178.5—179.5 °C (DMF-MeCN). ^{1}H NMR (DMSO-d_6) δ=1.18 (6H, t, J=7.2 Hz) and 3.46 (4H, q, J=7.2 Hz) for the major isomer, 1.32 (6H, t, J=7.2 Hz) and 3.86 (4H, q, J=7.2 Hz) for the minor isomer. IR ν 3412, 3192, 2226, 2196, 2136, 1652, 1566, 1444 cm^{-1}. MS m/z (rel intensity) 247 (M^+, 24), 230 (100), 175 (45). Found: C, 53.39; H, 4.92; N, 28.06; S, 12.96%. Calcd for $C_{11}H_{13}N_5S$: C, 53.42; H, 5.30; N, 28.32; S, 12.96%.

4-Cyano-5-phenyl-3-(thiobenzoylamino)isothiazole (9): Orange yellow powder. Mp 183.5—184.5 °C (CH_2Cl_2-ether). ^{1}H NMR ($CDCl_3$) δ=7.4—7.7 (8H, m), 7.8—8.0 (2H, m). IR ν 3176, 2224, 1543, 1443, 1418, 1386 cm^{-1}. MS m/z (rel intensity) 321 (M^+, 11), 320 (11), 121 (100). Found: C, 62.99; H, 3.43; N, 12.96; S, 19.91%. Calcd for $C_{18}H_{12}N_2SO$: C, 63.53; H, 3.45; N, 13.07; S, 19.95%.

Reaction of 1,4,2-Dithiazolium Salt 1a with Other Active Methylene Compounds. The salt **1a** (1 mmol) was added to stirred dichloromethane solution (6 ml) of active methylene compounds (1.5 mmol) and Et_3N (1.5 mmol). The reaction mixture was refluxed for 6 h. Subsequent work-up and purification were accomplished according to a similar procedure to the reaction of **1** with malononitrile.

5-[Cyano(phenylsulfonyl)methylene]-3-phenyl-1,4,2-dithiazole (5b): Yield 45%. Mp 201.5—203.0 °C (MeCN-$CHCl_3$). ^{1}H NMR ($CDCl_3$) δ=7.4—7.9 (8H, m), 8.0—8.2 (2H, m). MS m/z (rel intensity) 358 (M^+, 11), 135 (24). Found: C, 53.63; H, 2.77; N, 7.80; S, 26.83%. Calcd for $C_{16}H_{10}N_2S_3O_2$: C, 53.61; H, 2.81; N, 7.82; S, 26.83%.

5-(Benzoylcyanomethylene)-3-phenyl-1,4,2-dithiazole (5c):

Yield 56%. Mp 176.5—177.0 °C (DMF). ^{1}H NMR ($CDCl_3$) δ=7.6—7.8 (6H, m), 8.0—8.2 (4H, m). MS m/z (rel intensity) 322 (M^+, 11), 105 (51). Found: C, 63.26; H, 3.12; N, 8.64; S, 19.85%. Calcd for $C_{17}H_{10}N_2S_2O$: C, 63.33; H, 3.13; N, 8.69; S, 19.89%.

Methylation of 6b. To an ice-cooling suspension of sodium hydride (1.1 mmol) in abs tetrahydrofuran (4 ml) was added **6b** (1 mmol) to give a clear solution. Methyl iodide (3 mmol) was added to the mixture, which was stirred at room temperature for 1 h and then refluxed for 30 min. The mixture was quenched with dil HCl and the product was extracted with dichloromethane. The residue was purified by preparative TLC and recrystallized from dichloromethane-hexane to give **7** as yellow needles of mp 168.5—169.0 °C in 63% yield.

4-Amino-5-cyano-2-(1-cyano-2-diethylamino-2-methylthiovinyl)-6-phenylpyrimidine (7): ^{1}H NMR ($CDCl_3$) δ=1.26 (6H, t, J=7.7 Hz), 2.59 (3H, s), 3.67 (4H, q, J=7.7 Hz), 5.65 (2H, br. s), 7.4—7.6 (3H, m), 7.9—8.1 (2H, m). IR ν 3432, 3316, 3200, 2192, 1638, 1524, 1395 cm^{-1}. Found: C, 62.42; H, 5.50; N, 23.10; S, 8.65%. Calcd for $C_{19}H_{20}N_6S$: C, 62.61; H, 5.53; N, 23.06; S, 8.80%.

Reaction of 1,3-Dithiolium Salts 2 and 3 with Malononitrile. 1,3-Dithiolium salts **2** and **3** (1 mmol) were added to stirred solution (4 ml) of malononitrile (2 mmol) in the presence of bases (2 mmol) at room temperature. Other reaction conditions are listed in Tables 2 and 3. Subsequent work-up and purification were accomplished by a similar procedure to the reaction of **1**.

3-Amino-4-cyano-5-diethylamino-2-thiobenzoylthiophene (11a): Orange powder. Mp 245.0—246.0 °C (DMF-MeCN). ^{1}H NMR ($CDCl_3$) δ =1.30 (6H, t, J=7.2 Hz), 3.58 (4H, q, J=7.2 Hz), 7.3—7.4 (5H, br. s). IR ν 3332, 2196, 1602, 1553, 1499, 1458 cm^{-1}. MS m/z (rel intensity) 315 (M^+, 85), 243 (100), 121 (78). Found: C, 60.82; H, 5.36; N, 13.38; S, 20.37%. Calcd for $C_{16}H_{17}N_3S_2$: C, 60.92; H, 5.43; N, 13.32; S, 20.33%.

