RING CLOSURE OF 4-SUBSTITUTED 1-AMINO-1-(2-AMINOANILINO)-2,4-DICYANOBUTA-1,3-DIENE *VIA* 5-*EXO*-TRIG AND 6-*EXO*-DIG PROCESS

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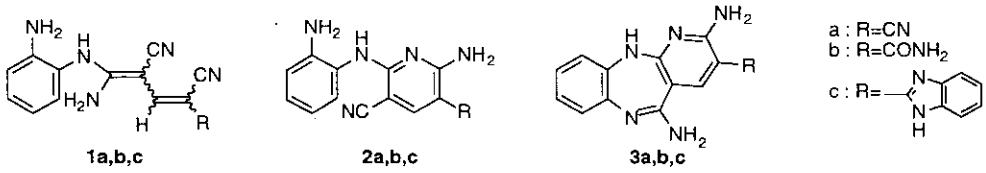
Abstract---Reaction conditions for ring closures of 4-substituted 1-amino-1-(2-aminoanilino)-2,4-dicyanobuta-1,3-diene(**1**) were described in the light of Baldwin's rule. A new route to 6-alkoxy-3-(2-benzimidazolinylidene)-5-cyano-2-imino-2,3-dihydropyridine(**9**) was also developed from 1,5-dinitrile(**1**).

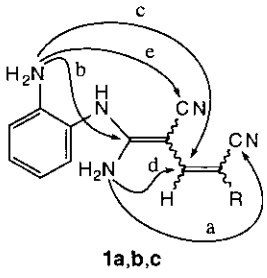
Many pyrido[2,3-*b*][1,5]benzodiazepines have been synthesized in order to evaluate their biological activities,[1] and one of them, propizepine, appears to be clinically active.[2] Recently, we have reported the novel synthesis of pyrido[2,3-*b*][1,5]benzodiazepines(**3a,b,c**) by ring closure of 3-substituted 2-amino-6-(2-aminoanilino)-5-cyanopyridines(**2a,b,c**)(Scheme 1).[3,4] The pyridine derivatives(**2a,b,c**) as the starting materials were obtained by ring closure of the 4-substituted 1-amino-1-(2-aminoanilino)-2,4-dicyanobuta-1,3-dienes(**1a,b,c**).

It also seems possible that polyaminopolynitrile(**1**) might be subject to another ring-forming reaction. Thus five types of heterocycles were predicted by Baldwin's rule as ring-closed products of **1** *via* favored ring-forming processes (pathways a to e) as summarized in Scheme 2. Among them, it was found that compounds(**5 a,b,c**) formed by 7-*Exo*-Trig process (pathway c) would be considered as ring tautomers of **1 a,b,c** which might be more unstable than **1a,b,c** in the light of resonance stabilization(Scheme 3) . Although the rule is useful for predicting the relative facility of ring closures, no one knows how to obtain the predicted heterocycles. This report describes several conditions for the ring closure of **1 a,b,c** in order to obtain some products predicted by Baldwin's rule.

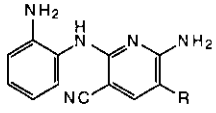
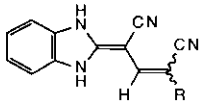
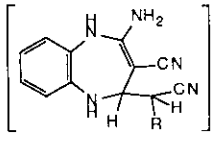
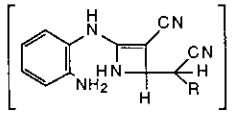
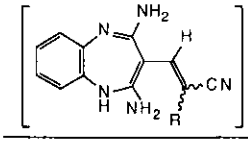


