

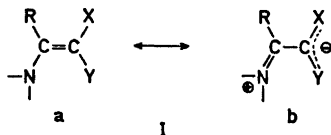
NMR-Studies by Lineshape Analysis of three Restricted Rotations in 1-Cyano-1-carbethoxy-2-methyl-2- dimethylaminoethylene

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The title compound was found to exist in the two conformers IV_a and IV_b . A virtually temperature-independent conformer ratio (IV_a/IV_b or IV_a/IV_b) of 1.30 was observed and the thermodynamic parameters for the equilibrium $IV_a \rightleftharpoons IV_b$ are $\Delta H^\circ = 0$ kcal/mol, $\Delta F_{298}^\circ = 0.16 \pm 0.02$ kcal/mol and $\Delta S^\circ = -0.5 \pm 0.1$ e.u. By complete lineshape analysis of the spectrum of the dimethylamino protons as a function of temperature, it was possible to make a simultaneous determination of the $=C-N-$ and $-C=C-$ barriers in IV_a and IV_b . The two $=C-N-$ barriers (ΔH^\ddagger) are 15.0 ± 0.6 kcal/mol and 15.5 ± 0.6 kcal/mol, respectively, while the corresponding value for the $-C=C-$ bond is 13.9 ± 0.6 kcal/mol. Observed entropies of activation for these barriers are 14.2 ± 3 e.u., 8.3 ± 3 e.u., and -3.2 ± 3 e.u. respectively. The reliability of these ΔS^\ddagger values is discussed as well as the possible origins of the differences in ΔH^\ddagger and ΔS^\ddagger between the $=C-N-$ and $-C=C-$ bonds.

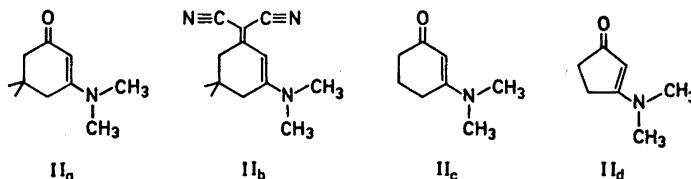
The study of hindered rotation(s) in enamines of the type I_a has recently attracted considerable attention, since studies of the $=C-N-$ and



(X,Y)=(CN,CN); (COOC₂H₅, COOC₂H₅); (H,NO₂)

$\begin{array}{c} -C=C- \\ | \quad | \end{array}$ barriers may provide information about the extent to which the canonical form I_b must be considered in the description of the ground state of I. Extensive delocalization of the electrons in I would increase the $\begin{array}{c} =C-N- \\ | \quad | \end{array}$ barrier and lower the $\begin{array}{c} -C=C- \\ | \quad | \end{array}$ barrier, which in ordinary olefins is of the order of >30 kcal/mol. Nuclear magnetic resonance (NMR) studies of enamines such as I have indeed shown not only the existence of a relatively high barrier to internal rotation for the $N(CH_3)_2$ group,¹⁻⁴ but also in some cases a rapid isomerization around the $\begin{array}{c} -C=C- \\ | \quad | \end{array}$ bond,⁴ thus indicating that the polar form I_b must to a large extent be taken into account when the electronic structure of I is discussed.

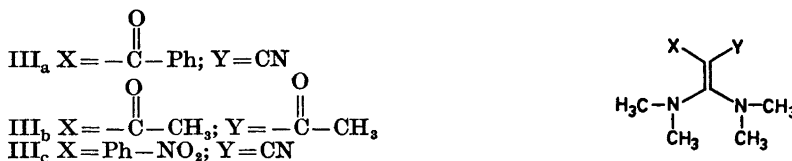
In the course of our study of the activation parameters for the $\begin{array}{c} =C-N- \\ | \quad | \end{array}$ rotation in enamines by NMR spectroscopy, using complete lineshape analysis methods, we have investigated the cyclic enamines II_a ,⁵ II_b ,⁵ II_c ,⁶ and II_d .⁶



In these enamines a large positive entropy of activation (ΔS^\ddagger) is observed for the $\begin{array}{c} =C-N- \\ | \quad | \end{array}$ rotation, which is in contrast with results from recent NMR studies of the hindered $\begin{array}{c} =C-N- \\ | \quad | \end{array}$ rotation in simple amides,⁷⁻¹⁰ *N*-acetylpyrrole,¹¹ and some halogenated trineopentylbenzenes¹² for which ΔS^\ddagger values close to zero have been obtained.