3-Amino-4-cyano-5-phenyl-2-thiobenzoylthiophene (11b): Orange powder. Mp 190.5—191.5 °C (MeCN-ether). ^{1}H NMR ($CDCl_3$) δ=7.3—7.6 (8H, m), 7.7—7.8 (2H, m), 8.3 (2H, br. s). IR ν 3372, 2208, 1602, 1422, 1334 cm^{-1}. MS m/z (rel intensity) 320 (M^+, 65), 319 (100), 287 (15), 243 (29), 121 (61). Found: C, 67.08; H, 3.75; N, 8.76%. Calcd for $C_{18}H_{12}N_2S_2$: C, 67.47; H, 3.77; N, 8.74%.

2-Dicyanomethylene-4,5-diphenyl-1,3-dithiole (12): Pale yellow powder. Mp 170.5—171.0 °C (CH_2Cl_2-MeCN). ^{1}H NMR ($CDCl_3$) δ=7.2—7.5 (10H, m). IR ν 2196, 1489, 1435, 1073 cm^{-1}. MS m/z (rel intensity) 318 (M^+, 100), 210 (48), 165 (86), 121 (51). Found: C, 67.73; H, 3.13; N, 8.84; S, 19.90%. Calcd for $C_{18}H_{10}N_2S_2$: C, 67.90; H, 3.17; N, 8.80; S, 20.14%.

2-Amino-3-cyano-5,6-diphenyl-1,4-dithiin (13): Yellow powder. Mp 191.0—192.0 °C (MeCN). ^{1}H NMR ($CDCl_3$) δ= 5.1 (2H, br. s) 7.0—7.2 (10H, m). IR ν 3384, 3260, 3176, 2188, 1618, 1542, 1440, 1310 cm^{-1}. MS m/z (rel intensity) 308 (M^+, 100), 276 (30), 242 (21), 178 (78), 121 (98). Found: C, 65.91; H, 3.93; N, 9.29%. Calcd for $C_{17}H_{12}N_2S_2$: C, 66.21; H, 3.92; N, 9.08%.

4-Amino-3-cyano-2-dicyanomethylene-5,6-diphenyl-2*H*-thiin (14): Yellow powder. Mp 258.5—260.0 °C (MeCN). ^{1}H NMR ($CDCl_3$) δ=5.8 (1H, br.), 6.7 (1H, br.), 7.0—7.5 (10H, m). IR ν 3432 (br.), 3332 (br.), 2204, 1635, 1441 cm^{-1}. MS m/z (rel intensity) 352 (M^+, 29), 178 (15), 121 (36), 55 (100). Found: C, 71.43; H, 3.40; N, 15.91; S, 9.12%. Calcd for $C_{21}H_{12}N_4S$; C, 71.57; H, 3.43; N, 15.90; S, 9.10%.

Reaction of 12 with Malononitrile. 2-Dicyanomethylene-4,5-diphenyl-1,3-dithiole **12** (1 mmol) was added to stirred acetonitrile solution (4 ml) of malononitrile (1 mmol) in the presence of Et_3N (1 mmol). The reaction mixture was stirred for 1 d at room temperature and worked up as described above to give **13** (42%) and **14** (26%).

Single-Crystal X-Ray Analysis of 7. Crystal data: $C_{19}H_{20}N_6S$; MW 364.48; monoclinic; space group $P2_1/c$; a=16.170 (4), b=14.822 (2), and c=16.276 (5) Å and β=101.27 (5)°; U=3826(1) Å^3; D_m=1.3 and D_c=1.27 g cm^{-3}, Z=8; μ(Mo $K\alpha$)= 1.85 cm^{-1}. Intensity data were collected on a Rigaku AFC-4 four-circle diffractometer by using graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) in the 2θ-ω scan mode with a scan width of $\Delta\omega$=(1.0+0.5 tan θ)° and a scan speed of 4.0° min^{-1} over the range of 2θ values of 2° up to 55°. Three standard reflections monitored every 50 reflections showed no significant X-ray damage or crystal decay. Intensities of 9446 reflections were measured and 4707 independent reflections ($|F_o|>3.0\,\sigma(|F_o|)$) were obtained and used for the analysis. The intensities were corrected for the Lorentz and polarization factors, but no correction were made for the absorption and extinction.

The structure was solved by MULTAN 78 program.[10] The positions of hydrogen atoms were obtained from the difference Fourier synthesis. Anisotropic thermal parameters and isotropic thermal parameters were assumed for non-hydrogen atoms and for hydrogen atoms, respectively. The structural parameters were refined by a full-matrix least-squares method to the final R value of 0.056 and the R_w=0.054 in conjunction with the weighting scheme of $w=(40(\sin\theta/\lambda)^2-30\ (\sin\theta/\lambda)+9)^{-1}$. The atomic scattering factors for non-hydrogen atoms and for hydrogen atoms were taken from Refs. 11 and 12, respectively. All the computations were carried out on a FACOM M-380 and a M-780 computer using UNICS III system.[13] The final atomic parameters for non-hydrogen atoms are given in Table 4[14] and the molecular structure with the numbering system for non-hydrogen atoms is shown in Fig. 1.

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