1a,b,c **2a,b,c** **3a,b,c**

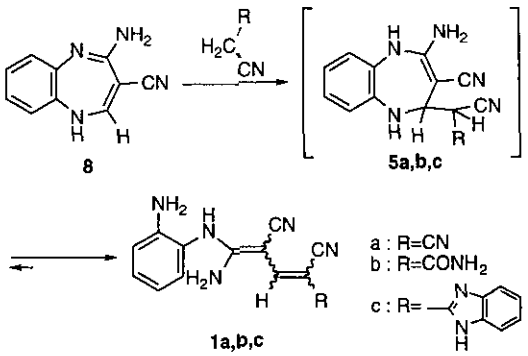
Scheme 1



1a,b,c

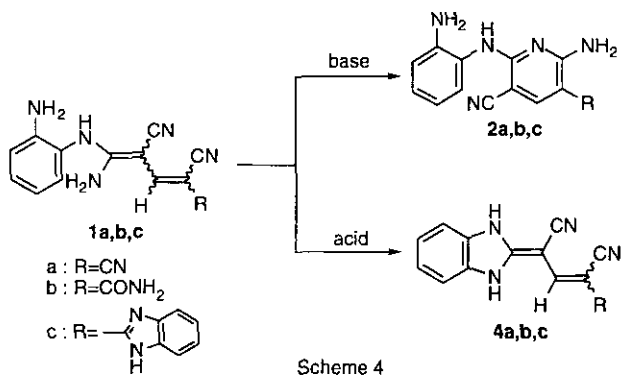
Product predicted by Baldwin's rule		Pathway
	**2a,b,c**	a
	**4a,b,c**	b ($-NH_3$)
	[5]	c
	[6]	d
	[7]	e

Scheme 2

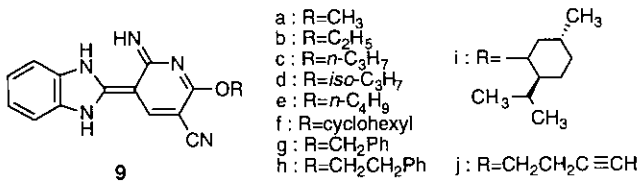


Scheme 3

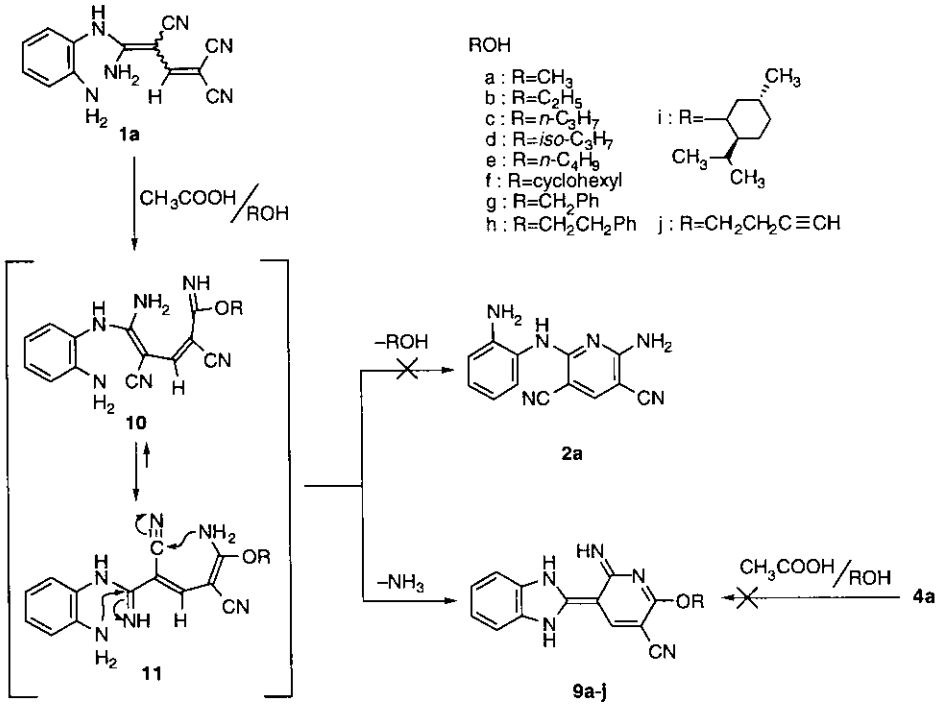
Compounds(**1a,b,c**) were obtained by the reaction of 4-amino-1*H*-1,5-benzodiazepine-3-carbonitrile(**8**) with active methylene compounds (Scheme 3).[6] When **1a,b,c** were heated in an alcohol such as methanol, ethanol, or 1-butanol in the presence of triethylamine or 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), pyridine derivatives(**2a,b,c**) were obtained through the 6-*Exo*-Dig process (pathway a) in 60~70% yield.[6] In contrast, when **1a,b,c** were heated in acetic acid or dilute hydrochloric acid, 2-substituted 4-(2-benzimidazolinylidene)pent-2-enedinitriles (**4a,b,c**) were obtained through the 5-*Exo*-Trig process (pathway b) with loss of ammonia in 60~70% yield (Scheme 4). Although the ring closure of **1** to a four-membered ring(**6**) through the 4-*Exo*-Trig process (pathway d), and a seven-membered ring(**7**) through the 7-*Exo*-Dig process (pathway e) is also predicted by Baldwin's rule, so far we have not obtained them (Scheme 2).



