Heterocycles. CLXIX. Barriers to Rotation in some *N,N*-Dimethyl-*N'*-heteroaryl, *N,N*-Diethyl-*N'*-heteroaryl-substituted Formamidines and *N,N*-Dimethyl-*N'*-heteroaryl-substituted Acetamidines

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The free energies of the rotational barriers, ΔG^*, about =CH-NMe_2 bond in *N'*-heteroaryl *N,N*-dimethylformamidines (A), about =CH-NEt_2 bond in *N'*-heteroaryl *N,N*-diethylformamidines (B), and about =C(Me)-NMe_2 bond in *N'*-heteroaryl *N,N*-dimethylacetamidines (C) have been found to be in the range 17.5-20.1 kcal/mole for type A, 18.8-21.6 kcal/mole for type B and 13-14 kcal/mole or below for type C of compounds, respectively. The compounds of the types A and B exist in the forms IIa, IIIa, IV, V, and VI, while the compounds of the type C exist in the forms IIb and IIIb.

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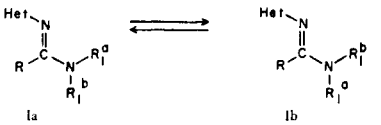
Recently, the free energies of the rotational barriers, ΔG^*, for a number of *N'*-pyridyl-, *N'*-pyridazinyl-, *N'*-*s*-triazinyl-*N,N*-dimethylsubstituted formamidines, their quaternized salts and some *N*-oxides and quaternized *N*-oxides have been reported to be in the range between 16 kcal/mole and 23 kcal/mole (1,2). It has been shown that electron donating groups attached to the heterocyclic ring decrease ΔG^*, while electron withdrawing groups increase it. The additional π-bonding in the dipolar resonance structures also increase rotational barriers around the $CH\text{-}N(CH_3)_2$ bond.

In this communication rotational barriers of three types of compounds A, B and C have been studied. Compounds of the type A were prepared from 2-aminopyridine, 2-aminopyridazine, 2-aminopyrazine, 2-aminopyrimidine, 8-amino-*s*-triazolo[1,5-*a*]pyrazine, 5-amino- and 8-aminopyrido[2,3-*d*]pyridazine, 6-aminotetrazolo[1,5-*a*]phthalazine, 6-aminopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine, 6-aminopyrido[2,3-*d*]tetrazolo[1,5-*b*]-pyridazine, 6-aminopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine, 6-amino-*s*-triazolo[4,3-*b*]pyridazine, 6-aminoimidazo[1,2-*b*]pyridazine, 6-amino-*s*-triazolo[1,5-*b*]pyridazine, and 6-aminotetrazolo[1,5-*b*]pyridazine derivatives, compounds of the type B from azido derivatives of substituted *s*-triazolo[4,3-*b*]pyridazine, *s*-triazolo[1,5-*b*]-pyridazine, tetrazolo[1,5-*b*]pyridazine, tetrazolo[1,5-*a*]-phthalazine, pyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine and isomeric pyridotetrazolopyridazines, while the compounds

Scheme I



Ia Ib

A. R = H, R_1 = CH_3
B. R = H, R_1 = CH_2CH_3
C. R = R_1 = CH_3

Het =

1

a. R_3 = CN; R_4 = R_5 = H
b. R_3 = R_4 = H; R_5 = NO_2
c. R_3 = R_4 = R_5 = H
d. R_3 = CH_3; R_4 = R_5 = H
e. R_3 = R_5 = H; R_4 = CH_3

2

a. R_4 = R_5 = R_6 = H
b. R_4 = R_5 = H; R_6 = Cl
c. R_4 = CH_3; R_5 = H; R_6 = Cl
d. R_4 = H; R_5 = CH_3; R_6 = Cl
e. R_4 = R_5 = CH_3; R_6 = Cl

3

4

a. R_3 = R_5 = H
b. R_3 = R_5 = Br
c. R_3 = H; R_5 = Cl

5

6

7

8

9

a. X = Y = CH; R_7 = R_8 = H
b. X = Y = CH; R_7 = CH_3; R_8 = H
c. X = N; Y = CH; R_7 = R_8 = H
d. X = N; Y = CH; R_7 = R_8 = CH_3
e. X = N; Y = CH; R_7 = CH_3; R_8 = H
f. X = CH; Y = N; R_7 = R_8 = H
g. X = Y = N; R_7 = R_8 = H
h. X = Y = N; R_7 = H; R_8 = CH_3
i. X = Y = N; R_7 = CH_3; R_8 = H

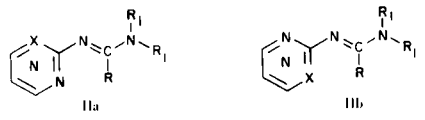
10

a. X = Y = Z = W = CH
b. X = Y = Z = CH; W = N

11

a. X = Y = Z = W = CH
b. X = Y = Z = CH; W = N
c. X = Z = W = CH; Y = N
d. X = Y = W = CH; Z = N

of the type C from substituted 2-aminopyridine, 2-aminopyrimidine, 2-aminopyrazine, 3-aminopyridazine, 3-amino-1,2,4-triazine, 6-aminoimidazo[1,2-*b*]pyridazine, 6-amino-*s*-triazolo[4,3-*b*]pyridazine, and 6-aminotetrazolo[1,5-*b*]-pyridazine derivatives (Scheme I).

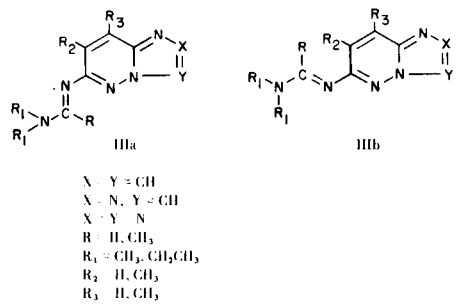


IIa IIb

X = C-H, C-CH$_3$, C-Br, C-CN, N
R = H, CH$_3$
R$_1$ = CH$_3$, CH$_2$CH$_3$

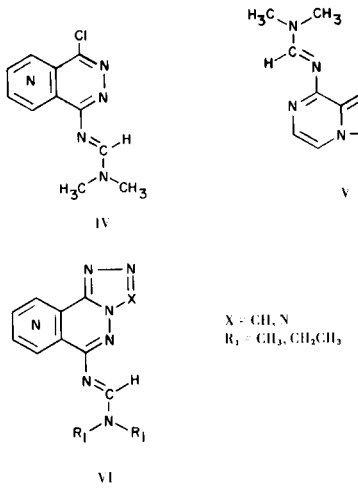
All compounds under investigation exhibit in the temperature range between -90° and +160° temperature dependent nmr spectra with one typical coalescence pattern associated with the slow interconversion of Ia and Ib.

