Synthesis and Reactions of 1,2-Fused 3-Cyanoindolizines

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With the intention that annulation of carbo- or heteroaromatic rings at the 1,2-positions can activate 3-cyanoindolizines as 1,3-dipolar species, 6-cyanobenz[*a*]indolizines, pyridazino[4,5-*a*]indolizines and 5-cyano-1,3-diphenylthiopheno[3,4-*a*]indolizine were prepared. 6-Cyanobenz[*a*]indolizines smoothly underwent 1,3-dipolar cycloaddition on to dibenzoylacetylene and diacetylacetylene to afford the corresponding indolizino[3,4,5-*ab*]isoindoles, whereas 5-cyano-1,4-diphenylpyridazino[4,5-*a*]indolizine reacted with dimethyl acetylenedicarboxylate to give the 1:2 adduct. Only a 3% yield of 5-cyano-1,3-diphenylthiopheno[3,4-*a*]indolizine formed upon phosphorus pentasulfide treatment of 1,2-dibenzoyl-3-cyanoindolizine.

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The 1,3-dipolar cycloaddition reactions undoubtedly rival Diels-Alder reactions in ubiquity as well as in synthetic utility [1], their synthetic potential being far from exhausted. Recently, we have reported on synthesis of 1,2-unsubstituted 3-cyanoindolizines by 1,3-dipolar cycloadditions of heteroaromatic dicyanomethylides with phenyl vinyl sulfoxide and bis(trimethylsilyl)acetylene [2]. Bicyclic bridgehead nitrogen-containing heterocycles such as indolizines [3] and azapentalenes [4] whose resonance hybrids involve an ylide structure could serve as a bicycloimmonium ylide. Indeed, 1,2-unsubstituted 3-cyanoindolizines undergo 1,3-dipolar cycloaddition to electron deficient acetylenes in the presence of Pd-C to afford the cycl[2.2.3]azines [5], though in certain cases, reactions of 3-cyanoindolizines with dimethyl acetylenedicarboxylate in the absence of Pd-C gave the pyrrole derivatives in an extremely unusual fashion [6]. Annulation of carbo- or heteroaromatic nucleus to indolizines at the 1,2-positions

Table 1

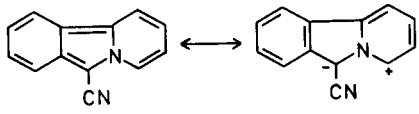
6-Cyanobenz[*a*]indolizines **2**

Compound	Yield (%) [a] Method A	Method B	Mp (°C)	IR (cm^{-1}) CN	CO	^1H NMR (δ) [b]
2a	45 (4)	35 (4)	127.7-128.0	2173	--	8.14-8.26 (m, 7H, H-1 ~ 3 + H-7 ~ 10), 8.53-8.68 (m, 1H, H-4)
2b	31 (1.4)	12 (2)	146.5-148.0	2160	--	2.45 (s, 3H, CH_3), 6.80-7.62 (m, 4H, H-7 ~ 10), 7.69 (br s, 1H, H-1), 7.90 (br d, J = 7.8 Hz, 1H, H-3), 8.27 (br d, J = 7.8 Hz, 1H, H-4)
2c	44 (3)	10 (2)	151.0-152.5	2174	--	7.07-7.79 (m, 9H, H-7 ~ 10 + C_6H_5), 7.98-8.19 (m, 2H, H-1,3), 8.45 (dd, J = 7.4, 1.6 Hz, 1H, H-4)
2d	21 (0.5)	24 (17)	213.0-214.0	2183	1641	7.38-8.08 (m, 9H, H-7 ~ 10 + C_6H_5), 8.33 (dd, J = 7.8, 1.7 Hz, 1H, H-3), 8.67 (br d, J = 7.8 Hz, 1H, H-4), 8.82 (d, J = 1.7 Hz, 1H, H-1)
2e	33 (trace)	---	191.0-192.0	2195	1722	4.06 (s, 3H, CH_3), 7.33-8.06 (m, 4H, H-7 ~ 10), 8.28 (dd, J = 8.3, 1.6 Hz, 1H, H-3), 8.62 (br d, J = 8.3 Hz, 1H, H-4), 8.89 (br d, J = 1.6 Hz, 1H, H-1)
2f	27 (--)	---	209.8-211.2	2175	1673	2.76 (s, 3H, CH_3), 7.38-8.08 (m, 4H, H-7 ~ 10), 8.33 (dd, J = 7.0, 1.8 Hz, 1H, H-3), 8.67 (br d, J = 7.0 Hz, 1H, H-4), 8.82 (br d, J = 1.8 Hz, 1H, H-1)
2g	19 (--)	---	190.5-192.5	2198	--	7.49 (td, J = 7.38, 1.02 Hz, 1H, H-9 or 8), 7.65 (td, J = 7.88, 1.02 Hz, 1H, H-8 or 9), 7.89 (dt, J = 8.35, 0.94 Hz, 1H, H-7 or 10), 8.24-8.29 (m, 2H, H-4 + H-10 or 7), 8.43 (dd, J = 4.6, 1.3 Hz, 1H, H-3), 9.47 (d, J = 1.34 Hz, 1H, H-1) [c]

[a] Parentheses indicate yields of benz[*a*]isoindolo[1,2,3-*cd*]indolizines **3**. [b] 60 MHz in deuteriochloroform unless otherwise mentioned. [c] 200 MHz.

is expected to activate 3-cyanoindolizines by means of aromatic stabilization in favor of the azomethine ylide structure, as exemplified in Scheme 1. In this paper we wish to report on the preparation and some cycloaddition reactions of 3-cyanoindolizines fused at the 1,2-positions by benzene, pyridazine, and thiophene rings.

Scheme 1



The reaction of pyridinium dicyanomethylide (**1a**) with benzyne generated from diphenyliodonium-2-carboxylate monohydrate in 1,2-bis(2-methoxyethoxy)ethane at about 200° for 1.5 hours gave 6-cyanobenz[*a*]indolizine (**2a**) in 45% yield along with benz[*a*]isoindolo[1,2,3-*cd*]indolizine (**3**, 4% yield) [7] upon column chromatography separation under medium pressure (mplc). The elemental and mass spectral analyses as well as ir, ^1H and ^{13}C nmr spectra are in agreement with structure **2a** (Tables 2 and 3). Alternatively, **2a** was prepared in a comparable yield by reaction of **1a** with benzyne that was generated from anthranilic acid and isoamyl nitrite in refluxing chloroform-acetone. The generality of these methods is illustrated in Table 1; this reaction also can be extended to synthesis of 6-cyanopyradino[1,2-*a*]isoindole (**2g**), although an analogous reaction of pyrimidinium dicyanomethylide with benzyne failed to give the corresponding indolizine.

