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Barriers to Internal Rotation in 1-(*N*,*N*-Dimethylthiocarbamoyl)pyrazoles. Hammett Correlation and Complete Lineshape Study

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The barriers to rotation of the dimethylamino group in twelve 1-(*N*,*N*-dimethylthiocarbamoyl)pyrazoles have been determined by the NMR technique at the coalescence temperature. For one of the compounds the rate constant has been determined at 15 temperatures in an interval of 40 degrees by the complete lineshape method, and the entropy and enthalpy of activation have been calculated. A good correlation between rate constants and Hammett σ_p-values is observed for one of the series of compounds investigated, with a ϱ value of -1.98.

It has not been possible to determine the barrier to internal rotation around the C–N bond in tetramethylurea,[1] tetramethylthiourea, or tetramethylselenourea [2,3] by NMR methods, since these barriers are very low. Tetramethylselenourea gives one resonance signal down to -120°C.[2]

The low barriers depend partly on the strong electron donating effect of the dimethylamino group.[4] This is supported by results obtained in investigations of thiourea derivatives in which one of the nitrogen atoms carries a substituent with conjugating capacity. Sandström,[4] determined a $\Delta G^{\ddagger}$ value of 16.1 kcal/mol for the rotation of the dimethylamino group in *N*,*N*-dimethyl-*N'*-acetylthiourea. Siddall and Stewart,[5] and Sandström [4] report $\Delta G^{\ddagger}$ values of 10.7 and 11.5 kcal/mol, respectively, for the rotation in *N*,*N*-dimethyl-*N'*-phenylthiourea. Isaksson and Sandström [3] have modified the conjugating capacity of the phenyl group by introducing nine different substituents in the *para* position of the phenyl ring in *N*,*N*-dimethyl-*N'*-phenylthiourea. They found a good Hammett correlation with a ϱ value of -1.04, which supports the picture of a barrier increasing conjugation between the phenyl ring and its thiourea nitrogen atom.

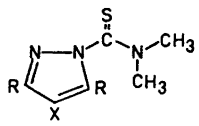
Anet and Osyany [6] found a $\Delta G^{\ddagger}$ value of 16.4 kcal/mol for the dimethylamino rotation in 1-(*N*,*N*-dimethylcarbamoyl)aziridine. In this case the ring

nitrogen atom is sp^3 hybridized, and consequently conjugation between this atom and the carbonyl group is unimportant compared to the competing conjugation with the dimethylamino group.

Not only electronic but also steric effects seem to lower the barriers to rotation in tetramethylurea and tetramethylthiourea. Zvonkova *et al.*[7] have shown that the NC(=X)N group in these two compounds cannot be planar, and this steric effect will lower the barrier by raising the energy of the initial state. In the transition state for the rotation of one of the dimethylamino groups, the other can turn into a position with more effective conjugation than is possible in the ground state, which lowers the energy of the transition state and consequently the barrier.[2,5]

In this investigation, one of the urea-nitrogen atoms is incorporated in a heteroaromatic ring, the pyrazole ring, in which the nitrogen atom contributes two electrons to the 6 π-electron system. The electronic properties of the pyrazole ring have been modified by the introduction of various substituents in position 4.

The combination of the electron-releasing capacity of the 4-pyrazolyl group [8–11] and the well-known sensitivity of the thiocarbonyl group to the electronic and steric properties of substituents [12] made an NMR-investigation of a series of 1-(*N*,*N*-dimethylthiocarbamoyl)pyrazoles interesting.



I, R=H
a, X=H
b, X=Br
c, X=NO_2

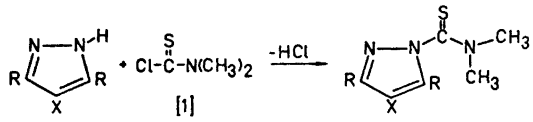
II, R=CH_3
a, X=CH_3
b, X=H
c, X=Cl
d, X=Br
e, X=I
f, X=$CO_2C_2H_5$
g, X=NO_2

III, R=$C(CH_3)_3$
X=H

IV, R=C_6H_5
X=Br

PREPARATIVE PART

The 1-(*N*,*N*-dimethylthiocarbamoyl)pyrazoles were prepared by reacting equimolar amounts of *N*,*N*-dimethylthiocarbamoyl chloride [1] and the appropriate pyrazole in dry benzene for 15 h at reflux temperature.