Scheme 4



Scheme 5



Scheme 6

Surprisingly, when **1a** was heated in ethanol in the presence of acetic acid, cyclic imidates, 3-(2-benzimidazolinylidene)-5-cyano-6-ethoxy-2-imino-2,3-dihydropyridine(**9b**) was isolated, as well as compound(**4a**) which was obtained from the filtrate (Scheme 5). It is worth noting that compounds(**1b**) and (**1c**) could not be converted to the corresponding cyclic imidate under the same conditions but provided compounds(**4b**) and (**4c**), respectively. Interestingly, when **1a,b,c** were treated in ethanol in the presence of hydrogen chloride (Pinner's method[7] for converting a nitrile to an ethyl imidate), the hydrochlorides of the starting materials(**1a,b,c**) were respectively obtained, but not the corresponding ethyl imidates.

Scheme 5, and Tables Ⅰ and Ⅱ show compounds(**9a-j**) obtained by the above reaction us-

ing a variety of alcohols. The structures of **9a-j** were supported on the basis of their spectral data. Especially, **9b** was determined by X-Ray structural analysis, and the data are summarized in Tables Ⅲ, Ⅳ, and Ⅴ and Figure 1. The ring closure of **1a** to **9a-j** would be explained as shown in Scheme 6. Namely, compound(**1a**) was converted to an intermediary imidate(**10**), followed by tautomerization to **11** which cyclized to **9** through both the 6-*Exo*-Dig process and the 5-*Exo*-Trig process with loss of ammonia. Since compound(**9b**) was not obtained by refluxing **4a** in ethanol in the presence of acetic acid, it was postulated that the formation of **9** needs the 6-*Exo*-Dig process of **11** for the formation of the dihydropyridine ring before the 5-*Exo*-Dig process of **10** for the formation of the benzimidazoline ring. Also, since compound(**2a**) was not obtained from the above reaction, it was postulated that the 6-*Exo*-Dig process of **11** is superior to the 6-*Exo*-Trig process of **10** which gives rise to compound(**2a**) with loss of an alcohol. In conclusion, the formation of **9** is due to the reaction between two cyano groups of **1a**. Although such a cyclization of 1,5-dinitriles to afford heterocycles has been studied using hydrogen halides,[8-10] our findings would also provide a new route to 6-alkoxy-3-(2-benzimidazolinylidene)-5-cyano-2-imino-2,3-dihydropyridine(**9**).

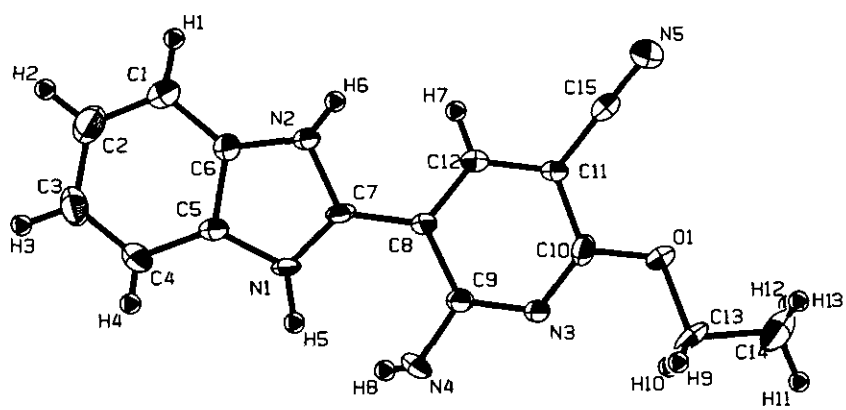


Figure 1 X-Ray structure of **9b** showing crystallographic numbering scheme (This numbering scheme is also used in Table Ⅲ,Ⅳ, and Ⅴ.)