As expected the ^{13}C resonances at 6 position (δ 85-90 ppm) are at considerably higher field than those of the non-fused 3-cyanoindolizines (δ 95-100 ppm) [2], thus suggesting more carbanionic character of the azomethine carbon. Indeed, 2-unsubstituted-, 2-methyl- and 2-phenyl-6-cyanobenz[*a*]indolizines(**2a,b,c**, C-6; δ 86.1, 84.9 and 85.8 ppm, respectively) readily underwent 1,3-dipolar cycloaddition at room temperature onto dibenzoylacetylene producing the corresponding 1,2-dibenzoylindolizino[3,4,5-

Scheme 2

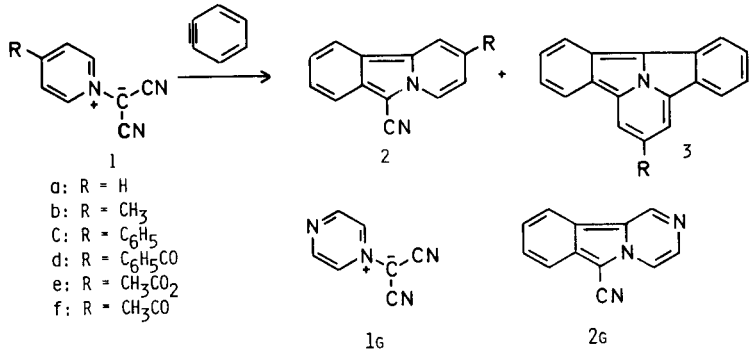


Table 2

^{13}C NMR Data of 6-Cyanobenz[*a*]indolizines **2** [a,b]

Compound	C-1[d]	C-2 [c]	C-3[d]	C-4[d]	C-6[r]	C-6a[r]	C-7[d], 8[d], 9[d] and 10[d]				C-10a[r]	C-10b[r]	CN[r]	C-α	Substituent C_6H_5 or CH_3
2a	125.0	117.4	116.5	128.0	86.1	117.4	118.5	119.9	121.0	121.1	130.8	131.9	115.2	—	
2b	124.3	132.5	116.3	127.9	84.9	115.7	117.4	119.6	119.9	120.5	131.1	132.3	115.7	21.2[q]	
2c	125.0	134.0	115.2	128.5	85.8	118.0	116.6	116.8	120.0	121.3	131.2	132.5	115.4	—	137.8[r] 126.6[d] 129.3[d] 128.2[d]
2d	124.2	128.5	117.3	128.7	89.0	121.1	117.3	120.0	121.5	123.1	129.1	132.0	113.9	193.2[r]	137.8[r] 128.7[d] 129.6[d] 132.7[d]
2e	122.4	129.0	119.3	128.4	88.0	121.5	116.0	116.4	120.1	120.6	124.7	131.3	113.3	164.5[r]	52.2[q]
2f [d]	128.6	129.3	115.5	128.7	90 [e]	120.5	117.4	119.3	119.8	123.2	124.2	132.2	113.7	194.3[r]	26.1[q]
2g	134.8	—	128.6	142.8	89.5	118.6	117.1	117.3	119.4	124.0	124.4	130.8	112.6	—	

[a] In dimethylsulfoxide-d_6 at 70°. [b] Superscripts indicate the partial proton decoupling pattern. [c] Singlet was observed for **2b-f**. [d] In deuteriochloroform at 48°. [e] Broad signal.

Table 3

Analytical Data of 6-Cyanobenz[*a*]indolizines **2**

Compound	Elemental Analysis Found (%)			Calcd. (%)			Mass Spectra Mass Fragments			Exact Mass		Formula
	C	H	N	C	H	N	M^+	Others		Found	Calcd.	
2a	81.47	4.01	14.72	81.22	4.20	14.58	192	---		192.0695	192.0688	$C_{13}H_8N_2$
2b	81.76	4.67	13.54	81.53	4.89	13.58	206	---		206.0803	206.0844	$C_{14}H_{10}N_2$
2c	85.14	4.29	10.18	85.05	4.51	10.44	268	---		268.0958	268.1000	$C_{19}H_{12}N_2$
2d	80.81	3.99	9.23	81.06	4.08	9.45	296	219	191	296.0969	296.0949	$C_{20}H_{12}N_2O$
2e	71.73	3.82	11.14	71.99	4.03	11.20	250	219	191	250.0741	250.0742	$C_{15}H_{10}N_2O_2$
2f	77.15	4.52	11.70	76.91	4.30	11.96	234	219	191	234.0855	234.0793	$C_{15}H_{10}N_2O$
2g	74.50	3.54	21.61	74.60	3.65	21.75	193	---		193.0677	193.0640	$C_{12}H_7N_3$

Table 4

1,2-Dibenzoylindolizino[3,4,5-*ab*]isoindoles **4**

Compound	Reaction Conditions Temperature (°C)	Time (hours)	Yield (%)	Mp (°C)	Mass Fragment M^+	Others	Elemental Analysis Found (%) C	H	N	Calcd (%) C	H	N	Formula
4a	rt	46	82	214-215	399	322 255	83.97	4.58	3.36	84.19	4.29	3.51	$C_{28}H_{17}NO_2$
4b	rt	24	82	256-257	413	336 278	84.19	4.60	3.38	84.24	4.63	3.39	$C_{29}H_{19}NO_2$
4c	rt	24	69	227-228	475	398 370	85.63	4.41	2.84	85.87	4.45	2.95	$C_{34}H_{21}NO_2$
4d	reflux	5.5	59	248-251	503	426 105	83.49	4.14	3.01	83.48	4.20	2.78	$C_{35}H_{21}NO_3$

Table 5

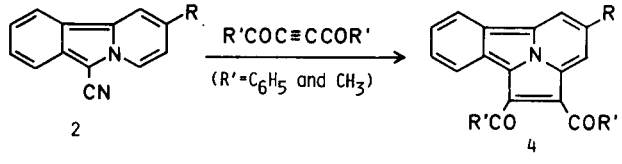
IR and ^{1}H NMR Spectral Data of 1,2-Dibenzoyl- and 1,2-Diacetylindolizino[3,4,5-*ab*]isoindoles **4** [a]