Free energy values of rotational barriers, ΔG^*, for =CH-N(CH$_3$)$_2$ bond (compounds of the type A) (Table I and Table IV) are in the range between 17.5 kcal/mole for *N'*-pyrazinyl-*N*,*N*-dimethyl formamidine (**A4a**) and 20.1 kcal/mole for *N*-(8-methyltetrazolo[1,5-*b*]pyridazinyl-6) formamidine (**A9h**). For the compounds with bicyclic heteroaryl group the barriers are generally higher, ΔG^* = 18.3-20.1 kcal/mole, when compared to the compounds with a monocyclic heteroaryl group, ΔG^* = 17.5-19.1 kcal/mole. Rotational barriers for CH-N(CH$_2$CH$_3$)$_2$ bond in *N*,*N*-diethyl substituted formamidines (Table II and Table V) with bicyclic heteroaryl groups are between ΔG^* = 18.8 kcal/mole for *N*,*N*-diethyl-*N'*-(7-methyl-*s*-triazolo[4,3-*b*]pyridazinyl-6)-formamidine (**B9d**) and ΔG^* = 20.5 kcal/mole for *N*,*N*-diethyl-*N'*-(7-methyltetrazolo[1,5-*b*]pyridazinyl-6)-formamidine (**B9i**). The barriers to rotation for compounds of the types A and B are not dependent on the steric effects of substituents attached at the ortho position in respect to the formamidine group. For example, ΔG^* values for *N*,*N*-dimethyl-*N'*-pyridyl-2-formamidine (**A1c**) and *N*,*N*-dimethyl-*N'*-(3-methylpyridyl-2)-formamidine (**A1d**) are 16.6 and 16.4 kcal/mole, respectively, as reported previously (1). Similarly, the ΔG^* values for unsubstituted and substituted *s*-triazolo[4,3-*b*]-pyridazinyl compounds **A9c** and **A9d** are 19.3 and 19.2 kcal/mole, for *s*-triazolo[4,3-*b*]pyridazinyl compounds **B9c**, **B9d** and **B9e** 18.8-19.5 kcal/mole, for tetrazolo-[1,5-*b*]pyridazinyl compounds **B9g**, **B9h**, **B9i** 20.1-20.5 kcal/mole, for bicyclic pyrido[2,3-*d*]pyridazine derivatives **A6** and **A7** 18.3 and 19.4 kcal/mole, respectively, and for tricyclic *N*-heteroaryl compounds **A10b**, **A11a**, **A11b**, **A11c**, **B11a**, **B11b**, **B11c**, **B11d** in the range of 19.5-21.6 kcal/mole. On the basis of these experimental results one can conclude that the compounds **A1a**, **A1b**, **A3**, **A4a**, **A4b**, **A4c** exist in the form IIa (R = H, R$_1$ = CH$_3$), compounds **A9a**, **A9c**, **A9d**, **A9f**, **A9g**, **A9h** in the form IIIa (R = H, R$_1$ = CH$_3$), compounds **B9c**, **B9d**, **B9e**, **B9f**, **B9g**, **B9h**, **B9i** in the form IIIa (R = H, R$_1$ = CH$_2$CH$_3$), compounds **A6** and **A7** in the form IV, compounds **A8** in the form V, compounds **A10b**, **A11a**, **A11b**, **A11c** in the form VI (R$_1$ = CH$_3$), and compounds **B10b**, **B11a**, **B11b**, **B11c**, and **B11d** in the form VI (R$_1$ = CH$_2$CH$_3$), with formamidine proton facing the heterocyclic ring nitrogen.



IIIa IIIb

X = Y = CH
X = N, Y = CH
X = Y = N
R = H, CH$_3$
R$_1$ = CH$_3$, CH$_2$CH$_3$
R$_2$ = H, CH$_3$
R$_3$ = H, CH$_3$

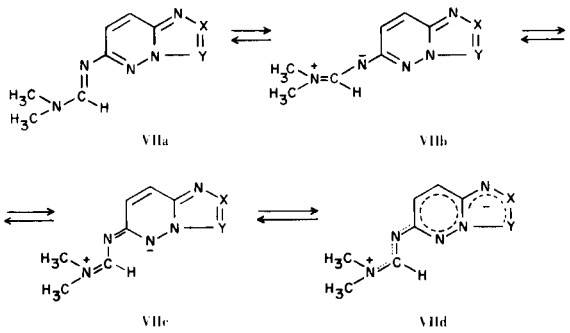


IV V

X = CH, N
R$_1$ = CH$_3$, CH$_2$CH$_3$

VI

As already mentioned, the barriers to rotation for the compounds with bicyclic heteroaryl groups are in average for 1 kcal/mole higher than the barriers for compounds with a monocyclic heteroaryl group. This phenomenon could be understood since a five-membered ring fused to a six-membered ring is known to be a strong electron withdrawer from the six-membered ring. This means that the double bond character of the C-N bond in CH-N(CH$_3$)$_2$ group is increased due to the additional π-bonding in the resonance structures VIIa-d.