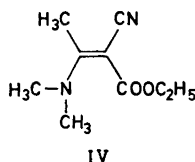
Determination of activation parameters by analysis of NMR spectra as a function of temperature has been shown to give relatively large errors in the calculated ΔS^\ddagger values even if careful computerized complete lineshape analyses are performed.⁷ The positive entropies of activation observed for the $\begin{array}{c} =C-N- \\ | \quad | \end{array}$ rotation in II_a – II_d might thus to some extent be due to systematic errors, which makes an interpretation of the observed ΔS^\ddagger values somewhat ambiguous. However, if several barriers in one molecule could be determined from the same NMR-signals using the same set of spectral parameters for all evaluated barriers, it would be reasonable to assume that the systematic errors in the evaluation procedure equally affect all the barriers determined. A realistic comparison of the ΔS^\ddagger values associated with the different rotations thus studied would then be possible.

Restricted rotation around several bonds in various enamines has recently been observed by Sandström and Wennerbeck¹³ who have determined the free energy of activation for the =C-N- , -C=C- , and =C-C=O bonds



in compounds III_a–III_c from the coalescence temperature of pertinent lines in the NMR spectrum of the dimethylamino groups.

The present study was prompted by the observation of four lines in the low-temperature NMR spectrum (-65°C) of the dimethylamino group in compound IV. Upon raising the temperature these four signals merge into one,



passing through three different coalescence points and thus manifesting the existence of three relatively high barriers to internal rotation. The study of the temperature-dependent spectrum of the $\text{N}(\text{CH}_3)_2$ group in IV thus offers a possibility of obtaining ΔS^\ddagger for three different rotations in the same molecule, all of which may be evaluated from one set of signals.

METHODS AND RESULTS

NMR spectrum. The low-temperature spectrum (-65°C) of IV in CD_2Cl_2 solution shows four group of signals (Fig. 1). The methyl and methylene

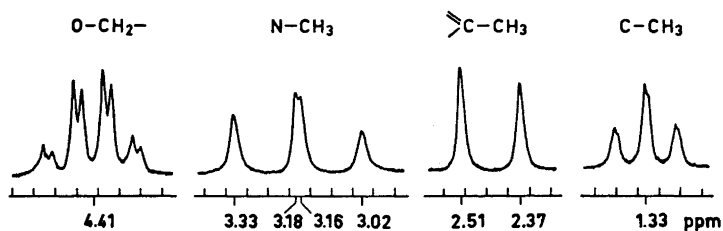
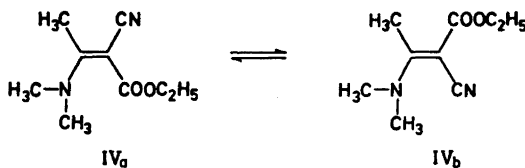


Fig. 1. NMR spectrum of IV in CD_2Cl_2 solution at -65°C .

protons of the ethyl group absorb at 1.33 ppm and 4.41 ppm, respectively (all shifts are measured relative to internal tetramethyl silane). The methyl signals exhibit shoulders due to the presence of two overlapping triplets, and the spectrum of the methylene protons consists of two quartets separated by ~ 2 Hz. Two signals due to the $C=C-CH_3$ protons are found at 2.37 ppm and 2.51 ppm, with the low field signal slightly larger than the high field one. Integration of these signals gave an intensity ratio of 1.30. The $N-CH_3$ protons give rise to four signals with the chemical shifts 3.33, 3.18, 3.16, and 3.02 ppm. For convenient discussion of the $N-CH_3$ spectrum these signals are labelled A, C, B, and D, respectively. An intensity ratio $A/D=1.30$ was obtained by integration.