Hydrogen chloride was evolved during the reaction. Compounds I b–c, II a–g, III, and IV crystallized from the evaporated reaction mixture and were purified by recrystallisation from ligroin (80–110°), benzene-ligroin, or ligroin-ethyl ether mixtures. Compounds I b, II c, and II f were chromatographed on a silica gel column. I a was distilled at reduced pressure. Preparative and analytical results are summarized in Tables 1–2.

NMR SPECTRA AND EVALUATION OF RATE CONSTANTS

The NMR spectra were recorded on a Varian A-60 spectrometer, equipped with a Varian V-6031 variable temperature probe and a V-6040 temperature controller. The spectra were recorded on 10 % solutions of the compounds in *o*-dichlorobenzene (ODC),

Table 1. Analytical data of compounds I–IV.

Compound	B.p. or m.p. °C, n_D^{20}	Yield %	Solvent for recrystallization
I a [a]	142–146/18 mm, 1.6065	42	
b	46–47 [b,c]	74	Ligroin (80–110°)
c	101–102	38	Ligroin-ether, 4:1
II a	88–89	64	Ligroin
b	58–59 [d]	40	Ligroin
c	61–62	70	Ligroin
d	88–89 [e]	88	Ligroin
e	109–110 [b]	85	Ligroin
f	89–90 [b]	60	Ligroin-benzene, 3:1
g	96–97	40	Ligroin-ether, 4:1
III	137–138	45	Ligroin
IV	160–161	71	Ligroin

For preparation of the N-unsubstituted pyrazoles, see Ref. 18 (I and II), Ref. 35 (III), and Ref. 36 (IV).

[a] Lit.[34] $n_D^{25}=1.6055$, b.p. 99–101/1.5 mm.

[b] Before analysis chromatographed on silica gel column (100–200 mesh) using benzene as eluent.

[c] Lit.[34] 43–44°.

[d] Lit.[33] 59–60°.

[e] For preparation, see Ref. 18.

Table 2. Elemental analyses of compounds I–IV.

Compound	Calculated						Found				
	M	C	H	N	S	Hal.	C	H	N	S	Hal.
Ia, $C_6H_9N_3S$	155.23	46.4	5.84	27.1	20.7		46.7	6.03	27.0	20.3	
b, $C_6H_8BrN_3S$	234.14	30.8	3.44	18.0	13.7	34.1	31.0	3.53	17.8	13.9	34.6
c, $C_6H_8N_4O_2S$	200.23	36.0	4.03	28.0	16.0		36.3	4.17	27.9	16.2	
IIa, $C_9H_{15}N_3S$	197.31	54.8	7.66	21.3	16.3		54.8	7.79	21.2	16.6	
b, $C_8H_{13}N_3S$	183.26	52.3	7.24	22.9	17.5		52.3	7.28	22.9	17.3	
c, $C_8H_{12}ClN_3S$	217.73	44.1	5.56	19.3	14.7	16.3	44.2	5.71	19.5	14.5	16.7
e, $C_8H_{12}IN_3S$	309.16	31.1	3.91	13.6	10.4	41.1	31.4	4.14	13.5	10.9	41.1
f, $C_{11}H_{17}N_3O_2S$	255.37	51.7	6.72	16.5	12.6		51.8	6.87	16.5	12.8	
g, $C_8H_{12}N_4O_2S$	228.28	42.1	5.30	24.6	14.1		42.4	5.45	24.5	13.9	
III, $C_{14}H_{25}N_3S$	267.44	62.9	9.42	15.7	12.0		62.4	9.43	15.7	11.3	
IV, $C_{18}H_{16}BrN_3S$	386.33	56.0	4.17	10.9	8.30	20.7	56.0	4.30	10.9	8.30	20.9

at a temperature where no exchange effects were noticeable. For comparison, some NMR spectra were recorded in deuterochloroform and benzene solutions. NMR data for the compounds investigated are found in Table 3. ODC was used as solvent for several reasons. It has good solvent characteristics, high boiling point and low freezing point (spectra were recorded in a temperature interval of about 190°). Furthermore, it gives an AA'BB' spectrum with sharp lines, which are convenient when adjusting the resolution of the instrument.