EXPERIMENTAL

All melting points were determined on a Yazawa micromelting point BY-2 apparatus and are uncorrected. The MS spectra were recorded using a JMS D-100. Elemental analyses were performed using a Perkin-Elmer 240B instrument (Table Ⅰ). The IR spectra (potassium bromide) were recorded on a JASCO IRA-1 spectrophotometer, and all compounds showed the characteristic absorption bands at 2220-2230 cm^{-1} due to the cyano group. The NMR spectra were determined with a Varian VXR-300 spectrometer using deuteriodimethyl sulfoxide as the solvent and tetramethylsilane as the internal standard (Table Ⅱ).

General Procedure for Synthesizing 2-Substituted 4-(2-Benzimidazolinylidene) pent-2-enedinitrile(4a,b,c)

Method A ---A solution of **1a** (0.1 g, 0.4 mmol) in 50 mL of 0.1 mol/L hydrochloric acid was heated on a boiling water bath for 1 h to precipitate pure crystals of **4a**. The crystals were washed with a saturated sodium bicarbonate solution and water.

Method B ---A solution of **1a** (0.1 g, 0.4 mmol) in 30 mL of acetic acid was refluxed for 5 h to precipitate pure crystals of **4a**. The crystals were washed with a saturated sodium bicarbonate solution and water.

3-(2-Benzimidazolinylidene)-5-cyano-2-imino-6-methoxy-2,3-dihydropyridine (9a)

Acetic acid (1 mL) was added to a suspension of **1a** (0.1 g, 0.4 mmol) in 50 mL of methanol, and the mixture was refluxed for 8 h. The solution was evaporated to dryness, and acetonitrile (10 mL) was added to the residue. The precipitates were filtered by suction filtration, and the filtrate was evaporated to dryness to afford crude **9a** which was purified

by column chromatography (silica gel) using chloroform as the eluant.

General Procedure for Synthesizing 6-Alkoxy-3-(2-benzimidazolinylidene)-5-cyano-2-imino-2,3-dihydropyridine(9b,c,d,e,f,g)

Acetic acid (1 mL) was added to a suspension of **1a** (0.1 g, 0.4 mmol) in 50 mL of ethanol, and the mixture was refluxed for 5 h. The solution was evaporated to dryness, and acetonitrile (10 mL) was added to the residue to afford crude **9b** which was purified by recrystallization using ethanol.

General Procedure for Synthesizing 3-(2-Benzimidazolinylidene)-5-cyano-2-imino-6-(2-phenylethoxy)-2,3-dihydropyridine(9h) and 3-(2-Benzimidazolinylidene)-5-cyano-2-imino-6-(L-menthoxy)-2,3-dihydropyridine(9i)

Acetic acid (1 mL) was added to a suspension of **1a** (0.1 g, 0.4 mmol) in 50 mL of 2-phenylethanol, and the mixture was refluxed for 5 h. The solution was evaporated to dryness, and acetonitrile (10 mL) was added to the residue. The precipitates were filtered by suction filtration and the filtrate was evaporated to dryness. The residue was purified by column chromatography (silica gel) using chloroform as the eluant to afford pure **9h**.

3-(2-Benzimidazolinylidene)-6-(3-butyn-1-oxy)-5-cyano-2-imino-2,3-dihydropyridine(9j)

Acetic acid (0.5 mL) was added to a suspension of **1a** (0.1 g, 0.4 mmol) in 25 mL of 3-butyn-1-ol, and the mixture was then refluxed for 5 h. The solution was evaporated to dryness, and the residue was purified by column chromatography (silica gel) using chloroform as the eluant to afford crystals of **9j**.