The doubling of the signals from all groups of protons is interpreted in terms of the existence of two conformers IV_a and IV_b , which at temperatures above $+20^\circ C$ interconvert rapidly enough to produce only average signals.



An assignment of signals to each conformer from the chemical shift differences and the conformer ratio, has unfortunately not yet been possible. At temperatures above $-50^\circ C$ the $N-CH_3$ signals A and B become broadened due to increased rate of rotation around the $=C-N-$ bond in one of the conformers,

and these lines coalesce into one signal at about $-43^\circ C$. (See spectrum at $-42.7^\circ C$ in Fig. 2). Increased rate of rotation around the $=C-N-$ bond

in the second conformer causes a broadening of signals C and D above $-22^\circ C$, which coalesce at about $-15^\circ C$. (See spectrum at $-14.9^\circ C$ in Fig. 1). Above this coalescence temperature the $C=C-CH_3$ signals are also broadened due to increased rate of rotation around the $-C=C-$ bond, and these lines merge

into one signal at about $+10^\circ C$, the temperature at which the dimethylamino signals for the same reason exhibit their third coalescence point. (See spectrum at $+10.3^\circ C$ in Fig. 2).

An alternative interpretation of the temperature dependence of the $C=C-CH_3$ spectrum and the third coalescence of the $N-CH_3$ signals would be a fast rotation around the $-C=C-$ bond and a moderately fast rotation

around the $=C-C=O$ bond. However, the $=C-C=O$ barrier in compound III_b was found to be only ~ 10 kcal/mol, and the corresponding barrier in IV may be assumed to be still lower, since III_b contains two nitrogen atoms

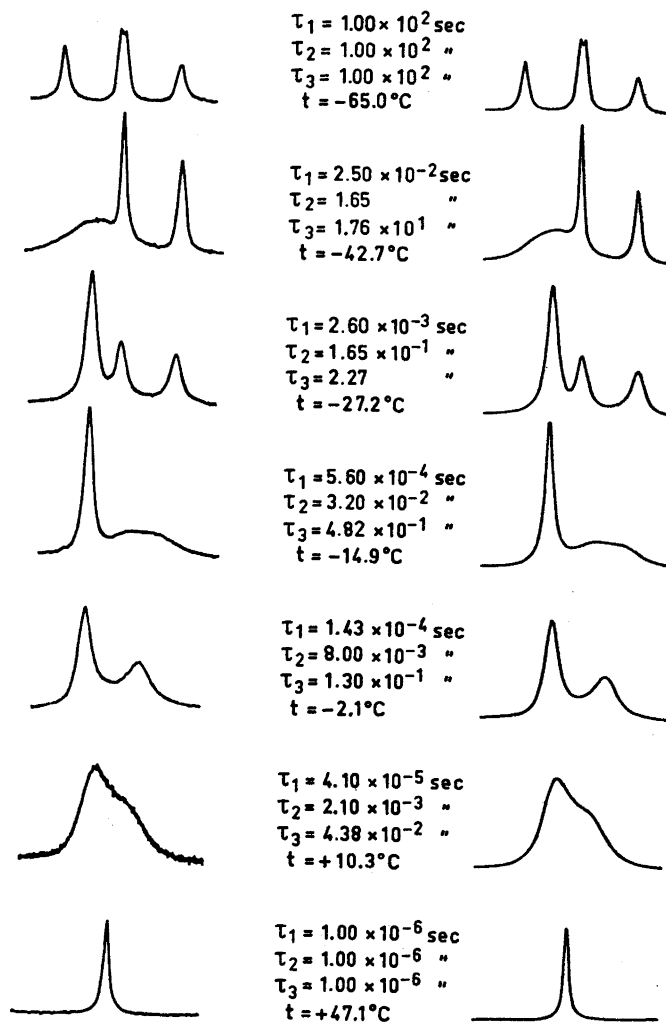
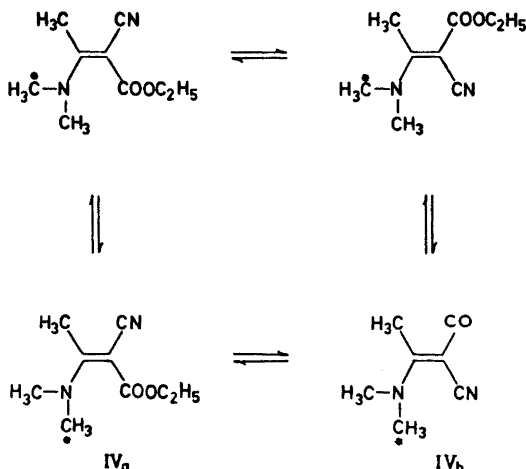