Compound	IR (cm^{-1}) CO	Ar	^{1}H NMR (δ) [b]
4a	1640	1600	7.19-7.75 (m, H-4,5 and C_6H_5), 7.96 (dd, J = 8.6, 7.0 Hz, 1H, H-8), 8.16 (dt, J = 6.6, 1,4 Hz, 1H, H-6), 8.18 (d, J = 7.0 Hz, 1H, H-7), 8.37 (d, J = 8.6 Hz, 1H, H-9), 8.41 (dt, J = 7.4, 1,2 Hz, 1H, H-3)
4b	1655	1605	2.84 (s, 3H, CH_3), 7.14-7.72 (m, 12H, H-4,5 and C_6H_5), 7.99 (s, 1H, H-7), 8.12 (dt, J = 7.6, 1.0-1.3 Hz, 1H, H-6), 8.22 (t, J = 1.0 Hz, H-9), 8.35 (dt, J = 7.6, 1.0 Hz, 1H, H-3)
4c	1630 1610 1657		7.18-7.75 (m, 15H, H-4,5 and C_6H_5), 7.85 (dd, J = 7.0, 1.0 Hz, 2H, *o*-C_6H_5), 8.17 (br d, J = 7.0 Hz, 1H, H-6), 8.40 (d, J = 1.2 Hz, 1H, H-7), 8.44 (dt, J = 8.0, 1.6 Hz, 1H, H-3), 8.55 (d, J = 1.0 Hz, 1H, H-9)
4d	1624 1598 1650		7.17-7.81 (m, 15H, H-4,5 and C_6H_5), 7.93 (dt, J = 6.8, 1.6 Hz, 2H, *o*-C_6H_5), 8.19 (dt, J = 7.6, 1.5 Hz, 1H, H-6), 8.48 (dt, J = 8.0, 1.1 Hz, 1H, H-3), 8.74 (d, J = 1.0 Hz, 2H, H-9,7)

[a] 200 MHz in deuteriochloroform. [b] The assignments of H-7 and H-9, and those of H-3 and H-6 may be reversed.

ab]isoindoles **4a-c**, whereas in the case of 2-benzoyl-6-cyanobenz[*a*]indolizine (**2d**) (C-6; δ 89 ppm) it was desirable to perform a reaction under refluxing benzene. Thus, the reactivity is qualitatively proportional to the carbanionic character of the C-6 that is reflected in the ^{13}C chemical shift. In agreement with this, the 1-methoxycarbonyl-3-cyanoindolizines whose ^{13}C resonances of C-3 appear at about 96-97 ppm reacted in an extremely sluggish manner with dimethyl acetylenedicarboxylate to afford only a trace amount of the corresponding cyclazines [8]. The results as well as ir and ^{1}H nmr spectra are summarized in Tables 4 and 5.

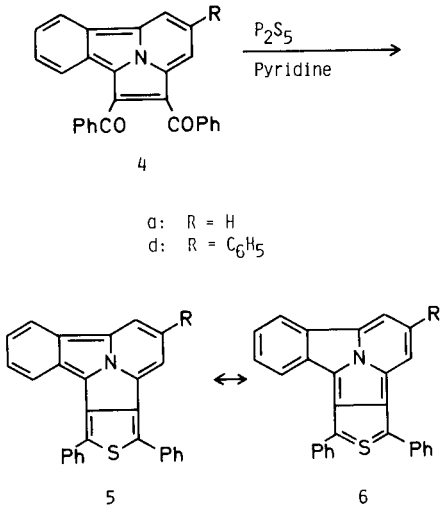
Scheme 3



a: R = H, R' = C_6H_5
b: R = CH_3, R' = C_6H_5
c: R = R' = C_6H_5
d: R = C_6H_5CO, R' = C_6H_5

Treatment of **4a** and **4d** with phosphorus pentasulfide in pyridine produced a new 18 π thiophene system **5a** and **5d** in 32% and 11% yield, respectively. This system can be formally regarded to be a non-classical thiophene **6** as one of the resonance contributors. The product **5a** was inert to dimethyl acetylenedicarboxylate in refluxing toluene for 72 hours, thus **5** being presumably a major resonance contributor to the ground state, though steric factors can not be neglected.

Scheme 4



Alternative possibilities exist for formation of 1,2-aromatic ring-fused 3-cyanoindolizines by initial 1,3-dipolar cycloaddition of **1** with diaroyl- or diacylacetylene followed by treatment with hydrazine and phosphorus pentasulfide that would give the pyridazine- and "nonclassical" thiophene-fused indolizines, respectively.

Pyridinium dicyanomethylides **1** readily underwent 1,3-dipolar cycloaddition with dibenzoylacetylene in refluxing toluene (more efficiently in the presence of Pd-C), producing the corresponding 1,2-dibenzoyl-3-cyanoindolizines **7a-e** in good yields. Similarly more reactive, though more unstable, diacetylacetylene combined with pyridinium ylides **1** in the absence of Pd-C to yield the 1,2-diacetyl-3-cyanoindolizines **7f-j**. The results are summarized in Tables 6, 7 and 8. Reaction of the dicarbonyl derivatives **7**