X-Ray Analysis of 9b

A crystal was mounted on a Rigaku AFC5S diffractometer, and the cell parameters and the intensity data were measured using graphite-monochromated Cu $K\alpha$ (λ=1.54178 Å) ra-

diation at 23°C. Approximate atomic coordinates were obtained by the direct method using MITHRIL.[11] The parameters of non-hydrogen atoms were refined using the full-matrix least-squares method with anisotropic temperature factors. The hydrogen atoms were located froma difference Fourie synthesis, and refined with isotropic temperature factors. The crystal data are as follows: Chemical formula $C_{15}H_{13}N_5O$; MW 279.30; monoclinic; space group $P2_1/n$; Z=4, unit cell dimensions a=10.230(6) Å, b=6.30(1) Å, c=22.430(7) Å, β =100.80(4)°, V=1421(2) Å^3; Dcal=1.305 gcm^{-3}; μ(Cu$K\alpha$)=6.74 cm^{-1}; crystal size 0.2×0.2 ×0.8 mm. Of the total of 2912 reflections up to the 2 θ range of 140.3° (unique reflections: 2753), 1277 were measured as being above the 3 σ (I) level and were used. The final R value was 0.062. The positional parameters for **9b** are listed in Table Ⅲ. The selected bond angles and torsion angles for **9b** are listed in Tables Ⅳ and Ⅴ, respectively.

Table I Analytical Data of Compounds (4 and 9)

Compd No.	Yield (%)	mp (℃)	MS m/z(M^+)	Molecular Formula	Anal. (%) Calcd (Found)		
					C	H	N
4a	41(A) 67(B)	>300	233	$C_{13}H_7N_5$	66.95 (67.00	3.03 2.98	30.03 30.03)
4b	20(A) 67(B)	>300	251	$C_{13}H_9N_5O$ $1/4H_2O$	61.05 (61.28	3.74 3.76	27.38 27.16)
4c	37(A) 62(B)	290	324	$C_{19}H_{12}N_6$ $2.5H_2O$	62.17 (61.89	3.60 3.74	22.44 22.75)
9a	8	>300	265	$C_{14}H_{11}N_5O$	63.40 (63.13	4.15 4.28	26.42 26.18)
9b	27	>300	279	$C_{15}H_{13}N_5O$ H_2O	60.61 (60.87	5.05 4.73	23.57 23.35)
9c	56	>300	293	$C_{16}H_{15}N_5O$	65.52 (65.48	5.15 5.14	23.88 23.95)
9d	15	310	293	$C_{16}H_{15}N_5O$	65.52 (65.33	5.15 5.43	23.88 23.78)
9e	28	>300	307	$C_{17}H_{17}N_5O$ $1/4H_2O$	65.47 (65.73	5.66 5.75	22.46 22.41)
9f	62	315	333	$C_{19}H_{19}N_5O$	68.45 (68.22	5.74 5.75	21.01 20.80)
9g	14	304-307	341	$C_{20}H_{15}N_5O$ $1/4H_2O$	69.45 (69.68	4.52 4.54	20.25 19.97)
9h	11	239-240	355	$C_{21}H_{17}N_5O$ $1/8H_2O$	70.52 (70.63	4.86 4.91	19.58 19.36)
9i	19	272-273	389	$C_{23}H_{27}N_5O$	70.92 (71.03	6.99 7.06	17.98 17.98)
9j	44	282-285	303	$C_{17}H_{13}N_5O$ $1/4H_2O$	66.33 (66.24	4.42 4.45	22.75 23.01)

Table II NMR Data of Compounds (**4** and **9**)