Fig. 2. Examples of experimental and theoretical spectra of the $N\text{-CH}_3$ protons in IV at various temperatures.

in conjugation with the carbonyl group while IV contains only one. A barrier to internal rotation of less than ~ 10 kcal/mol would lead to a coalescence temperature of $< -65^\circ\text{C}$.

Evaluation of the interconversion rates. The various interconversions in IV can be illustrated by the following scheme:



The exchange broadening of the $N-\text{CH}_3$ signals can be described as a four-site case involving three different exchange rates. A computer program for this case based on the theory of Gutowsky *et al.*¹⁴ was developed for a CDC 3600 computer. Calculated spectra were obtained in plotted form on a Calcomp plotter type 565. The rates of rotation around the $=\text{C}-\text{N}-$ and $-\text{C}=\text{C}-$

bonds were determined by visual fitting of theoretical spectra to experimental ones. The lineshape function for the present four-site case contains the following eleven parameters which must be known in order to calculate the theoretical spectra: three different mean lifetimes τ_1 to τ_3 corresponding to three different interconversion rates, four transverse relaxation times T_{2A} to T_{2D} , one for each of the four signals in the $N-\text{CH}_3$ spectrum, three chemical shift differences $\delta\nu_{AB} = \nu_A - \nu_B$, $\delta\nu_{CD} = \nu_C - \nu_D$, and $\delta\nu_{AB-CD} = (\nu_A + \nu_B)/2 - (\nu_C + \nu_D)/2$, and the relative populations of the two conformers, P_{IVa} and P_{IVb} . (Since $P_{IVa} + P_{IVb} = 1$ we may set $P_{IVa} = P$ and $P_{IVb} = (1 - P)$.)

The low temperature spectrum (slow exchange limit) of the dimethylamino group could be well reproduced with the same $T_2 = 0.14$ sec for all four lines, and the T_2 value obtained from the single line in the high temperature spectrum (fast exchange limit) was 0.16 sec. The difference between the observed high and low temperature values of T_2 was considered to be within the experimental errors, and thus $T_2 = 0.15$ sec was used for all intermediate temperatures. The chemical shift differences $\delta\nu_{AB}$, $\delta\nu_{CD}$, and $\delta\nu_{AB-CD}$ could be determined together with the appropriate τ value below each coalescence point by visual curve fitting. No significant temperature dependency could be found for $\delta\nu_{AB}$, $\delta\nu_{CD}$, and $\delta\nu_{AB-CD}$ within the estimated error limits of 0.2–0.3 Hz. A mean value of the shift differences obtained at temperatures below each coalescence point was therefore used for the evaluation of τ at higher temperatures. The values of these parameters used in the curve fitting procedure were 16.2 Hz for $\delta\nu_{AB}$, 15.4 Hz for $\delta\nu_{CD}$, and 15.0 Hz for $\delta\nu_{AB-CD}$. At tempera-