VIIa VIIb

VIIc VIId

Table I

N,N-Dimethyl-*N'*-substituted Formamidines

Compound	Nmr data: chemical shift (τ) and coupling constants J (Hz)(s) N=CH	$N(CH_3)_2$	Other proton resonances or literature reference	Formula M.p. (°C) or b.p. (°C/mm) or literature reference		Analysis C	H	N
A1a	A 1.50 (s)	6.90 (s), 6.97 (s)	3.16 (dd, H_5), 2.15 (dd, H_4), 1.75 (dd, H_6); $J_{4,5}$ = 8 Hz, $J_{4,6}$ = 2.5 Hz, $J_{5,6}$ = 5 Hz	$C_9H_{10}N_4$	Calcd.	62.05	5.79	32.17
				66-69° (b)	Found	61.84	5.67	32.30
A1b	A 1.41 (s)	6.90 (s), 6.92 (s)	(3)	(3)				
A3	B 1.41 (s)	6.87 (s), 6.91 (s)	(3)	(3)				
A4a	B 1.64 (s)	6.92 (s)	(3)	(3)				
A4b	A 1.60 (s)	6.86 (s), 6.89 (s)	(4)	(4)				
A4c	A 1.49 (s)	6.89 (s), 6.98 (s)	(3)	(3)				
A6	A 1.40 (s)	6.74 (s), 6.79 (s)	(3)	(3)				
A7	A 1.18 (s)	6.68 (s), 6.75 (s)	(3)	(3)				
A8	A 1.54 (s)	6.81 (s), 6.88 (s)	2.34 (d, H_6), 1.56 (d, H_5), 1.26 (s, H_2); $J_{5,6}$ = 4.5 Hz	(7)				
A9a	A 1.73 (s)	6.86 (s), 6.96 (s)	(5)	(5)				
A9c	B 1.82 (s)	6.88 (s), 6.93 (s)	1.24 (s, H_3), 3.18 (d, H_7), 2.23 (d, H_8); $J_{7,8}$ = 9.4 Hz	(6)				
A9d	B 1.81 (s)	6.81 (s), 6.85 (s)	1.15 (s, H_3); 7.71 (s, 7-CH_3); 7.39 (s, 8-CH_3)	$C_{10}H_{14}N_6$	Calcd.	55.03	6.47	--
				179-181° (c)	Found	54.85	6.72	--
A9f	B 1.52 (s)	6.85 (s), 6.88 (s)	(3)	(3)				
A9g	B 1.54 (s)	6.80 (s), 6.85 (s)	2.86 (d, H_7), 2.01 (d, H_8); $J_{7,8}$ = 10.3 Hz	(6)				
A9h	B 1.53 (s)	6.79 (s), 6.85 (s)	3.02 (q, H_7), 7.31 (d, 8-CH_3); $J_{H_7,8\text{-}CH_3}$ = 1.5 Hz	$C_{10}H_{15}N_7$	Calcd.	51.48	6.49	42.03
				178-182° (c)	Found	51.57	6.54	42.25
A10b	A 1.53 (s)	6.80 (s), 6.83 (s)	0.88 (s, H_3), 1.22 (dd, H_7), 2.22 (dd, H_8), 0.86 (dd, H_9); $J_{7,8}$ = 8.7 Hz, $J_{8,9}$ = 5.1 Hz, $J_{7,9}$ = 1.7 Hz	$C_{11}H_{11}N_7$	Calcd.	54.76	4.60	40.64
				271-274° (d)	Found	54.66	4.57	40.82
A11a	A 1.34 (s)	6.72 (s), 6.79 (s)	1.40-1.60 (m, H_7, H_{10}), 1.90-2.10 (m, H_8, H_9)	$C_{11}H_{11}N_7$	Calcd.	54.76	4.60	40.64
				199-203° (c)	Found	54.71	4.77	40.57
A11b	A 1.38 (s)	6.72 (s), 6.78 (s)	1.16 (dd, H_7), 2.10 (dd, H_8), 0.79 (dd, H_9)	$C_{10}H_{10}N_8$	Calcd.	49.58	4.16	46.26
				237-238° (c)	Found	49.97	4.18	46.17
A11c	C 1.27 (s)	6.65 (s), 6.70 (s)	0.17 (d, H_7), 0.87 (d, H_9), 1.68 (dd, H_{10})	$C_{10}H_{10}N_8$	Calcd.	49.58	4.16	46.26
				252-253° (d)	Found	49.98	4.09	46.37

(a) Solvents: A = DMSO-d_6, B = deuteriochloroform, C = DMFA-d_7. (b) Crystallized from cyclohexane. (c) Crystallized from a mixture of chloroform and petrol ether. (d) Crystallized from a mixture of methanol and dimethylformamide.

Table II

N,N-Diethyl-*N'*-substituted Formamidines

Compound		Nmr data: chemical shift (τ) and coupling constants J (Hz) (a) N=CH	$N(CH_2CH_3)_2$ JCH_2CH_3	Other proton resonances	Reference
B9c	B	1.78 (s)	6.40 (q), 6.60 (q) 8.70 (t), 8.75 (t)	(6)	(6)
B9d	B	1.97 (s)	6.45 (q), 6.63 (q) 8.71 (t), 8.74 (q) J = 7.0 Hz	7.45 (q, 8-CH_3), 7.74 (q, 7-CH_3), 1.36 (s, H_3); $J_{7\text{-}CH_3,8\text{-}CH_3}$ = 0.6 Hz	
B9e	B	1.72 (s)	6.36 (q), 6.53 (q) 8.64 (t), 8.70 (t) J = 7.2 Hz	7.65 (d, 7-CH_3), 1.14 (d, H_3), 2.31 (qd, H_8); $J_{7\text{-}CH_3,H_8}$ = 1.1 Hz, $J_{3,8}$ = 0.8 Hz	
B9f	A	1.58 (s)	6.50 (q), 6.55 (q) 8.76 (t), 8.78 (t)	(3)	(3)
B9g	B	1.50 (s)	6.35 (q), 6.50 (q) 8.66 (t), 8.73 (t)	(6)	(6)
B9h	B	1.55 (s)	6.38 (q), 6.50 (q) 8.68 (t), 8.74 (t) J = 7.4 Hz	7.32 (d, 8-CH_3), 3.05 (q, H_7); $J_{H_7,8\text{-}CH_3}$ = 1.1 Hz	
B9i	B	1.56 (s)	6.37 (q), 6.53 (q) 8.65 (t), 8.70 (t) J = 7.2 Hz	7.56 (s, 7-CH_3), 2.20 (s, H_8)	
B10b	B	1.57 (s)	6.27 (q), 6.46 (q) 8.62 (t), 8.65 (t) J = 7.2 Hz	1.17 (s, H_3), 1.28 (dd, H_7), 2.36 (dd, H_8), 0.93 (dd, H_9); $J_{7,8}$ = 8.5 Hz, $J_{8,9}$ = 4.6 Hz, $J_{7,9}$ = 1.5 Hz	
B11a	B	1.32 (s)	6.21 (q), 6.43 (q) 8.59 (t), 8.61 (t) J = 7.3 Hz	1.35-1.65 (m, H_7, H_{10}), 1.94-2.33 (m, H_8H_9)	
B11b	A	1.47 (s)	6.30 (q), 6.45 (q) 8.75 (t)	(6)	(6)
B11c	B	1.22 (s)	6.17 (q), 6.41 (q) 8.59 (t), 8.61 (t) J = 7.2 Hz	0.03 (d, H_7), 0.85 (d, H_9), 1.60 (dd, H_{10}); $J_{9,10}$ = 5.6 Hz, $J_{7,10}$ = 0.9 Hz	
B11d	B	1.38 (s)	6.22 (q), 6.45 (q) 8.61 (t)	0.16 (d, H_{10}), 0.99 (d, H_8), 1.73 (dd, H_7); $J_{7,8}$ = 5.6 Hz, $J_{7,10}$ = 0.9 Hz	