Compd.No.		NMR δ (ppm)
4a	^{1}H	7.42(t, J=8 Hz, 1H, arom), 7.59(t, J=8 Hz, 1H, arom), 7.86(d, J=8 Hz, 1H, arom), 8.36(s, 1H, 2-H), 8.58(d, J=8 Hz, 1H, arom), 8.71(br s, 2H, NH)
	^{13}C	75.13, 85.84, 116.06, 116.39, 115.12, 119.09, 122.07, 126.63, 128.46, 141.59, 144.38, 147.27, 152.69
4b	^{1}H	7.41(t, J=5.8 Hz, 1H, arom), 7.58(t, J=5.8 Hz, 1H, arom), 7.82(br s, 1H, NH), 7.86(d, J=6 Hz, 1H, arom), 8.20(s, 1H, 2-H), 8.42(br s, 2H, NH_2), 8.58(d, J=6 Hz, 1H, arom), 9.33(br s, 1H, NH)
	^{13}C	74.86, 107.64, 115.22, 117.20, 118.63, 121.79, 126.52, 127.91, 136.84, 43.52, 147.86, 152.26, 163.33
4c	^{1}H	7.23(m, 1H, arom), 7.46(t, J=7 Hz, 1H, arom), 7.51(m, 1H, arom), 7.60(m, 1H, arom), 7.66(t, J=7 Hz, 1H, arom), 7.86(d, J=9 Hz, 1H, arom), 7.91(m, 1H, arom), 8.00(d, J=9 Hz, 1H, arom), 8.68(d, J=9 Hz, 1H, arom), 9.00(br s, 1H, NH), 9.07(s, 1H, 2-H), 10.12(br s, 1H, NH)
	^{13}C	76.60, 96.18, 114.02, 115.15, 115.34, 116.47, 116.89, 118.20, 118.92, 121.70, 122.55, 125.61, 126.71, 127.00, 128.06, 128.46, 131.13, 137.57, 137.65, 143.70, 145.00, 145.60, 149.38, 149.63, 152.31
9a	^{1}H	3.95(s, 3H, CH_3), 7.20(m, 2H, arom), 7.57(br s, 2H, arom), 8.14(br s, 1H, NH), 8.54(s, 1H, 4-H), 9.74(br s, 1H, NH), 12.75(br s, 1H, NH)
	^{13}C	54.04, 80.64, 99.97, 116.74, 122.31, 141.40, 149.30, 158.51, 163.80
9b	^{1}H	1.36(t, J=7 Hz, 3H, CH_3), 4.43(q, J=7 Hz, 2H, CH_2), 7.22(m, 2H, arom), 7.59(br s, 2H, arom), 8.11(br s, 1H, NH), 8.55(s, 1H, 4-H), 9.73(br s, 1H, NH), 12.80(br s, 1H, NH)
	^{13}C	14.48, 24.30, 62.57, 80.48, 100.13, 114.85, 116.92, 122.27, 141.56, 149.59, 158.6, 163.53
9c	^{1}H	0.98(t, J=7.5 Hz, 3H, CH_3), 1.76(m, 2H, CH_2), 4.33(t, J=6.5 Hz, 2H, CH_2), 7.22(m, 2H, arom), 7.59(br s, 2H, arom), 8.11(br s, 1H, NH), 8.55(s, 1H, 4-H), 9.75(br s, 1H, NH), 12.71(br s, 1H, NH)
	^{13}C	10.18, 21.68, 67.98, 80.75, 99.91, 116.7, 122.26, 141.41, 149.35, 158.50, 163.57
9d	^{1}H	1.33(d, J=6 Hz, 6H, CH_3), 5.35(m, 1H, OCH), 7.19(d, J=4 Hz, 2H, arom), 7.51(br s, 1H, arom), 7.62(br s, 1H, arom), 8.06(br s, 1H, NH), 8.52(s, 1H, 4-H), 9.69(br s, 1H, NH), 12.76(br s, 1H, NH)
	^{13}C	21.78, 69.53, 81.09, 99.76, 110.85, 116.86, 118.20, 121.80, 122.70, 141.52, 149.37, 158.52, 163.11