tures below -50°C the relative population P was determined by integration of signals A and D. (Overlap between signals B and C prevented the determination of P from these signals.) Between -50°C and the third coalescence point ($\sim +25^{\circ}\text{C}$) of the $N-\text{CH}_3$ spectrum, P was evaluated by curve fitting. The P values obtained are 0.559 at -65°C and 0.572 at $+10^{\circ}\text{C}$. As the precision in the determination of P by integration and curve fitting was estimated to be about $\pm 2-3\%$, the observed difference between P at -65°C and $+20^{\circ}\text{C}$ is within the error limits and therefore a P value of 0.565 was used at temperatures above $+10^{\circ}\text{C}$.

The rate of interconversion around the $-\text{C}=\text{C}-$ bond was also determined from the exchange-broadened spectra of the $\text{C}=\text{C}-\text{CH}_3$ protons by curve fitting. By setting $\nu_{\text{A}} = \nu_{\text{B}}$ and $\nu_{\text{C}} = \nu_{\text{D}}$, the program for the four-site case could also be used for the calculation of theoretical spectra for the $\text{C}=\text{C}-\text{CH}_3$ protons. The parameters in the lineshape equation pertinent to the $\text{C}=\text{C}-\text{CH}_3$ spectrum were determined in the same way as those for the $N-\text{CH}_3$ spectrum at all temperatures investigated. No temperature dependence was found for these parameters and the values used for the four spin-spin relaxation times, $\delta\nu_{\text{AB-CD}}$ and P were 0.16 sec, 13.8 Hz and 0.565, respectively.

The precision in the determinations of τ_1 , τ_2 , and τ_3 from the $N-\text{CH}_3$ spectrum and τ_3 from the $\text{C}=\text{C}-\text{CH}_3$ spectrum was about $\pm 2\%$ at the coalescence points and about $\pm 5\%$ close to the slow and fast exchange ends of the Arrhenius plot. Plots of $\ln(1/\tau)$ versus $1/T$ for the rotations investigated in IV are shown in Fig. 3.

Evaluation of activation parameters and equilibrium data for $\text{IV}_a \rightleftharpoons \text{IV}_b$. The activation parameters for the $=\text{C}-\text{N}-$ and $-\text{C}=\text{C}-$ rotations were

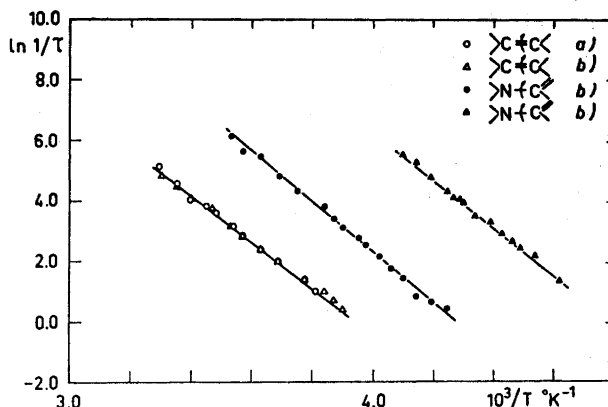


Fig. 3. Arrhenius plots of kinetic data for the interconversions around the $-\text{N}-\text{C}=\text{C}-$ and $-\text{C}=\text{C}-$ bonds in IV. a) Rate constants evaluated from the $\text{C}=\text{C}-\text{CH}_3$ signals. b) Rate constants evaluated from the $N-\text{CH}_3$ signals.

calculated according to the theory of absolute reaction rates, and are summarized in Table 1. Calculations of the error limits given in this table were

Table 1. Activation parameters for the hindered internal rotation around the $=\text{C}-\text{N}-$ and $-\text{C}=\text{C}-$ bonds in IV. The error limits given in the table were calculated assuming only random errors.

