

INTERNAL ROTATION

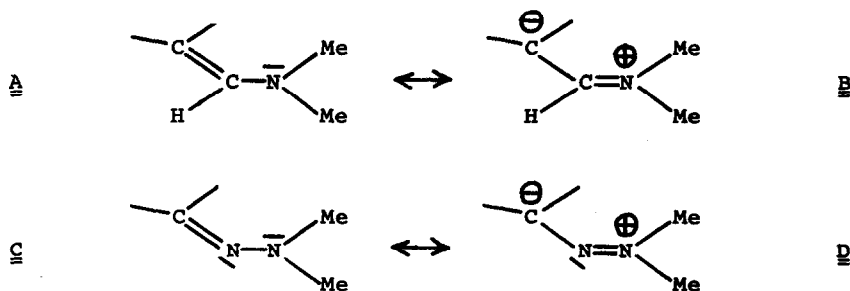
ABOUT THE =C-N BOND IN ENAMINES AND THE =N-N BOND IN HYDRAZONES <sup>1)</sup>

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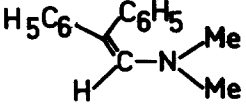
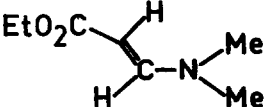
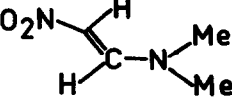
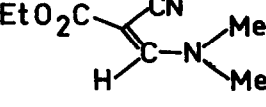
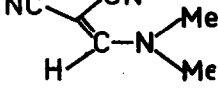
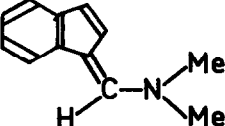
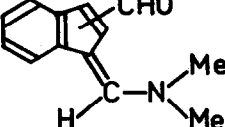
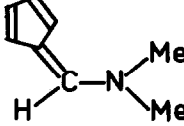
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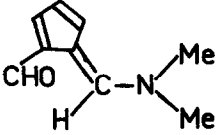
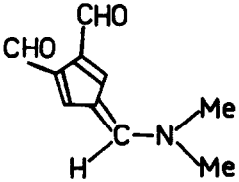
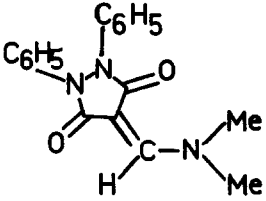
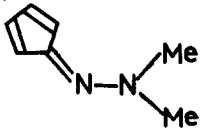
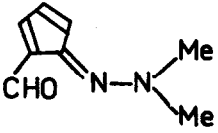
Resonance structures A and B must be considered for the ground state of enamines <sup>2)</sup>. Hindrance of free rotation about the C-N bond is dependent upon the contribution of B. The kinetics of this process have been studied for



$R_2C=CH-CH=NMe_2$  ( $R = H, C_6H_5, OEt$ ) <sup>3)</sup>. For some hydrazones Hafner <sup>4)</sup> has proposed structures C and D, but hindered rotation about the N-N bond in this class of compounds has not yet been reported.

Our  $\Delta G_c^\ddagger$  - values evaluated from the <sup>1</sup>H-NMR methyl signals (see table) indicate that the rate of rotation in enamines 1, 2, 3, 4 <sup>5)</sup>, and 5 depends upon the electron-attracting properties of the substituents. In 6 and 7 <sup>6)</sup> the benzo ring reduces the rotational barriers by 2 - 3 kcal mole<sup>-1</sup> as compared to 8 and 9. A formyl group raises the free enthalpies of activation by 3 - 4 kcal mole<sup>-1</sup>, as can be seen in the table by comparing 6 to 7, 8 to 9, and 9 to 10. If one of the N-methyl groups is replaced by another substituent, rotational isomers are possible. It will be difficult to separate <sup>7)</sup> such

		Solvent	$\tau_1, \tau_2$	$T_c$ (°C)	$\Delta G_c^\ddagger$ (kcal mole <sup>-1</sup> )
<u>1</u>		d <sub>6</sub> -Acetone		<-55	< 12 <sup>9)</sup>
<u>2</u>		CHCl <sub>3</sub>	6.9, 7.2 -40°	0	139 <sup>3)</sup>
<u>3</u>		CDBr <sub>3</sub>	6.71, 7.06 0°	+52	165
<u>4</u>		CDBr <sub>3</sub>	6.59, 6.70 +35°, w 15	+52.5	17.3
<u>5</u>		CDBr <sub>3</sub>	6.64, 6.71 +35°, w 10	+60	18.0
<u>6</u>		d <sub>6</sub> -Acetone	6.74, 6.85 -65°	-55.5	10.4
<u>7</u>		Pyridine/ CHCl <sub>3</sub>	6.96, 7.09 -45°	+ 7	14.7
<u>8</u>		d <sub>6</sub> -Acetone	6.79, 6.92 -55°	-16.5	13.4