Scheme 5

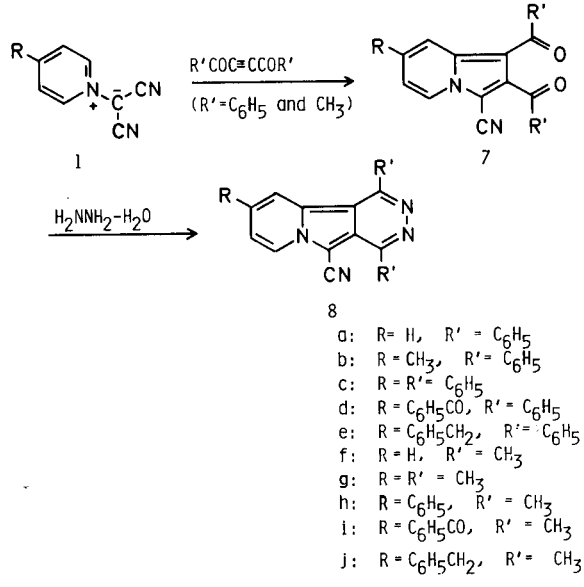


Table 6

1,2-Dibenzoyl- and 1,2-Diacetyl-3-cyanoindolizines **7**

Product	Reaction Conditions		Yield	Mp	Mass Fragments		Elemental Analysis [a] Found (%)			Calcd (%)			Formula
	Reflux Time (hours)	Pd-C	(%)	(°C)	M^+	Other	C	H	N	C	H	N	
7a	6	addn	86	158-159	350	273	78.78	3.96	8.06	78.85	4.03	8.00	$C_{23}H_{14}N_2O_2$
7b	2	addn	55	180-181	364	287	79.20	4.29	7.71	79.11	4.43	7.69	$C_{24}H_{16}N_2O_2$
7c	2	addn	62	188-190	426	349	81.94	4.13	6.51	81.67	4.25	6.57	$C_{29}H_{18}N_2O_2$
7d	3	addn	69	179-180	454	377	79.51	3.81	6.19	79.28	3.99	6.16	$C_{30}H_{18}N_2O_3$
7e	3	addn	79	134-135	440	363	81.80	4.48	6.47	81.80	4.58	6.36	$C_{30}H_{20}N_2O_2$
7f	3	none	56	169-170	226	211	68.98	4.52	12.59	69.02	4.46	12.38	$C_{13}H_{10}N_2O_2$
7g	1.5	none	47	143-144	240	225	69.86	4.92	11.54	69.99	5.03	11.66	$C_{14}H_{12}N_2O_2$
7h	1.5	none	53	181-182	302	287	75.44	4.51	9.37	75.48	4.67	9.27	$C_{19}H_{14}N_2O_2$
7i	1	none	69	154-155	330	315	73.00	4.49	8.54	72.72	4.27	8.48	$C_{20}H_{14}N_2O_3$
7j	1	none	69	81-82	316	301	75.84	4.93	8.79	75.93	5.10	8.86	$C_{20}H_{16}N_2O_2$

[a] Exact mass [M^+]; **7f**, Found: 226.0718; Calcd: 226.0742; **7g**, Found: 240.0871; Calcd: 240.0898; **7h**, Found: 302.1091; Calcd: 302.1055; **7i**, Found: 330.0953; Calcd: 330.1004; **7j**, Found: 316.1247; Calcd: 316.1211.

Table 7

IR and ^{1}H NMR Spectral Data of 1,2-Dibenzoyl- and 1,2-Diacetyl-3-cyanoindolizines **7** [a]

Compound	IR (cm^{-1})				^{1}H NMR (δ)
	CN	C_6H_5CO	and/or	CH_3CO	
7a	2220	1635	1655	1665	7.03-7.66 (m, 12H), 8.27 (br d, J = 9.6 Hz, 1H, H-8), 8.48 (br d, J = 6.6 Hz, 1H, H-5)
7b	2220	1640	1660	1670	2.48 (s, 3H, CH_3), 6.91-7.85 (m, 11H), 8.06 (br s, 1H, H-8), 8.31 (d, J = 7.2 Hz, 1H, H-5)
7c	2215	1615	1635	1660	7.11-7.52 (m, 14H, H-6 + C_6H_5), 7.69-7.73 (m, 2H, C_6H_5), 8.50 (dd, J = 3.8, 2.0 Hz, H-5), 8.52 (br d, J = 2.0 Hz, 1H, H-8) [b]
7d	2206	1620	1655	1660	7.11-7.72 (m, 14H, H-6 + C_6H_5), 7.82-7.87 (m, 2H, C_6H_5), 8.54 (dd, J = 6.8, 3.2 Hz, 1H, H-5), 8.57 (s, 1H, H-8) [b]
7e	2210	1623	1652	1660	4.10 (s, 2H, CH_2), 6.94-7.65 (m, 16H), 8.15 (br s, 1H, H-8), 8.35 (br d, J = 10.8, 1.0 Hz, 1H, H-5)
7f	2201	1645	1650	1683	2.53, 2.80 (each s, 3H, CH_3), 7.07-7.77 (m, 2H, H-6, 7), 8.30-8.63 (m, 2H, H-5, 8)
7g	2202	1634	1685		2.50 (s, 6H, CH_3 × 2), 2.73 (s, 3H, CH_3), 7.00 (dd, J = 8.0, 1.9 Hz, 1H, H-6), 8.10 (dd, J = 1.9, 0.5 Hz, 1H, H-8), 8.30 (dd, J = 8.0, 0.5 Hz, 1H, H-5)
7h	2200	1639	1672		2.54, 2.78 (each s, 3H, CH_3), 7.43 (dd, J = 7.2, 1.8 Hz, 1H, H-6), 7.49-7.58 (m, 3H, C_6H_5), 7.67-7.71 (m, 2H, C_6H_5), 8.38 (br d, J = 7.2 Hz, 1H, H-5), 8.50 (br d, J = 1.8 Hz, 1H, H-8)
7i	2200	1658	1663	1679	2.48, 2.80 (each s, 3H, CH_3), 7.50-7.71 (m, 4H, H-6 + C_6H_5), 7.80-7.85 (m, 2H, C_6H_5), 8.42 (dd, J = 7.2, 1.0 Hz, 1H, H-5), 8.61 (dd, J = 1.4, 1.0 Hz, 1H, H-8)
7j	2201	1654	1665	1697	2.47, 2.75 (each s, 3H, CH_3), 4.07 (s, 2H, CH_2), 6.94 (dd, J = 6.6, 1.9 Hz, 1H, H-6), 7.31 (s, 5H, C_6H_5), 8.20 (br d, J = 1.9 Hz, 1H, H-8), 8.25 (d, J = 6.6 Hz, 1H, H-5)

[a] 60 MHz in deuteriochloroform unless otherwise stated. [b] 200 MHz.

Table 8

^{13}C NMR Spectral Data of 1,2-Dibenzoyl- and 1,2-Diacetyl-3-cyanoindolizines **7** [a]