Rotation	E_a kcal/mol	ΔH^\ddagger kcal/mol	ΔF_{298}^\ddagger kcal/mol	ΔS^\ddagger e.u.
$>\text{N}-\text{C}=<$ ^a	15.48 ± 0.21	14.88 ± 0.21	10.75 ± 0.35	13.9 ± 2.0
$>\text{N}-\text{C}<$ ^a	15.96 ± 0.28	15.36 ± 0.28	12.99 ± 0.43	8.0 ± 2.4
$>\text{C}=\text{C}<$ ^a	14.37 ± 0.14	13.78 ± 0.14	14.82 ± 0.21	-3.5 ± 1.2
$>\text{C}=\text{C}<$ ^b	14.69 ± 0.17	14.10 ± 0.17	14.73 ± 0.25	-2.1 ± 1.4

^a Evaluated from the spectrum of the dimethylamino protons.

^b Evaluated from the spectrum of the $\text{C}=\text{C}-\text{CH}_3$ protons.

carried out assuming only random errors, and are probably too small. Previous consideration of errors in the NMR line-shape method ^{7,8} indicates that more realistic errors in E_a , ΔH^\ddagger , ΔF^\ddagger , and ΔS^\ddagger are ± 0.6 kcal/mol, ± 0.6 kcal/mol, $\pm 0.1-0.2$ kcal/mol, and 2-3 e.u., respectively. The observed temperature-independent conformer ratio $K=1.30$ gives $\Delta H^\circ=0$ kcal/mol, $\Delta F^\circ=RT \ln K=0.16$ kcal/mol, and $\Delta S^\circ=0.5$ e.u. for the isomer equilibrium $\text{IV}_a \rightleftharpoons \text{IV}_b$. Errors in ΔF° and ΔS° estimated from the uncertainty in the determination of the conformer ratio are ± 0.02 kcal/mol and ± 0.1 e.u., respectively.

The effect of different solvents on $\Delta F_{T_c}^\ddagger$ (T_c = the coalescence temperature) are given in Table 2. The effect of different solute concentrations (5, 10, and 20 % by weight) was also investigated, but as no detectable concentration dependence was observed for $\Delta F_{T_c}^\ddagger$ only those values for a solute concentration of 10 % by weight are given in Table 2.

DISCUSSION

The free energy of activation (ΔF^\ddagger) for the $=\text{C}-\text{N}-$ rotation in compound V has recently been reported ³ to be 17.3 kcal/mol. The ΔF^\ddagger values

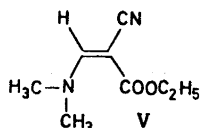


Table 2. Summary of $\Delta F_{T_c}^\ddagger$ values for the hindered rotations in IV studied in different solvents.

Solvent	Rotation	T_c °K	$\Delta\nu$ Hz	ΔF^\ddagger kcal/mol
CCl ₄ :CHCl ₃ (6:1)	$>N \nmid C \leq$	231	8.0	11.8 ^b
	$>N \nmid C \leq$	258	3.5	12.9 ^c
	$>C \nmid C <$	291	8.5	14.9
Pyridine	$>N \nmid C \leq$	238	16.0	11.6 ^b
	$>N \nmid C \leq$	249	4.5	13.0 ^c
	$>C \nmid C <$	288	15.5	14.4
DMSO(<i>d</i> ₆):CH ₂ Cl ₂ (1:1)	$>N \nmid C \leq$	228	8.2	11.6 ^b
	$>N \nmid C \leq$	258	13.1	13.0 ^c
	$>C \nmid C <$	258	8.1	13.2
Acetone	$>N \nmid C \leq$	—	—	— ^d
	$>N \nmid C \leq$	258	17.3	12.81 ^c
	$>C \nmid C <$	281	9.3	14.23

^a $\Delta F^\ddagger_{T_c}$ was calculated from values obtained by the formula $2\pi\tau\Delta\nu = \sqrt{2}$

^b Evaluated from the coalescence of signals A and B (see text).