		Solvent	$\tau_1, \tau_2$	$T_c$ (°C)	$\Delta G_c^\ddagger$ (kcal mole <sup>-1</sup> )
<u>9</u>		Cyclohexanone	6.58, 6.72 +35°, w 2.2	+48.5	17.0
<u>10</u>		Cyclohexanone	6.44, 6.56 +35°	+106	20.2
<u>11</u>		(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O	6.6, 7.5 +80°	+160	21.5
<u>12</u>		CD <sub>3</sub> OD		<-65	<11 <sup>8)</sup>
<u>13</u>		d <sub>6</sub> -Acetone	6.22, 6.54 -55°	-39	11.8

$\tau_1, \tau_2$ : Chemical shifts of the two N-methyl groups when rotation is slow

$T_c$ : Coalescence temperature, at 60 Mcps

$\Delta G_c^\ddagger$ : Free enthalpy of activation at  $T_c$ . Errors vary from  $\pm 0.1$  to  $\pm 0.3$  kcal mole<sup>-1</sup>.

w 1.5: Line widths at this temperature are increased to 1.5 cps by the rotation process.

isomers even in systems like 10 or 11, since the  $\Delta G_c^\ddagger$  - values for the isomerization are expected to be only 20.2 or 21.5 kcal mole<sup>-1</sup>. Neither 12 nor the N,N-dimethylhydrazones of p-nitrobenzaldehyde and benzophenone show significant broadening of the average methyl signal above -65°. However,  $\Delta G_c^\ddagger$  for the formylated hydrazone 13 can be measured and is 5.2 kcal mole<sup>-1</sup> lower than the barrier for the corresponding enamine 9. From this result we conclude that the dipolar structure B contributes more to the ground state of enamines than D to the ground state of hydrazones. 12 is gradually decomposed in CD<sub>3</sub>OD/CDCl<sub>3</sub> (3:1) at 60°; under these conditions one ring proton of 6 is exchanged for deuterium (half-life ~ 100 hr), whereas two deuterons are introduced into the ring of 8 (half-life ~ 4 hr), further deuteration of 8 being slow. Apparently electrophilic substitution is favoured in these enamines in comparison to the less polar, diene-like hydrazone. The positions of the deuterium atoms have not yet been established.

The cis-trans relationships given in the table for the C=C bond in the enamines and the C=N bond in hydrazone 13 are not strictly proven in all cases. Isomerization at these "double" bonds proceeds more slowly than the above described rotation about the =C-N and =N-N "single" bonds in enamines and hydrazones. This is shown by the formyl protons of 10 differing in their chemical shifts up to +185° ( $\Delta G_c^\ddagger > 25$  kcal mole<sup>-1</sup>) and by the absorption of the ring protons in 12 resulting in an ABCD spectrum up to at least +150° ( $\Delta G_c^\ddagger > 22$  kcal mole<sup>-1</sup>).

Helpful discussions with Professor H.A. Staab are gratefully acknowledged. We also thank Miss A. Mattheus for experimental assistance.

- 1) Part IV of the series "Protonenresonanz-Untersuchungen zur inneren Rotation". Part III: A.Manschreck, A.Mattheus, and G.Rissmann, J.Mol. Spectroscopy, accepted for publication. Part II: Reference 7).
- 2) See, for example, K.Hafner, K.H.Vöpel, G.Ploss, and C.König, Liebigs Ann. Chem. 661, 52 (1963).
- 3) H.E.A.Kramer and R.Gompper, Z.Physik.Chem. (Frankfurt/M) 43, 292 (1964) and personal communication.
- 4) K.Hafner, G.Schulz, and K.Wagner, Liebigs Ann.Chem. 678, 39 (1964).
- 5) 4 and 11 were kindly provided by Dr.Mondelli, Milano. Cf. R.Mondelli and L.Merlini, Gazz.Chim.Ital. 95, 1371 (1965).
- 6) M.p. 6: 90 - 91°; 7: 160°. U.V. 6: 350 m $\mu$  (log  $\epsilon$  = 4.36), 282 (4.22), 277 (4.23), n-hexane; 7: 393 m $\mu$  (log  $\epsilon$  = 4.48), 254 (4.32), CCl<sub>4</sub>.
- 7) A.Manschreck, Tetrahedron Letters 1965, 1341.
- 8) Calculated assuming  $\tau_2 - \tau_1 = 0.20$  at a temperature below -55°.