Compound	C-1[s]	C-2[s]	C-3[s]	C-5[d]	C-6[d]	C-7 [b]	C-8[d]	C-8a[s]	CN[s]	CO[s]		Other Substituents
7a	111.3	136.4	98.1	127.6	116.8	120.9	125.6	140.1	113.9	189.9	190.2	137.5[s] 137.7[s] 128.2[d] 128.5[d] 128.9[d] 131.1[d] 133.2 [d]
7b	111.5	136.6	97.6	124.9	119.4	139.5	124.9	140.3	112.7	189.9	190.5	21.6[q] 137.8[s] 138.0[s] 128.2[d] 128.5[d] 128.9[d] 131.1[d] 131.9[d]
7c	111.4	137.7	97.8	125.6	116.5	140.7	117.4	140.3	114.4	189.8	190.4	136.9[s] 137.2[s] 138.0[s] 126.9[d] 129.0[d] 129.4[d] 128.2[d] 128.5[d] 132.1[d] 133.2[d]
7d	110.8	137.5	99.5	125.6	116.1	135.1	123.9	139.5	117.0	189.2	190.1	136.0[s] 135.6[s] 136.0[s] 193.2[s] 128.3[d] 128.8[d] 129.8[d] 132.6[d] 133.4[d]
7e	111.4	137.8	97.8	125.3	118.6	142.4	119.4	140.3	113.3	189.8	190.4	41.7[t] 136.7[s] 137.7[s] 138.2[s] 125.3[d] 127.0[d] 128.2[d] 128.5[d] 129.0[d] 132.0[d] 133.2[d]
7f	111.0	137.5	96.9	129.2	117.1	120.8	126.1	138.7	113.1	195.9	198.1	29.7[q] 31.2[q]
7g	111.8	137.5	95.5	124.9	119.0	139.6	119.5	139.6	112.9	192.9	196.6	21.6[q] 30.1[q] 31.3[q]
7h	111.4	137.5	96.1	125.7	116.4	141.4	117.5	138.6	113.6	194.5	196.7	30.2[q] 31.3[q] 136.8[s] 126.8[d] 129.3[d] 129.4[d]
7i	111.1	137.7	97.4	125.4	115.9	135.2	123.8	134.8	117.1	193.3	195.3	30.4[q] 31.1[q] 135.8[s] 193.0[s] 128.7[d] 129.7[d] 133.3[d]
7j	111.5	137.9	95.4	125.2	118.0	142.3	119.0	138.0	113.2	192.5	196.3	30.1[q] 31.0[q] 41.3[t] 136.7[s] 125.2[d] 128.6[d] 128.7[d]

[a] In deuteriochloroform. Superscipts indicate the partial proton decoupling pattern. [b] Doublet was observed for **7a** and **7f**, while singlet was done for **7b-e** and **7g-j**.

Table 9

5-Cyano-1,4-diphenyl- and 5-Cyano-1,4-dimethylpyridazino[4,5-*a*]indolizines **8**

Compound	Yield (%)	Mp (°C)	Mass Fragments M⁺	Others	Analytical Data Found (%) C	H	N	Calcd. (%) C	H	N	Formula [a]
8a	87	284-286	346		79.84	3.85	16.07	79.75	4.07	16.17	$C_{23}H_{14}N_4$
8b	85	284-286	360		80.25	4.25	15.44	79.98	4.47	15.54	$C_{24}H_{16}N_4$
8c	91	279-282	422		82.69	4.22	13.03	82.44	4.29	13.26	$C_{29}H_{18}N_4$
8d	95	245-247	450	421 345	79.69	3.95	12.45	79.98	4.03	12.44	$C_{30}H_{18}N_4O$
8e	95	244-246	436		82.68	4.77	12.60	82.55	4.62	12.84	$C_{30}H_{20}N_4$
8f	89	282-285	222	193	69.95	4.49	25.20	70.26	4.54	25.21	$C_{13}H_{10}N_4$
8g	100	287-289	236	207	71.40	5.30	23.88	71.17	5.12	23.71	$C_{14}H_{12}N_4$
8h	100	>300	298	269	76.58	4.51	18.60	76.49	4.73	18.78	$C_{19}H_{14}N_4$
8i	97	276-278	326		73.89	4.37	17.31	73.61	4.32	17.17	$C_{20}H_{14}N_4O$

[a] Exact mass [M⁺]; **8f**, Found: 222.0888; Calcd: 222.0906; **8g**, Found: 236.1067; Calcd: 236.1062; **8h**, Found: 298.1194; Calcd: 298.1219; **8i**, Found: 326.1175; Calcd: 326.1168.

Table 10

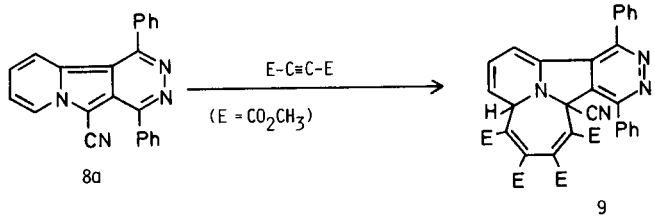
IR and ^{1}H NMR Spectral Data of 5-Cyano-1,4-diphenyl- and 5-Cyano-1,4-dimethylpyridazino[4,5-*a*]indolizines **8** [a]

Compound	IR (cm⁻¹) CN	Others	^{1}H NMR (δ)
8a	2205	1625	7.33-7.50 (m, 3H), 7.57-7.66 (m, 5H), 7.79-7.86 (m, 3H), 7.96-8.01 (m, 2H), 8.79 (dd, J = 8.0, 1.2 Hz, 1H, H-7)
8b	2190	1640	2.43 (s, 3H, CH_3), 7.28 (dd, J = 7.0, 1.6 Hz, 1H, H-8), 7.56-7.65 (m, 7H), 7.79-7.84 (m, 2H), 7.97-8.02 (m, 2H), 8.68 (d, J = 7.0 Hz, 1H, H-7)
8c	2175	1630	7.48-7.53 (m, 5H), 7.61-7.68 (m, 6H), 7.76 (dd, J = 7.2, 1.8 Hz, 1H, H-8), 7.86-7.91 (m, 2H), 8.00-8.04 (m, 3H), 8.83 (dd, J = 7.2, 0.8 Hz, 1H, H-7)
8d	2205	1630 1657	7.64-7.74 (m, 6H), 7.83-7.88 (m, 6H), 7.93-7.98 (m, 2H), 8.07-8.23 (m, 2H), 8.44 (br s, 1H, H-10), 9.05 (dd, J = 7.2, 1.0 Hz, 1H, H-7)
8e	2201	1640	3.99 (s, 2H, CH_2), 7.05-7.10 (m, 2H), 7.27-7.34 (m, 3H), 7.48-7.61 (m, 8H), 7.69-7.74 (m, 2H), 7.94-7.99 (m, 2H), 8.67 (br d, J = 7.0 Hz, 1H, H-7)
8f	2200	1630	3.12, 3.33 (each s, 3H, CH_3), 7.92 (br t, J = 7.0 Hz, 1H, H-8), 8.10 (br t, J = 8.0 Hz, 1H, H-9), 8.59 (br d, J = 8.0 Hz, 1H, H-10), 9.05 (br d, J = 7.0 Hz, 1H, H-7) [b]
8g	2195	1640	2.77, 3.05, 3.27 (each s, 3H, CH_3), 7.69 (br d, J = 7.0 Hz, 1H, H-8), 8.30 (br d, J = 7.0 Hz, 1H, H-7), 8.85 (s, 1H, H-10) [b]
8h	2190	1633	3.08, 3.33 (each s, 3H, CH_3), 7.60-7.64 (m, 3H), 7.76-7.81 (m, 2H), 8.12 (dd, J = 8.0, 2.0 Hz, 1H, H-8), 8.61 (br s, 1H, H-10), 9.04 (br d, J = 8.0 Hz, 1H, H-7) [b]
8i	2200	1650	3.16, 3.28 (each s, 3H, CH_3), 7.57-7.65 (m, 2H), 7.73-7.88 (m, 3H), 8.22 (dd, J = 7.0, 1.4 Hz, 1H, H-8), 8.83 (br s, 1H, H-10), 9.19 (br d, J = 7.0 Hz, 1H, H-7) [b]