(a) Solvents: A = DMSO-d_6, B = deuteriochloroform.

The picture for *N,N*-dimethyl-*N'*-heteroaryl substituted acetamidines, compounds of the type C (Table III and Table VI), is completely different. The rotational barriers are much lower and strongly dependent on the steric effect of the groups attached at the *ortho* position in respect to the acetamidine group. ΔG^* values for compounds II (X = CH, R = H, R_1 = CH_3 or C_2H_5) and III (R = R_2 = H, R_1 = CH_3 or C_2H_5) are between 13 and 14 kcal/mole, while in acetamidines of the structure II (X = C-CH_3 or C-CN, R = CH_3, R_1 = CH_3) or (X = N, R = CH_3, R_1 = CH_3) and in acetamidines of the structure III (R = R_1 = R_2 = CH_3) the barriers to rotation drop for more than 8-10 kcal/mole, in the range below 10 kcal/mole, in comparison to the corresponding formamidine derivatives. On this basis one can draw a conclusion that the acetamidine methyl group is oriented differently than the corresponding formamidine proton. Therefore, the compounds **C1c**, **C1e**, **C2a**, **C2b**, **C2d**, and **C4a** exist in the form IIb (R = CH_3, R_1 = CH_3, X = C-H), the compound **C9a** in the form IIIb (R = CH_3, R_1 = CH_3, R_2 = H), while in the compounds **C1a**, **C1d**, **C2c**, **C2e**, **C3**, **C5**, **C9b** and **C9d** the acetamidine group is no longer coplanar with the heteroaryl group.

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage, nmr spectra were recorded on a JEOL JNM C-60 HL NMR spectrometer (tetramethylsilane as internal standard), equipped with variable temperature probe.

Methods previously described in the literature were used to prepare the following compounds: **A1b** (3), **A3** (3), **A4b** (4), **A4c** (3), **A6** (3), **A7** (3), **A8** (7), **A9a** (5), **A9c** (6), **A9f** (6),