The barriers were determined as free energies of activation, $\Delta G^{\ddagger}$, at the coalescence temperature, using the Eyring equation and calculating the rate constant k_c by the expression of Gutowsky and Holm:[13]

$$k_c = \frac{1}{2\tau} = \frac{\pi \Delta \nu_0}{\sqrt{2}} \quad (1)$$

The barrier to rotation for II d (10 % solution in ODC) was determined by means of the complete lineshape method on a Varian A-60 A instrument. The spectra were recorded at 15 different temperatures in a temperature interval of 40 degrees. At each temperature three spectra were automatically digitized and transferred to a punched tape. The transverse relaxation time was obtained from eqn. (2):

$$T_2 = \frac{1}{(W_1 + \Delta W_{ref})\pi} \quad (2)$$

W_1 is the line width of the reference TMS at a temperature below that at which exchange effects are noticed. ΔW_{1ef} is the change in line width due to changes in viscosity and magnet homogenity (note that the formula in Ref. 2 is in error by a factor of 2).

The calculated value of T_2, approximate estimates of the mean lifetime 2τ, the non-exchanging chemical shift $\Delta \nu_0$, and the digitized lineshapes were used as input data for a UNIVAC 1108 computer. The best values for τ and $\Delta \nu_0$ were found by the computer by means of the STEPIT procedure.[14] From $\Delta \nu_0$ values below the coalescence temperature suitable values were calculated for higher temperatures. With the τ-values determined by the computer, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the rotation were obtained by plotting $\log 1/2\tau T$ *vs.* $1/T$ according to the Eyring equation in the form (3):

$$\log \frac{1}{2\tau T} = -\frac{\Delta H^{\ddagger} \log e}{RT} + \frac{\Delta S^{\ddagger} \log e}{R} + \log \frac{k_B}{h} \quad (3)$$

All parameters for II d are found in Table 5. The $\Delta G^{\ddagger}$ value obtained by this method agrees well with the value obtained by the approximate method at the coalescence temperature. A discussion of different sources of error in the application of the complete lineshape method for the evaluation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is found in Ref. 30. Small systematic errors in $\Delta \nu_0$ and T_2 may cause serious errors especially in $\Delta S^{\ddagger}$ values.

The temperatures were measured as described in Ref. 3.

DISCUSSIONS OF CHEMICAL SHIFTS, COUPLING CONSTANTS AND CONFORMATIONS

The chemical shifts and coupling constants are given in Table 3. The NMR spectrum of 1-(*N*,*N*-dimethylthiocarbamoyl)pyrazole consists of three well separated quartets in the aromatic region. Earlier investigations of 1-acylpyrazoles,[15-16] 1-carbamoylpyrazoles,[17] and 1,1′-thiocarbonyl-bispyrazoles[18] have provided the following ranges for the interproton coupling constants: $J_{34} = 1.3 - 1.6$ Hz, $J_{35} = 0.6 - 0.7$ Hz, and $J_{45} = 2.5 - 3.0$ Hz in these systems. Using these constants, the high field resonance at 3.78 τ is assigned to hydrogen 4. This is in agreement with the fact that the electron density is theoretically found to be highest in position 4 in the pyrazole ring.[31] The 3 and 5 hydrogen resonances occur at 2.45 τ and 1.72 τ, respectively. Compounds I b – c both show two doublets with a splitting of 0.7 Hz. The chemical shifts of the ring methyl and *t*-butyl hydrogens in compounds II a – g and III are assumed to fall in the same order as those of the ring hydrogens, that is the 3-methyl and *t*-butyl hydrogens at higher field than the 5-methyl and *t*-butyl hydrogens.

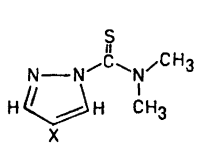
Table 3. Chemical shifts (τ-values) and coupling constants for 1-(*N*,*N*-dimethylthiocarbamoyl)pyrazoles.