[a] 200 MHz in deuteriochloroform. [b] A trace amount of trifluoroacetic acid was added.

with 100% hydrazine hydrate afforded the corresponding pyridazine-fused 3-cyanoindolizines **8** in excellent yields. For example, **7a** and **7f** gave 5-cyano-1,4-diphenyl- and 5-cyano-1,4-dimethylpyridazino[4,5-*a*]indolizine (**8a**) and (**8f**) as yellow crystals in 87 and 89% yield respectively, providing a convenient characterization of these diaroyl and diacyl derivative. Reaction of 5-cyano-1,4-diphenylpyridazino[4,5-*a*]indolizine (**8a**) with dimethyl acetylenedicarboxylate in refluxing toluene for 14 hours produced the

Scheme 6



8a 9

Table 11

^{13}C NMR Spectral Data of 5-Cyano-1,4-diphenyl- and 5-Cyano-1,4-dimethylpyridazino[4,5-*a*]indolizines **8** [a]

Compound	C-1'	C-4'	C-4a'	C-5'	C-7'	C-8'	C-9 [b]	C-10'	C-10a'	C-10b'	CN'	R' C-1''	R' C-2' C-3''	R' C-2'' C-4'	R' C-3' C-4''	Substituent (R'') C-α	Substituent (R'') C_6H_5
8a	153.4	152.7	124.1	91.5	132.6	121.3	122.1	127.5	133.5	110.9	111.0	132.4'	128.7' 129.5'	129.1' 129.6'	129.7' 131.5'	---	
8b	152.8	152.6	124.1	92.4	133.4	120.2	144.6	127.6	134.7	109.8	110.2	131.7' 131.8'	128.8' 129.3'	128.9' 129.9'	125.1' 127.2'	21.8'	
8c	153.7	152.9	125.0	93.0	134.1	117.5	145.3	122.2	135.4	109.9	111.0	131.1' 132.5'	128.8' 129.3'	129.2' 130.0'	127.0' 127.1'		135.0' 130.3' 131.2' 128.6'
8d	153.8	153.4	124.8	94.2	133.7	121.8	137.0	122.8	134.9	109.7	112.8	132.1' 132.7'	128.8' 129.5'	128.9' 129.7'	127.2' 128.1'	191.6'	133.1' 129.7' 131.2' 128.8'
8e	154.3	151.9	124.1	89.4	130.1	120.1	140.4	127.1	136.5	110.7	112.9	131.6' 135.6'	128.4' 128.9'	128.8' 129.5'	121.5' 125.8'	41.3'	137.7' 128.8' 128.9' 129.9'
8f [c]	153.4	151.6	125.2	91.0	131.1	122.1	122.4	129.3	133.8	110.0	111.8	17.5'	19.3'			---	
8g [c]	152.8	152.2	125.5	91.3	127.6	120.8	145.0	124.7	134.8	109.2	110.8	17.4'	19.3'			21.6'	
8h [c]	153.0	152.7	126.0	91.7	131.1	118.1	145.7	121.9	135.3	110.2	110.6	17.7'	19.4'				135.1' 127.5' 128.3' 130.0'
8i [c]	153.8	153.4	126.1	93.3	134.9	121.9	138.2	122.8	134.7	110.1	111.9	17.8'	19.4'				133.1' 128.3' 129.2' 130.1'

[a] Superscipts indicate the partial proton decoupling pattern. [b] Singlet was observed for **8b-e** and **8g-i**, while doublet was done for **8a** and **f**. [c] A few drops of trifluoroacetic acid was added.

1:2 adduct in 43% yield, whose structure was tentatively assigned as **9**. There are several precedents for this type of structure from nitrogen heterocycles such as pyridines [9], azapentalenes [10], and azaazulenes [11,12].

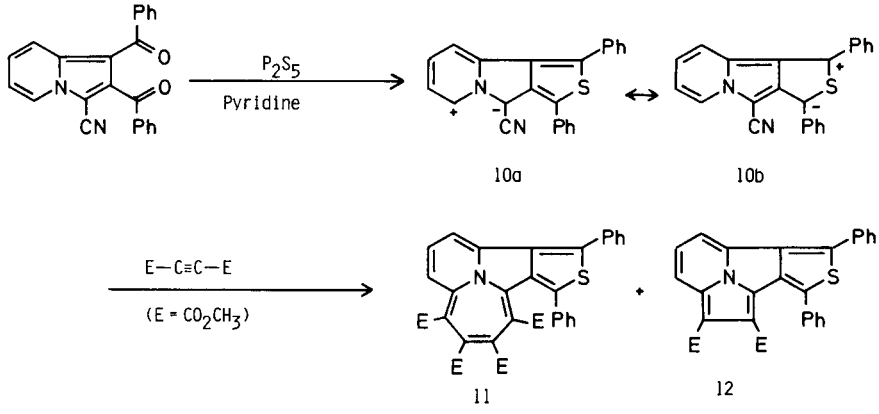
A nonclassical thiophene like 5-cyano-1,3-diphenylthiopheno[3,4-*a*]indolizine (**10**) offers an interesting possibility for the development of two kinds of 1,3-dipolar forms, an azomethine ylide **10a** and a thiocarbonyl ylide **10b** within the fused ring system [4,13]. Unfortunately, the yield of **10** was too low to extend further study on a nonclassical thiophene system; only 3% yield of **10** was obtained upon phosphorus pentasulfide treatment of **7a** in refluxing pyridine followed by the usual work up. Dimethyl acetylenedicarboxylate underwent cycloaddition with **10** in refluxing toluene to give the dehydrocyanated 1:2 adduct **11** in low yield along with a trace amount of the dehydrocyanated 1:1 adduct, possibly **12**.

EXPERIMENTAL

General.