Table III

N,N-Dimethyl-*N'*-substituted Acetamidines

Compound	Nmr data: chemical shift (τ) and coupling constants J (Hz) (a)		Other proton resonances	Formula M.p. (°C) or b.p. (°C/mm)		Analysis C	H	N
	N=C-CH_3	$N(CH_3)_2$						
C1a	A 7.96 (s)	6.80 (s)	2.68 (dd, H_5), 1.75 (dd, H_4), 1.30 (dd, H_6); $J_{4,5}$ = 7.5 Hz, $J_{4,6}$ = 1.5 Hz, $J_{5,6}$ = 4.5 Hz	$C_{10}H_{12}N_4$ 120/2	Calcd.	63.81	6.43	29.77
					Found	63.83	6.35	30.10
C1c	B 8.05 (s)	6.98 (s)	3.15 (m, H_3), 2.45 (m, H_4), 3.40 (m, H_5), 1.65 (m, H_6); $J_{3,4}$ = 6.5 Hz, $J_{4,5}$ = 6.5 Hz, $J_{4,6}$ = 1.5 Hz, $J_{5,6}$ = 4.5 Hz	$C_9H_{13}N_3$ 120/2	Calcd.	66.22	8.03	25.75
					Found	66.47	8.12	25.93
C1d	A 8.16 (s)	6.92 (s)	7.87 (s, 3-CH_3), 2.46 (dd, H_4), 3.07 (dd, H_5), 1.87 (dd, H_6); $J_{4,5}$ = 6.5 Hz, $J_{5,6}$ = 4.5 Hz, $J_{4,6}$ = 1.5 Hz	$C_{10}H_{15}N_3$ 120/2	Calcd.	67.76	8.53	23.71
					Found	67.57	8.29	23.84
C1e	B 8.05 (s)	6.95 (s)	7.82 (s, 4-CH_3), 3.30 (qd, H_3), 3.12 (qd, H_5), 1.85 (d, H_6); $J_{H_3,4\text{-}CH_3}$ = 0.5 Hz, $J_{H_5,4\text{-}CH_3}$ = 0.5 Hz; $J_{5,6}$ = 4.5 Hz	$C_{10}H_{15}N_3$ 110/2	Calcd.	67.76	8.53	23.71
					Found	67.76	8.32	24.06
C2a	B 7.93 (s)	6.90 (s)	3.05 (dd, H_4), 2.65 (dd, H_5), 1.18 (dd, H_6); $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 4.5 Hz, $J_{4,6}$ = 1.5 Hz	$C_8H_{12}N_4$ 140/2	Calcd.	58.51	7.37	34.12
					Found	58.19	7.45	34.17
C2b	B 7.88 (s)	6.90 (s)	3.06 (d, H_4), 2.68 (d, H_5); $J_{4,5}$ = 9.0 Hz	$C_8H_{11}N_4Cl$ 63-66 (b)	Calcd.	48.36	5.58	28.20
					Found	48.16	5.79	28.17
C2c	A 8.0 (s)	6.87 (s)	2.60 (q, H_5), 7.85 (broad s, 4-CH_3); $J_{H_5,4\text{-}CH_3}$ = 0.5 Hz	$C_9H_{13}N_4Cl$ 100 (b)	Calcd.	50.82	6.16	26.64
					Found	50.90	6.42	26.31
C2d	B 7.92 (s)		7.65 (s, 5-CH_3), 3.07 (s, H_4)	$C_9H_{13}N_4Cl$ 73-76 (b)	Calcd.	50.82	6.16	26.64
					Found	50.66	6.30	26.67
C2e	B 7.95 (s)	6.87 (s)	7.65 (s, 4-CH_3 or 5-CH_3), 7.83 (s, 5-CH_3 or 4-CH_3)	$C_{10}H_{15}N_4Cl$ 75 (b)	Calcd.	52.98	6.70	24.72
					Found	53.25	6.87	24.73
C3	C 7.93 (s)	6.90 (s)	1.40 (d, H_4H_6), 3.04 (t, H_5); $J_{4,5}$ = $J_{5,6}$ = 4.8 Hz	$C_8H_{12}N_4$ 115/2	Calcd.	58.51	7.37	34.12
					Found	58.64	7.45	34.02
C4a	B 7.97 (s)	6.92 (s)	1.80 (m, H_3, H_5, H_6)	$C_8H_{12}N_4$ 110/2	Calcd.	58.51	7.37	34.12
					Found	58.26	7.70	34.00
C5	C 7.67 (s)	6.75 (s)	1.30 (d, H_5), 1.02 (d, H_6); $J_{5,6}$ = 2.0 Hz	$C_7H_{11}N_5$ 120/2	Calcd.	50.89	6.71	42.40
					Found	51.17	6.80	42.40
C9a	B 7.92 (s)	6.87 (s)	3.32 (d, H_7), 2.15 (d, H_8), 2.25 (s, H_3), 2.75 (s, H_2); $J_{7,8}$ = 9.5 Hz	$C_{10}H_{13}N_5$ 80-83 (c)	Calcd.	59.09	6.45	34.46
					Found	59.46	6.16	34.51
C9b	A 7.92 (s)	6.86 (s)	7.76 (d, 7-CH_3), 2.52 (d, H_2), 2.25 (d, H_3), 2.38 (q, H_8); $J_{2,3}$ = 1.0 Hz, $J_{H_8,7\text{-}CH_3}$ = 1 Hz	$C_{11}H_{15}N_5$ 130-135 (d)	Calcd.	60.80	6.96	32.24
					Found	60.58	6.68	32.69
C9d	A 7.90 (s)	6.83 (s)	7.80 (s, 8-CH_3), 7.45 (s, 7-CH_3); $J_{7\text{-}CH_3,8\text{-}CH_3}$ = 1.0 Hz	$C_{11}H_{16}N_6$ 143 (c)	Calcd.	56.87	6.94	36.18
					Found	57.03	7.03	36.27

(a) Solvents: A = perdeuteriomethanol, B = deuteriochloroform, C = deuteriochloroform:perdeuteriomethanol 1:1. (b) Crystallized from petrol ether. (c) Crystallized from cyclohexane. (d) Crystallized from a mixture of chloroform and petrol ether.

Table IV

Activation Parameters for
N,N-Dimethyl-*N'*-substituted Formamidines

Compound	T_c (°K)	$\Delta\nu$(Hz)	k_c(s^{-1})	ΔG^* (Kcal/mole)
A1a	351	4.5	10.0	19.1
A1b	358	7.5	16.7	19.1
A3	333	4.0	8.9	18.1
A4a	322	4.0	8.9	17.5
A4b	365	4.0	8.9	19.9
A4c	347	6.0	13.3	18.6
A6	334	3.5	7.8	18.3
A7	357	4.5	10.0	19.4
A8	357	4.0	8.9	19.5
A9a	340	6.0	13.3	18.2
A9c	359	6.5	14.4	19.3
A9d	355	5.3	11.8	19.2
A9f	357	7.0	15.6	19.0
A9g	375	7.3	16.2	20.0
A9h	379	8.5	18.9	20.1
A10b	368	2.3	5.1	20.5
A11a	369	4.5	10.0	20.0
A11b	358	4.0	8.9	19.5
A11c	385	3	6.7	21.2

Table V

Activation Parameters for
N,N-Diethyl-*N'*-substituted Formamidines

Compound	T_c (°K)	$\Delta\nu$(Hz)	k_c(s^{-1})	ΔG^* (Kcal/mole)
B9c	359	4.3	9.6	19.5
B9d	348	5.2	11.6	18.8
B9e	351	4.7	10.4	19.0
B9f	353	4.5	10.0	19.2
B9g	372	3.5	7.8	20.4
B9h	363	2.8	6.2	20.1
B9i	372	3.2	7.1	20.5
B10b	378	7.0	15.6	20.2
B11a	380	7.0	15.6	20.3
B11b	380	7.0	15.6	20.3
B11c	404	7.0	15.6	21.6
B11d	379	7.0	15.6	20.3

B9c (6), **B9f** (3), **B9g** (6), **B11b** (6), 6-azido-8-methyltetrazolo-[1,5-*b*]pyridazine (9), 6-azidopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine (10), 6-azidopyrido[3,4-*d*]tetrazolo[1,5-*b*]pyridazine (10), 6-aminopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine (11), and 6-aminopyrido[3,4-*b*]tetrazolo[1,5-*b*]pyridazine (11). All other *N,N*-dimethyl-*N'*-substituted formamidines (compounds of type A) were prepared according to the general procedure reported previously (1). In this manner the following compounds were prepared: **A1a** from 2-amino-3-cyanopyridine, **A9d** from 6-amino-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**12**), **A10b** from 6-aminopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**12**), **A11a** from 6-aminotetrazolo[1,5-*a*]phthalazine (8), **A11b** from 6-aminopyrido[2,3-*d*]tetrazolo[1,5-*b*]pyridazine (9), **A11c** from 6-aminopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine (11). Analytical and nmr data are summarized in Table I.