Table Ⅱ Continued

Compd.No.	NMR	δ (ppm)
9e	^{1}H	0.95(t, J=7.5 Hz, 3H, CH_3), 1.47(m, 2H, CH_2), 1.73(m, 2H, CH_2), 4.38(t, J=6.5 Hz, 2H, CH_2), 7.22(m, 2H, arom), 7.59(br s, 2H, arom), 8.20(br s, 1H, NH), 8.55(s, 1H, 4-H), 9.74(br s, 1H, NH), 12.79(br s, 1H, NH)
	^{13}C	13.64, 18.63, 30.34, 66.28, 80.76, 99.88, 116.74, 122.26, 141.41, 149.35, 158.50, 163.57
9f	^{1}H	1.35(m, 3H, cyclohexyl), 1.52(m, 3H, cyclohexyl), 1.72(m, 2H, cyclohexyl), 1.92(m, 2H, cyclohexyl), 5.14(m, 1H, OCH), 7.19(m, 2H, arom), 7.56(d, J=13 Hz, 2H, arom), 8.04(br s, 1H, NH), 8.52(s, 1H, 4-H), 9.69(br s, 1H, NH), 12.77(br s, 1H, NH)
	^{13}C	23.17, 24.94, 31.65, 73.90, 81.17, 99.80, 110.9, 118.3, 121.9, 122.9, 116.77、141.47, 149.36, 158.51, 163.04
9g	^{1}H	5.46(s, 2H, CH_2), 7.18(m, 1H, 6'), 7.23(m, 1H, 5'), 7.34(m, 1H, Ph), 7.40(m, 2H, Ph), 7.50(m, 3H, 4', Ph), 7.65(d, J=7.5 Hz, 1H, 7'), 8.20(br s, 1H, 3'-NH), 8.56(s, 1H, 4-H), 9.75(br s, 1H, 6-NH), 12.80(s, 1H, 1'-NH)
	^{13}C	67.82, 80.87, 100.35, 111.00, 116.79, 118.40, 121.91, 123.01, 128.22, 128.27, 128.58, 133.67, 136.35, 141.63, 142.33, 149.34, 158.49, 163.28
9h	^{1}H	3.05(t, J=7 Hz, 2H, C$\underline{H}_2$Ph), 4.53(t, J=7 Hz, 2H, OCH_2), 7.21(m, 3H, arom, 4-Ph), 7.32(m, 4H, 2, 3, 5, 6-Ph), 7.57(br s, 2H, arom), 8.12(br s, 1H, NH), 8.53(s, 1H, 4-H), 9.71(br s, 1H, NH)
	^{13}C	34.54, 67.23, 80.75, 95.66, 100.08, 104.44, 116.70, 122.36, 126.43, 127.47, 128.36, 129.09, 137.93, 141.46, 149.35, 158.50, 163.37
9i	^{1}H	0.76(d, J=7 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 0.87(d, J=7 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 0.89(d, J=6.6 Hz, 3H, 1-CH_3), 0.93(m, 1H, 6-men), 1.06(m, 2H, 2, 5-men), 1.52(m, 2H, 1, 4-men), 1.67(d, J=11 Hz, 2H, 5, 6-men), 1.91(m, 1H, C$\underline{H}$(CH_3)$_2$), 2.10(m, 1H, 2-men), 5.08(dt, J=4.3 and 11 Hz, 1H, 3-men), 7.19(m, 2H, 5', 6'-H), 7.57(br s, 2H, 4', 7'-H), 8.07(br s, 1H, NH), 8.52(s, 1H, 4-H), 9.70(br s, 1H, NH), 12.78(br s, 1H, NH)
	^{13}C	16.85, 20.41, 21.91, 23.59, 26.30, 31.05, 33.75, 40.29, 46.93, 75.73, 80.89, 99.89, 116.79, 122.34, 141.62, 149.37, 158.52, 163.40
9j	^{1}H	2.68(dt, J=2.7 and 6.7 Hz, 2H, OCH_2CH_2C), 2.90(t, J=2.5 Hz, 1H, C≡CH), 4.44(t, J=7 Hz, 2H, OCH_2CH_2C), 7.20(m, 2H, 5', 6'-H), 7.49(d, J=8 Hz, 1H, 4'or7'-H), 7.64(d, J=8 Hz, 1H, 4'or7'-H), 8.15(br s, 1H, NH), 8.53(s, 1H, 4-H), 9.72(br s, 1H, NH), 12.79(s, 1H, NH),
	^{13}C	18.51, 64.40, 72.69, 80.77, 100.24, 110.89, 116.61, 118.30, 121.81, 122.90, 133.55, 141.53, 142.21, 149.22, 158.40, 163.37