^c Evaluated from the coalescence of signals C and D (see text).

^d No coalescence was observed down to -80°C .

for the dimethylamino group rotations in IV_a and IV_b are lower by ~ 6 kcal/mol and ~ 4 kcal/mol, respectively (*cf.* Table 1). Compared with the observed ΔF^\ddagger values for the corresponding barrier in *N,N*-dimethylformamide (20.9 kcal/mol⁸) and *N,N*-dimethylacetamide (18.0 kcal/mol⁸), the effect of the methyl group on ΔF^\ddagger for the $=C-N-$ rotation in IV_a and IV_b is

quite large. However, since no value for the enthalpy of activation (ΔH^\ddagger) for the hindered rotation of the $N(\text{CH}_3)_2$ group in V has yet been reported it is difficult to assess the extent to which the change in ΔF^\ddagger is also associated with a change in the corresponding entropy of activation (ΔS^\ddagger).

If the enthalpy of activation for an internal rotation is taken as a measure of the magnitude of the corresponding barrier, the present study reveals a slightly larger barrier for the $=C-N-$ bond than for the formal double bond

(*cf.* Table 1). The $=C-N-$ and $-C=C-$ barriers determined (15.5, 15.0,

and 13.9 kcal/mol, respectively) thus lend further support to the results obtained in previous studies of enamines^{3,4} (eqn. I) which were interpreted in terms of extensive delocalization of the electrons in the ground state of these compounds. Although the enthalpy of activation for the restricted rotation of the dimethylamino group and for that around the $-C=C-$ bond

are quite similar, the corresponding ΔS^\ddagger values are of very different magnitude: 14.2 e.u. and 8.3 e.u. for the two $=\text{C}-\text{N}-$ rotations and -3.2 e.u. for the rotation around the $-\text{C}=\text{C}-$ bond. The observed ΔS^\ddagger value for the $-\text{C}=\text{C}-$ rotation is thus more than 10 e.u. lower than those for the $=\text{C}-\text{N}-$ rotations.

This difference is assumed to be significant, since ΔS^\ddagger for the hindered rotations in IV are all calculated from rate data determined by lineshape analysis of the spectrum of the $N-\text{CH}_3$ protons. Systematic errors would therefore affect all three ΔS^\ddagger values to an equal extent. Furthermore a ΔS^\ddagger value of -2.1 e.u. was obtained for the rotation around the $-\text{C}=\text{C}-$ bond by analysis of the $\text{C}=\text{C}-\text{CH}_3$ spectrum.

The positive entropies of activation for the $=\text{C}-\text{N}-$ rotations observed in the present work are also in agreement with the results obtained in studies of the enamines II_a-II_b .^{5,6} Possible origins of these entropy effects, such as solvent effects, a temperature dependent enthalpy of activation or a low-lying vibration in the transition state, are discussed in Ref. 5.

Since NMR studies of the $=\text{C}-\text{N}-$ rotation in IV indicate a large delocalization of the electrons in the planar initial state, this would be more polar than the transition state in which the $\text{N}(\text{CH}_3)_2$ group is assumed to be twisted 90° out of the plane of the $-\text{C}=\text{C}-$ bond. The transition state for the rotation around the $-\text{C}=\text{C}-$ double bond would on the other hand be more polar

than the initial state in which the fragments $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{N} \end{array}$ and $\begin{array}{c} \text{X} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Y} \end{array}$ are in the same plane, since the rotation around the $-\text{C}=\text{C}-$ bond is assumed to proceed via a structure with a large contribution from the canonical form I_b . According to these considerations, the solvent-solute interactions would stabilize the initial state relative to the transition state for the $=\text{C}-\text{N}-$ rotation and the transition state relative to the initial state for the $-\text{C}=\text{C}-$ rotation, thus leading to a positive ΔS^\ddagger for the rotation around the $=\text{C}-\text{N}-$ bond and a negative ΔS^\ddagger for the isomerization around the $-\text{C}=\text{C}-$ bond.