Melting points were taken on a Yanagimoto micro melting point apparatus and uncorrected. The ir spectra were obtained on a Jasco IR-G or a Hitachi EPI-G spectrometer. The ^{1}H nmr spectra were measured on a JEOL JNM-PMX60 (60 Mz) or on a Varian VXR200 (200 MHz) instrument. The ^{13}C spectra were recorded on a JEOL JNM-FX90Q pulsed Fourier-transform spectrometer operating at 22.49 MHz. Chemical shifts

Scheme 7



are expressed in parts per million downfield from internal tetramethylsilane. Partial proton decoupling was used to distinguish between individual carbon atoms. Mass spectra and the exact mass were obtained on a JEOL JMS-DX303 spectrometer at 70 eV of ionization energy and their data were processed with JEOL JMA-DA5000 system. Preparative medium-pressure liquid chromatography (mplc) was carried out using a column (25 × 310 mm) pre-packed with silica gel (Lobar, LiChroprep Si 60, Merck). Toluene and xylene were dried over Drierite. The dicyanomethylides, dibenzoylacetylene and diacetylacetylene were prepared according to the methods reported by Linn *et al.* [14], Lutz *et al.* [15] and Acheson *et al.* [16], respectively.

General Procedures for the Preparaton of 6-Cyanobenz[*a*]indolizines **2** (Tables 1, 2 and 3).

Method A.

A magnetically stirred mixture of the ylide **1** (3 mmoles) and diphenyliodonium-2-carboxylate monohydrate (3.3 mmoles) in 1,2-bis(2-methoxyethoxy)ethane (15 ml) was heated to about 210° in an oil bath for 0.5-2.0 hours. The solvent was distilled off and the residue was fractionated by a column chromatography (Wakogel C-100). Elution with 20% ethyl acetate in hexane gave two fractions, which were purified by mplc (elution with 10% ethyl acetate in hexane). The first fraction was recrystallized from hexane and the second was purified by recrystallization from ethanol to afford the corresponding cyclazine **3** and indolizine **2**, respectively.

Method B.

To a hot, magnetically stirred solution of the ylide **1** (3 mmole) and isoamyl nitrite (15 mmole) in chloroform (45 ml) was added dropwise a solution of anthranilic acid (15 ml) in acetone (30 ml). After refluxing for 4-6 hours the solvent and the excess reagent was evaporated *in vacuo* and the residue was chromatographed on alumina (Wako, about 200 mesh) with ethyl acetate and benzene as eluent affording the cyclazine **3** and the indolizine **2**, which were recrystallized from hexane and 10% benzene in ethanol, respectively.

General Procedure for Preparation of 1,2-Dibenzoylindolizino[3,4,5-*ab*]-isoindoles **4** (Tables 4 and 5).

A solution of 6-cyanobenz[*a*]indolizine (**2**) (100 mg) and dibenzoylacetylene (1.1 times the equimolar amount of the indolizine **2**) in benzene (30 ml) was magnetically stirred at room temperature for the time periods given in Table 4. In the case of 4-benzoyl substituted indolizine **2d**, the reaction mixture was heated to reflux for 5.5 hours. After evaporation of solvent, the residue was chromatographed on alumina (Wako, about 200 mesh) with benzene and ethyl acetate as eluent. Recrystallization from ethanol afforded the cyclazine **4**.

1,2-Diacetylindolizino[3,4,5-*ab*]isoindole **4e** (Tables 4 and 5).

A solution of diacetylacetylene (100 mg, 0.9 mmole) and 6-cyanobenz-[*a*]indolizine (**2a**) (100 mg, 0.5 mmole) in benzene (20 ml) was magnetically stirred at room temperature for 1 hour. The solvent was removed *in vacuo*. The residue was subjected to chromatography on silica gel (Wakogel C-100) with 33% ethyl acetate in hexane to give the crude product **4e**, which was further purified by mplc (40% ethyl acetate in hexane).

4,6-Diphenylthiopheno[3,4-*a*]indolizino[3,4,5-*ab*]isoindole (**5a**).

A mixture of 1,2-dibenzoylindolizino[3,4,5-*ab*]isoindole (**4a**) (500 mg, 1.25 mmoles) and phosphorus pentasulfide (2.0 g) in dry pyridine (60 ml) was heated under reflux with stirring for 2 hours. The resulting reaction mixture was poured into 10% aqueous sodium hydroxide solution (250 ml). A dark red solid precipitated, and was purified by column chromatography on silica gel (Wakogel C-100) with benzene as eluent and recrystallized from ethanol-benzene (1:2) to afford dark red crystals **5a** (260 mg, 32%) mp 201-204°; ms: [m/z] 399 (M^+), 367 (M^+-S), 322 (M^+-C_6H_5); ir (potassium bromide): 1593, 1528, 1402, 1338, 1315, 755, 747, 739, 732, 727, 695 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.10-7.78 (m, 10H), 7.78-8.48 (m, 7H).

Anal. Calcd. for $C_{28}H_{17}NS$: C, 84.18; H, 4.29; N, 3.51; S, 8.03. Found: C, 84.25; H, 4.16; N, 3.34; S, 8.09.

2-Benzoyl-4,6-diphenylthiopheno[3,4-*a*]indolizino[3,4,5-*ab*]isoindole (**5d**).

A mixture of 1,2,4-tribenzoylindolizino[3,4,5-*ab*]isoindole (**4d**) (50 mg, 0.1 mmole) and phosphorus pentasulfide (0.5 g) in dry pyridine (50 ml) was heated at reflux with stirring for 2.5 hours. The resulting reaction mixture was poured into 10% aqueous sodium hydroxide solution (150 ml) and extracted with ether. The combined organic layer was dried with anhydrous sodium sulfate and evaporated to leave a dark red solid, which was purified by column chromatography on alumina (Wako, about 200 mesh) with benzene-ethyl acetate (9:1) as eluent to give red crystals **5d** (11 mg, 22%), mp 253-254°; ms: [m/z] 503 (M^+), 398 (M^+-COC_6H_5); ir (potassium bromide): 1638, 1615, 1595, 1456, 1360, 1284, 1250, 1108, 750, 720, 712, 695, 652 cm^{-1}; Exact mass: m/z. Calcd. for $C_{35}H_{21}NOS$: 503.1344. Found: 503.1329.

Reaction of 4,6-Diphenylthiopheno[3,4-*a*]indolizino[3,4,5-*ab*]isoindole (**5a**) with Dimethyl Acetylenedicarboxylate.