Table VI

Activation Parameters for
N,N-Dimethyl-*N'*-substituted Acetamidines (a)

Compound	T_c (°K)	$\Delta\nu$(Hz)	k_c(s^{-1})	ΔG^* (Kcal/mole)
C1a	193	(3)	(6.7)	<10.4
C1c	240	3	6.7	13.0
C1d	177	(3)	(6.7)	< 9.4
C1e	246	4.5	10.0	13.2
C2a	257	3	6.7	14.0
C2b	259	3.75	8.3	14.0
C2c	177	(3)	(6.7)	< 9.4
C2d	261	3	6.7	14.2
C2e	181	(3)	(6.7)	< 9.7
C3	173	(3)	(6.7)	< 9.3
C4a	256	3	6.7	13.9
C5	193	(3)	(6.7)	< 9.6
C9a	258	3	6.7	14.1
C9b	187	(3)	(6.7)	<10.0
C9d	191	(3)	(6.7)	<10.3

(a) The ΔG^* values below 10 kcal/mole were not determined since the compounds crystallized out of the solution at the temperatures around -90° or below. $\Delta\nu$ = 3 Hz (value in parenthesis) was chosen in order to calculate the ΔG^* values in such cases.

6-Amino-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**12**).

A mixture of 6-chloro-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (12) (1 g.) and liquid ammonia (30 ml.) was heated in an autoclave at 120° for three hours. After cooling liquid ammonia was evaporated, water (60 ml.) was added to the residue, crude 6-amino-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine was filtered off and crystallized from water, m.p. 263-265°; ms: M^+ = 163; nmr (in DMSO-d_6): τ = 7.52 (s, 8-CH_3), 7.86 (s, 7-CH_3), 1.02 (s, H_3), 3.64 (broad, NH_2).

Anal. Calcd. for $C_7H_9N_5$: C, 51.52; H, 5.56; N, 42.92. Found: C, 51.42; H, 5.78; N, 42.88.

6-Aminopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**13**).

In similar manner 6-aminopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**13**) was prepared from 6-chloropyrido[2,3-*d*]-*s*-triazolo-[4,3-*b*]pyridazine (13) in 92% yield and crystallized from water, m.p. 295°; ms: M^+ = 186; nmr (in DMSO-d_6): τ = 1.02 (s, H_3), 1.26 (dd, H_7), 2.18 (dd, H_8), 0.84 (dd, H_9), 3.25 (broad, NH_2); $J_{7,8}$ = 8.5 Hz, $J_{8,9}$ = 4.7 Hz, $J_{7,9}$ = 1.6 Hz.

Anal. Calcd. for $C_8H_6N_6$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.46; H, 3.45; N, 45.25.

6-Amino-7-methyl-*s*-triazolo[4,3-*b*]pyridazine (**14**).

6-Azido-7-methyl-*s*-triazolo[4,3-*b*]pyridazine (0.6 g.) was dissolved in ethanol (10 ml.) at 45° and a stream of hydrogen sulfide was bubbled into the solution for 1.5 hours. The solution was heated to boiling, the colloidal sulphur filtered off and the filtrate evaporated *in vacuo* to dryness. The crude residue was extracted with tetrahydrofurane (3 x 1.5 ml.) in order to remove sulphur, and crystallized several times from ethanol and *N,N*-dimethylformamide, m.p. 290°; ms: M^+ = 149; nmr (DMSO-d_6): τ = 7.75 (d, 7-CH_3), 1.15 (d, H_3), 2.31 (qd, H_8), 3.4-4.25 (broad, NH_2); $J_{7\text{-}CH_3,H_8}$ = 1.1 Hz, $J_{3,8}$ = 0.8 Hz.

Anal. Calcd. for $C_6H_7N_5$: C, 48.31; H, 4.73; N, 46.96. Found: C, 48.22; H, 4.96; N, 47.03.

In similar manner the following compound was prepared.

6-Amino-7-methylimidazo[1,2-*b*]pyridazine (**15**).

This compound was prepared from 6-azido-7-methylimidazo-[1,2-*b*]pyridazine in 59% yield and crystallized from ethanol, m.p. 190-193°; ms: M^+ = 148.

Anal. Calcd. for $C_7H_8N_4$: C, 56.74; H, 5.44; N, 37.82. Found: C, 56.89; H, 5.65; N, 37.99.

6-Hydrazino-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**16**).

A mixture of 6-chloro-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (12) (1.5 g.), hydrazine hydrate (80%, 1 ml.) and ethanol (5 ml.) was heated under reflux for 50 minutes. After cooling the precipitated hydrazino compound was filtered off and crystallized from water, 93% yield, m.p. 237-238°; ms: M^+ = 178; nmr (DMSO-d_6): τ = 7.88 (q, 7-CH_3), 7.52 (q, 8-CH_3), 1.03 (s, H_3), -0.35 (broad N*H*NH_2), 2.50 (broad, NHNH_2); $J_{7\text{-}CH_3,8\text{-}CH_3}$ = 0.7 Hz.

Anal. Calcd. for $C_7H_{10}N_6$: C, 47.18; H, 5.66; N, 47.17. Found: C, 46.95; H, 5.50; N, 46.98.

In a similar manner the following compounds were prepared:

6-Hydrazino-7-methylimidazo[1,2-*b*]pyridazine (**17**).

Compound **17** was prepared from 6-chloro-7-methylimidazo-[1,2-*b*]pyridazine (14) in 42% yield and crystallized from water, m.p. 255-260°; ms: M^+ = 163.

Anal. Calcd. for $C_7H_9N_5$: C, 51.52; H, 5.56; N, 42.92. Found: C, 51.75; H, 5.81; N, 43.07.

6-Hydrazinopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**18**).

Compound **18** was prepared from 6-chloropyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (13) in 95% yield and crystallized from water, m.p. 277-281°; ms: M^+ = 201; nmr (deuteriosulfuric acid): τ = 0.23-0.58 (m, H_7 and H_9, overlapped), 1.05 (dd, H_8), -0.35 (s, H_3); $J_{7,8}$ = 8.5 Hz, $J_{8,9}$ = 5.5 Hz.