Investigations of the solvent effect on $\Delta F_{T_c}^\ddagger$ for the $-\text{N}-\text{C}=\text{C}-$ rotations (Table 2) show that this parameter is quite insensitive to the polarity of the solvent. It thus seems likely that solvent-solute interactions have little in-

fluence also on the entropy of activation for the hindered internal rotation of the dimethylamino groups in IV_a and IV_b. Solvent effect studies of the $-\text{C}=\text{C}-$ rotation show on the other hand a slight decrease of $\Delta F_{T_c}^\ddagger$ with

$$\begin{array}{c} | \quad | \\ -\text{C}=\text{C}- \\ | \quad | \end{array}$$
 increasing polarity of the solvent (Table 2) and is thus ~ 1.5 kcal/mol lower in DMSO:CH₂Cl₂ (1:1) than in CCl₄:CHCl₃ (6:1). Whether the observed solvent effect on $\Delta F_{T_c}^\ddagger$ for the rotation around the $-\text{C}=\text{C}-$ bond is associated with

$$\begin{array}{c} | \quad | \\ -\text{C}=\text{C}- \\ | \quad | \end{array}$$
 a solvent dependence also in ΔS^\ddagger can, however, not be answered until the appropriate ΔH^\ddagger are known. The solvent studies indicate, however, that the canonical form I_b probably makes a large contribution to the electronic structure of the transition state for the isomerization around the $-\text{C}=\text{C}-$ bond

$$\begin{array}{c} | \quad | \\ -\text{N}-\text{C}=\text{C}- \\ | \quad | \end{array}$$
 and that this state is more polar than the initial state for the $-\text{N}-\text{C}=\text{C}-$ rotation.

EXPERIMENTAL

The enamine IV used in the present investigation was prepared according to Ref. 15 and distilled before use; b.p. 140°/0.3 mm; MS: $m/e=182$ (M^+); IR: 2200 cm^{-1} ($\text{C}\equiv\text{N}$), ~ 1700 cm^{-1} ($\text{C}=\text{O}$). The NMR spectrum (see Fig. 1) strongly supports the proposed structure. Methylene chloride-*d*₂ (Merck, Sharpe & Dome of Canada Ltd.) as well as all other solvents used were of commercial quality and used without further purification. The NMR spectra used in the lineshape analysis were obtained from a solution of 10 wt. % IV and 5 % tetramethylsilane (reference signal for the field-frequency lock of the spectrometer) in CD₂Cl₂.

The spectra were recorded on a Varian HA-100 spectrometer equipped with a variable temperature probe and a V-4343 variable temperature regulator. The shifts were measured by the usual sideband technique using a Hewlett-Packard Model 202 CD audio oscillator. The sample temperatures were obtained from the temperature dependent shift difference between the hydroxyl and methylene protons in a solution of 50 % ethylene glycol and 50 % CD₃OD acidified with a small amount of hydrochloric acid. This solution was kept in a sealed capillary which was fixed in the center of the sample tube by means of two teflon plugs. The temperature-dependent shift difference between the hydroxyl and the methylene protons in this solution was calibrated against copper-constantan thermocouple as described elsewhere.⁷ The temperatures obtained from this internal "glycol thermometer" are estimated to be accurate to better than $\pm 0.5^\circ\text{C}$ (cf. Ref. 7).

The resolution of the spectrometer was maintained as constant as possible by adjusting the homogeneity so as to always obtain the same half-width (0.35 Hz) in the triplet from traces of CDHCl₂ in the solvent.

Acknowledgement. The author wishes to thank professor Sture Forsén for his kind interest in this work and for valuable comments on the manuscript. Thanks are also due to Dr. R. E. Carter for linguistic criticism and helpful discussions.

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Received December 13, 1969.