A mixture of the isoindole **5a** (150 mg, 0.4 mmole) and dimethyl acetylenedicarboxylate (320 mg, 2.2 mmoles) was heated in refluxing toluene (40 ml) for 72 hours. After evaporation of the solvent, the isoindole **5a** (130 mg, 87%) was recovered by column chromatography on alumina (Wako, about 200 mesh) with benzene as the eluent.

General Procedure for Preparation of 3-Cyano-1,2-dibenzoylindolizines **7a-e** (Tables 6, 7 and 8).

A mixture of pyridinium dicyanomethylide **1** (14 mmoles), dibenzoylacetylene (17 mmoles) and Pd-C (5%, 2 g) in dry toluene (200 ml) was refluxed with stirring for the time periods stated in Table 6. After filtration of Pd-C and evaporation of toluene, the product **7** was isolated by column chromatography on alumina (Wako, about 200 mesh) with benzene as eluent, and purified by recrystallization from ethanol-ethyl acetate (1:1).

General Procedure for Preparation of 3-Cyano-1,2-diacetylindolizines **7f-j** (Tables 6, 7 and 8).

A solution of pyridinium dicyanomethylide **1** (3.2 mmoles) and diacetylacetylene (9-12 mmoles) in dry toluene (30 ml) was heated to reflux for the time period given in Table 6, cooled, and evaporated to leave a crude product **7** which was purified by column chromatography and mplc (elution with 10% ethyl acetate in hexane), and then was recrystallized from ethanol-hexane.

General Procedure for Preparation of 5-Cyano-1,4-diphenyl- and 5-Cyano-1,4-dimethylpyridazino[4,5-*a*]indolizines **8a-i** (Tables 9, 10 and 11).

To a magnetically stirred hot solution of 3-cyano-1,2-diphenyl- or 3-cyano-1,2-diacetylindolizine, **7**, in ethanol-benzene was added dropwise an excess amount of 100% hydrazine hydrate. After stirring at room temperature for 1 hour and standing in a refrigerator overnight, the appeared precipitates were filtered and washed with ethanol to give yellow crystals of the products **8**.

Reaction of 5-Cyano-1,4-diphenylpyridazino[4,5-*a*]indolizine (**8a**) with Dimethyl Acetylenedicarboxylate.

A solution of the indolizine **8a** (200 mg, 0.58 mmole) and dimethyl acetylenedicarboxylate (250 mg, 1.76 mmoles) in dry toluene (30 ml) was heated at reflux for 14 hours. After evaporation of the solvent, the residue was separated by chromatography on silica gel (Wakogel C-100) with benzene-ethyl acetate (9:1) to give yellow crystals of the 1:2 adduct **9** (158 mg, 43%), mp 282-283°; ms: [m/z] 630 (M^+ for $C_{35}H_{26}N_4O_8$), 599 (M^+-OCH_3), 571 (M^+-CO_2CH_3), 553 (100%, M^+-C_6H_5); ir (potassium bromide): 2960, 2230, 1745, 1725, 1443, 1360, 1337, 1265, 1240, 1215, 1178, 757, 697 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.45, 3.63, 3.86, 3.88 (each s, 3H × 4), 6.80-6.96 (m, 2H), 7.15-7.35 (m, 5H), 7.50-7.56 (m, 4H),

7.66-7.77 (m, 2H), 8.19-8.24 (m, 1H); ^{13}C nmr (deuteriochloroform): 53.1, 53.2, 54.0, 54.1 (each q, CH_3), 164.9, 165.0, 166.1, 169.5 (each s, CO), 65.2, 91.6, 103.5, 108.3, 109.5, 115.7, 118.0, 132.6, 132.9, 134.4, 141.7, 144.5, 145.6 (each s), 126.1, 128.5, 128.6, 128.7 (each strong d; the phenyl *ortho* and *meta* carbons), 129.5, 131.2 (each d, the phenyl *para* carbons), 116.1, 119.8, 124.8, 125.9 (each d); Exact mass: m/z. Calcd. for $C_{35}H_{26}N_4O_8$: 630.1750. Found: 630.1779.

Anal. Calcd. for $C_{35}H_{26}N_4O_8$: C, 66.66; H, 4.16; N, 8.89. Found: C, 66.60; H, 4.16; N, 8.50.

Reaction of 3-Cyano-1,2-dibenzoylindolizine (**7a**) with Phosphorus Pentasulfide and Reaction of the Product **10** with Dimethyl Acetylenedicarboxylate.

A mixture of 3-cyano-1,2-dibenzoylindolizine **7a** (500 mg, 1.4 mmoles) and phosphorus pentasulfide (3 g) was heated in refluxing pyridine (60 ml) with magnetically stirring for 1.5 hours. The resulting reaction mixture was poured into 10% aqueous sodium hydroxide solution (150 ml) and extracted with ether (total 150 ml). The combined organic layers were dried with anhydrous calcium chloride and evaporated to leave a red precipitate, which was separated by column chromatography on alumina (Wako, about 200 mesh) with benzene as the eluent. Without further purification, the red crystals of **10**, (mp 221-223°; ir (potassium bromide): 2170 cm^{-1}) were heated to reflux with dimethyl acetylenedicarboxylate (600 mg, 4.2 mmoles) in dry benzene (60 ml) for 1 hour. After evaporation of the solvent, the residue was separated by column chromatography on silica gel (Wakogel C-100) with benzene-ethyl acetate (1:1) as the eluent to afford the following: From the first fraction the 1:2 adduct **11**, mp 225° was obtained; ms: [m/z] 607 (M^+ for $C_{34}H_{25}NO_8S$); ir (potassium bromide): 2945, 2915, 2832, 1712, 1488, 1445, 1447, 1258, 1205, 1168, 995, 788, 749, 690 cm^{-1}. From the second fraction the 1:1 adduct **12**, mp 135.5-136.5° was obtained; ms: [m/z] 465 (M^+ for $C_{28}H_{19}NO_4S$), 434 (M^+-S+1); ir (potassium bromide): 1758, 1720, 1520, 1468, 1346, 1313, 1232, 1195, 1120, 1085, 808, 773, 767, 713 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.56, 3.94 (each s, 3H × 2), 7.25 (s, 6H), 7.42-7.77 (m, 4H), 7.84-7.90 (m, 2H), 8.22 (dd, J = 8.4, 0.9 Hz, 1H); Exact mass: m/z Calcd. for $C_{28}H_{19}NO_4S$: 465.1035. Found: 465.1014.

Compounds **11** and **12** were obtained in amounts too small to allow elemental analyses.

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