Anal. Calcd. for $C_8H_7N_7$: C, 47.76; H, 3.51; N, 48.74. Found: C, 47.61; H, 3.60; N, 48.81.

6-Azido-7-methyl-*s*-triazolo[4,3-*b*]pyridazine (**19**).

A mixture of 6-hydrazino-7-methyl-*s*-triazolo[4,3-*b*]pyridazine (**17**) (3 g.) and hydrochloric acid (1:1, 15 ml.) was cooled to 0° and the solution of sodium nitrite (1.2 g. in 5 ml. of water) was added slowly. The precipitated 6-azido-7-methyl-*s*-triazolo[4,3-*b*]-pyridazine was filtered off and crystallized twice from chloroform and *n*-hexane, m.p. 124-129°; ms: M^+ = 175; nmr (deuteriochloroform): τ = 7.73 (d, 7-CH_3), 1.10 (d, H_3), 2.23 (qd, H_8); $J_{7\text{-}CH_3,H_8}$ = 1.1 Hz, J_{H_3,H_8} = 0.8 Hz.

Anal. Calcd. for $C_6H_5N_7$: C, 41.14; H, 2.88; N, 55.98. Found: C, 41.17; H, 3.12; N, 55.84.

In the same manner the following compounds were prepared:

6-Azido-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**20**).

Compound **20** was prepared from 6-hydrazino-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**16**) in 90% yield and crystallized from water, m.p. 146-150°; ms: M^+ = 189; nmr (deuteriochloroform): τ = 7.38 (q, 8-CH_3), 7.82 (q, 7-CH_3), 1.19 (s, H_3); $J_{7\text{-}CH_3,8\text{-}CH_3}$ = 0.6 Hz.

Anal. Calcd. for $C_7H_7N_7$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.27; H, 3.74; N, 51.75.

6-Azido-7-methylimidazo[1,2-*b*]pyridazine (**21**).

This compound was prepared from 6-hydrazino-7-methylimidazo[1,2-*b*]pyridazine (**17**) in 70% yield and crystallized from chloroform and *n*-hexane, m.p. 110°; ms: M^+ = 174.

Anal. Calcd. for $C_7H_6N_6$: C, 48.27; H, 3.47; N, 48.26. Found: C, 48.41; H, 3.68; N, 48.31.

6-Azidopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**22**).

This compound was prepared from 6-hydrazinopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**18**) in 65% yield and crystallized from methanol, m.p. 215-217°; ms: M^+ = 212; nmr (deuteriochloroform): τ = 1.07 (s, H_3), 1.66 (dd, H_7), 2.31 (dd, H_8), 0.82 (dd, H_9); $J_{7,8}$ = 8.5 Hz, $J_{8,9}$ = 4.7 Hz, $J_{7,9}$ = 1.6 Hz.

Anal. Calcd. for $C_8H_4N_8$: C, 45.28; H, 1.90; N, 52.81. Found: C, 45.27; H, 2.25; N, 53.02.

6-Diethylaminomethyleneamino-7,8-dimethyl-*s*-triazolo[4,3-*b*]-pyridazine (**B9d**).

A mixture of 6-azido-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**20**) (0.9 g.) and diethylamine (250 ml.) was heated under reflux for 25 days. The solvent was removed *in vacuo* and the residue purified by tlc (Merck DC Fertigplatten Kieselgel F 254, chloroform:methanol 25:1 as solvent). The strongly fluorescent spot was eluted with chloroform, the solvent evaporated to dryness and the residue (390 mg.) crystallized from chloroform and *n*-hexane, m.p. 68-74°; ms: M^+ = 246.

Anal. Calcd. for $C_{12}H_{18}N_6$: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.23; H, 7.14; N, 34.05.

6-Diethylaminomethyleneamino-7-methyl-*s*-triazolo[4,3-*b*]pyridazine (**B9e**).

A mixture of 6-azido-7-methyl-*s*-triazolo[4,3-*b*]pyridazine (**19**) (1 g.) and diethylamine (150 ml.) was heated under reflux for 25 days. The solvent was evaporated *in vacuo*, chloroform (50 ml.) was added and the crude 6-amino-7-methyl-*s*-triazolo[4,3-*b*]pyridazine was filtered off. The filtrate was evaporated and the residue was purified by tlc (Merck DC Fertigplatten Aluminum oxide F 254 type T, chloroform:methanol 50:1 as solvent). The strongly fluorescent spot was eluted, the solvent evaporated to dryness and the residue (775 mg.) crystallized from chloroform and *n*-hexane, m.p. 111-113°; ms: M^+ = 232.

Anal. Calcd. for $C_{11}H_{16}N_6$: C, 56.87; H, 6.94; N, 36.19. Found: C, 56.83; H, 6.95; N, 36.30.

6-Diethylaminomethyleneamino-8-methyltetrazolo[1,5-*b*]pyridazine (**B9h**) and 6-Diethylaminomethyleneamino-7-methyltetrazolo[1,5-*b*]pyridazine (**B9i**) from 6-Azido-7-methyltetrazolo[1,5-*b*]pyridazine.

A mixture of 6-azido-7-methyltetrazolo[1,5-*b*]pyridazine (9) (1 g.) and diethylamine (150 ml.) was heated under reflux for 10 days. The solvent was removed *in vacuo* and the mixture (560 mg.) of **B9h** and **B9i** (in the ratio 8:3) was separated from the crude reaction product by tlc (Merck DC Fertigplatten Aluminum oxide F 254 type T, chloroform:methanol 90:1 as solvent). Compound **B9h** was separated from **B9i** by tlc (Merck DC Fertigplatten Kieselgel F 254, chloroform-methanol 150:1 as solvent). Compound **B9h** had m.p. 86-89°; ms: M^+ = 233.

Anal. Calcd. for $C_{10}H_{15}N_7$: C, 51.48; H, 6.49; N, 42.03. Found: C, 51.57; H, 6.54; N, 42.25.

Compound **B9i** had m.p. 127-128°; ms: M^+ = 233.

Anal. Calcd. for $C_{10}H_{15}N_7$: C, 51.48; H, 6.49; N, 42.03. Found: C, 51.33; H, 6.64; N, 42.41.