Table Ⅲ Positional Parameters and Equivalent Isotropic Thermal Parameters of **9b** with Their Estimated Standard Deviations in Parentheses

atom*	x	y	z	B(eq)
O(1)	0.6402(4)	−0.7907(7)	0.0836(2)	2.8(2)
N(1)	0.9352(5)	0.0552(8)	0.1976(2)	2.1(2)
N(2)	1.0347(5)	0.0028(8)	0.1190(2)	2.3(2)
N(3)	0.6982(4)	−0.5175(7)	0.1522(2)	2.0(2)
N(4)	0.7568(8)	−0.258(1)	0.2217(3)	2.9(3)
N(5)	0.8521(5)	−0.789(1)	−0.0214(3)	4.0(3)
C(1)	1.1829(6)	0.326(1)	0.1323(3)	2.9(3)
C(2)	1.2138(6)	0.495(1)	0.1704(3)	3.3(3)
C(3)	1.1531(6)	0.531(1)	0.2213(3)	3.0(3)
C(4)	1.0589(7)	0.391(1)	0.2335(3)	2.6(3)
C(5)	1.0259(5)	0.217(1)	0.1966(3)	1.9(2)
C(6)	1.0885(6)	0.184(1)	0.1463(3)	2.1(2)
C(7)	0.9413(5)	−0.072(1)	0.1517(3)	1.8(2)
C(8)	0.8646(5)	−0.261(1)	0.1340(2)	1.8(2)
C(9)	0.7719(5)	−0.3454(9)	0.1689(2)	1.9(2)
C(10)	0.7126(6)	−0.620(1)	0.1025(3)	2.2(3)
C(11)	0.8055(6)	−0.558(1)	0.0660(3)	2.1(3)
C(12)	0.8786(6)	−0.376(1)	0.0831(3)	2.3(3)
C(13)	0.5447(6)	−0.859(1)	0.1201(3)	3.8(3)
C(14)	0.4692(7)	−1.039(1)	0.0873(3)	5.2(4)
C(15)	0.8285(6)	−0.685(1)	0.0172(3)	2.8(3)
H(1)	1.219(6)	0.31(1)	0.096(3)	6(2)
H(2)	1.2789	0.5933	0.1623	4.0
H(3)	1.1773	0.6509	0.2467	3.5
H(4)	1.024(6)	0.41(1)	0.262(3)	3(2)
H(5)	0.8784	0.0388	0.2263	2.5
H(6)	1.056(6)	−0.08(1)	0.094(3)	3(2)
H(7)	0.925(6)	−0.32(1)	0.056(3)	5(2)
H(8)	0.79(1)	−0.20(1)	0.236(4)	4(3)
H(9)	0.5899	−0.9041	0.1590	4.6
H(10)	0.4860	−0.7462	0.1247	4.6
H(11)	0.4051	−1.0881	0.1098	6.3
H(12)	0.4255	−0.9931	0.0484	6.3
H(13)	0.5289	−1.1511	0.0830	6.3

*The numbers attaching to atoms are from the crystallographic numbering scheme in Figure 1.

Table IV Selected Bond Angles(°) with Their Estimated Standard Deviations in Parentheses

atom*	atom*	atom*	angles
C10	O1	C13	117.0(5)
N1	C5	C4	131.8(5)
N1	C7	C8	128.0(5)
N2	C7	C8	121.9(5)
C7	C8	C12	121.7(5)
N2	C6	C1	132.6(6)
O1	C10	N3	121.4(5)
C12	C11	C15	121.7(5)

*The numbers attaching to atoms are from the crystallographic numbering scheme in Figure 1.

Table V Selected Torsion Angles(°) with Their Estimated Standard Deviations in Parentheses*

atom A†	atom B†	atom C†	atom D†	angle
N1	C5	C4	C3	−178.8(6)
N1	C7	C8	C9	−4.1(9)
N1	C7	C8	C12	177.8(6)
N2	C6	C1	C2	179.8(7)
N2	C7	C8	C9	177.1(6)
N2	C7	C8	C12	−1.0(9)

*The sign is positive if a clockwise mortion of atom A would superimpose it on atom D when looking from atom B to atom C.

†The numbers attaching to atoms are from the crystallographic numbering scheme in Figure 1.

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