6-Diethylaminomethyleneamino-8-methyltetrazolo[1,5-*b*]pyridazine (**B9h**) from 6-Azido-8-methyltetrazolo[1,5-*b*]pyridazine.

A mixture of 6-azido-8-methyltetrazolo[1,5-*b*]pyridazine (9) (1 g.) and diethylamine (150 ml.) was heated under reflux for 8 days. The solvent was removed under reduced pressure and chloroform (150 ml.) was added to the residue. The solid was filtered off and identified as 6-amino-8-methyltetrazolo[1,5-*b*]-pyridazine. The filtrate was concentrated and the residue purified by tlc (Merck, DC Fertigplatten, Aluminum oxide F 254 type T,

chloroform:methanol 20:1 as solvent). The strongly fluorescent spot was eluted, the solvent evaporated to dryness and the residue identified as **B9h**, crystallized from chloroform and diethyl ether. The compound was identical in all respects with the compound prepared from 6-azido-7-methyltetrazolo[1,5-*b*]pyridazine (9).

6-Diethylaminomethyleneaminopyrido[4,3-*d*]tetrazolo[1,5-*b*]-pyridazine (**B11c**) and 6-Diethylaminomethyleneaminopyrido[3,4-*d*]tetrazolo[1,5-*b*]pyridazine (**B11d**).

A mixture of 6-azidopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine (10) (1 g.) and diethylamine (150 ml.) was heated under reflux for 5 days. After cooling the crude **B11c** (410 mg.) was filtered off and crystallized from chloroform and *n*-hexane, m.p. 226-230°; ms: $M^+ = 276$.

Anal. Calcd. for $C_{12}H_{14}N_8$: C, 53.32; H, 5.22; N, 41.46. Found: C, 53.33; H, 5.20; N, 41.39.

From the filtrate **B11d** (70 mg.) was separated by tlc (Merck DC Fertigplatten Aluminum oxide F 254 type T, chloroform:*n*-hexane 10:1 as solvent, $R_f = 0.5$) and crystallized from chloroform and *n*-hexane, m.p. 187-189°; ms: $M^+ = 270$.

Anal. Calcd. for $C_{12}H_{14}N_8$: C, 53.32; H, 5.22; N, 41.46. Found: C, 52.93; H, 5.52; N, 41.67.

6-Diethylaminomethyleneaminotetrazolo[1,5-*a*]phthalazine (**B11a**).

A mixture of 6-azidotetrazolo[1,5-*a*]phthalazine (8) (1 g.) and diethylamine (80 ml.) was heated under reflux for 15 days. The solvent was removed *in vacuo* to dryness. Chloroform (50 ml.) was added and the crude 6-aminotetrazolo[1,5-*a*]phthalazine (160 mg.) was filtered off. The filtrate was evaporated and the residue (830 mg.) crystallized from chloroform and *n*-hexane, m.p. 144-147°; ms: $M^+ = 269$.

Anal. Calcd. for $C_{13}H_{15}N_7$: C, 57.97; H, 5.61; N, 36.41. Found: C, 57.87; H, 5.78; N, 36.56.

6-Diethylaminomethyleneaminopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]-pyridazine (**B10b**).

A mixture of 6-azidopyrido[2,3-*d*]-*s*-triazolo[4,3-*b*]pyridazine (**22**) (0.8 g.) and diethylamine (150 ml.) was heated under reflux for 15 days. The solvent was removed to dryness, chloroform (40 ml.) was added and crude 6-aminopyrido[2,3-*d*]-*s*-triazolo-[4,3-*b*]pyridazine filtered off. The filtrate was evaporated and the residue purified by tlc (Merck DC Fertigplatten Aluminum oxide F 254 type T, chloroform:methanol 50:1 as solvent). The spot with $R_f = 0.6$ was eluted with methanol, affording **B10b** (450 mg.) which was then crystallized from chloroform and *n*-hexane, m.p. 162-169°; ms: $M^+ = 269$.

Anal. Calcd. for $C_{13}H_{15}N_7$: C, 57.97; H, 5.61; N, 36.41. Found: C, 57.65; H, 5.52; N, 36.30.

General Procedure for the Preparation of *N,N*-Dimethyl-*N'*-substituted Acetamidines (Compounds of Type C).

A mixture of the corresponding aminoazine (0.2 g.) and *N,N*-dimethylaminoacetamide dimethylacetal (0.2 ml.) in toluene (3 ml.) was heated under reflux for 3 hours. After cooling, eventual unreacted aminoazine was filtered off, the solvent evaporated *in vacuo* and the resultant acetamidine purified by crystallization or distillation.

In this manner the following compounds were prepared: **C1a** from 2-amino-3-cyanopyridine; **C1c** from 2-aminopyridine; **C1d** from 2-amino-3-methylpyridine; **C1e** from 2-amino-4-methylpyridine; **C2a** from 3-aminopyridazine; **C2b** from 3-amino-6-chloropyridazine; **C2c** from 3-amino-6-chloro-4-methylpyridazine (16); **C2d** from 3-amino-6-chloro-5-methylpyridazine (16); **C2e** from 3-amino-6-chloro-4,5-dimethylpyridazine (17); **C3** from 2-aminopyrimidine; **C4a** from 2-aminopyrazine; **C5** from 3-amino-1,2,4-triazine; **C9a** from 6-aminoimidazo[1,2-*b*]pyridazine (18); **C9b** from 6-amino-7-methylimidazo[1,2-*b*]pyridazine (**15**); and **C9d** from 6-amino-7,8-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**12**). Analytical and nmr data are listed in Table III.

Kinetic Measurements.

The solvents used for the low-temperature measurements were deuteriochloroform, perdeuteriomethanol or deuteriochloroform: perdeuteriomethanol 1:1. The solutions were prepared as described previously (1). The nmr spectra were recorded on a JEOL JNM C-60 HL instrument equipped with a variable temperature accessory. The temperatures were measured accurately to ± 0.5°. The free energies of the barriers to rotation, ΔG^*, at the coalescence temperature were calculated using the approximate Eyring equation and Gutowsky-Holm equation (2a).

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