Compound	Solvent	Position 3	4	5	N-CH_3 (*trans*)	N-CH_3 (*cis*)
Ia[a]	ODC	2.45r[c]	3.78r	1.72r	6.91	6.74
b[b]	ODC	2.48r		1.70r	6.94	6.77
c[c]	ODC	2.67r		2.08r	7.00	6.80
IIa	ODC	7.90m[d]	8.25m	7.67m	7.09	6.72
b	$CDCl_3$				6.95	6.52
b	ODC	7.85m	4.25r	7.63m	7.12	6.72
b	C_6H_6				7.40	6.95
c	ODC	7.87m		7.65m	7.13	6.73
d	ODC	7.85m		7.63m	7.15	6.73
e	ODC	7.83m		7.58m	7.15	6.71
f[e]	ODC	7.58m		7.38m	7.20	6.70
g	ODC	7.57m		7.37m	7.20	6.70
III	$CDCl_3$				7.23	6.52
	C_6H_6				7.67	7.02
	ODC	8.73*t*[f]	3.98r	8.60*t*	7.33	6.73
IV	ODC				7.12	6.82

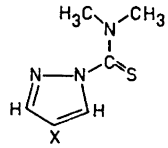
[a] $J_{35}=0.7$ Hz, $J_{34}=1.6$ Hz, $J_{45}=2.7$ Hz.
[b] $J_{35}=0.7$ Hz.
[c] r=ring hydrogen.
[d] m=methyl hydrogens.
[e] τ-CH_3=8.75, τ-CH_2=5.80.
[f] *t*=*tert.* butyl hydrogens.

The difference in shielding between positions 3 and 5 probably depends in part on the magnetic anisotropy of the lone pair on the pyridine-type nitrogen atom of the pyrazole ring and that of the thiocarbonyl group.

Molecular models show that there are two possible planar or nearly planar conformations of compounds I a–c namely [2] and [3]:



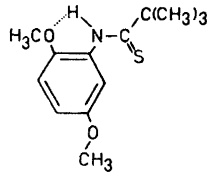
[2]



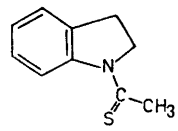
[3]

The most probable of these is conformation [2]. Support for this choice may be found in the work of Rae[19] and Nagarajan and Nair,[20] who studied the deshielding effect of the thiocarbonyl group in compounds [4] and [5]. Rae[19] investigated the NMR spectrum of 2,5-dimethoxythiopivalanilide [4], in which the phenyl ring is forced into the thioamide plane by hydrogen bonding between NH and the oxygen atom in the methoxy group. In this molecule hydrogen 6 is deshielded by about 2.3 ppm compared to the other ring hy-

drogens. Nagarajan and Nair[20] found that the aromatic *ortho* hydrogen in thioacetylindoline [5] is deshielded by about 2.2 ppm compared to the other ring hydrogens.



[4]



[5]

These results make conformation [2] most probable for the 1-(*N*,*N*-dimethylthiocarbamoyl)pyrazoles, since hydrogen 5 in this case is deshielded by only 0.7 – 0.8 ppm compared to hydrogen 3.

In assigning signals to the *N*-methyl hydrogens the solvent dependence of the signals is of no assistance, as the shift between the signals is not affected by changing solvent from deuterochloroform to benzene. The generally held view is that the resonance of the *N*-methyl hydrogen atoms *trans* to the carbonyl oxygen or sulphur in amides and thioamides is shifted farther upfield than that of the *cis* hydrogen atoms on changing from a nonaromatic to an aromatic solvent.[21]

The difference in chemical shift between the *N*-methyl hydrogens in compound I a is 10.4 Hz, in compound II b 24.4 Hz, and in III 36.6 Hz. These differences have been helpful in assigning signals to the *N*-methyl hydrogens. A planar conformation is impossible for compound II b since the 5-methyl group would then interact too strongly with the *N*-methyl group *trans* to the thiocarbonyl sulphur. The dihedral angle between the pyrazole ring and the thiocarbamoyl group increases to relieve steric hindrance, and the *N*-methyl group *trans* to the thiocarbonyl sulphur will consequently be placed in a region shielded by the ring current in the pyrazole ring. Table 3 shows that the *N*-methyl resonances for I a occur at 6.74 τ and 6.91 τ, for II b at 6.72 τ and 7.12 τ and for III at 6.73 τ and 7.33 τ. The resonance for one of the *N*-methyl groups is not affected by substitution in positions 3 and 5 on the pyrazole ring, whereas the other *N*-methyl resonance signal is shifted 0.2 and 0.4 ppm, respectively, towards higher field. The *N*-methyl signal most sensitive to substitution, that is the one at highest field, is consequently assigned to the methyl group *trans* to the thiocarbonyl group. Jackman *et al.*[22] found a similar increase in chemical shift between the two *N*-methyl signals in dimethylbenzamides on the introduction of an *ortho* substituent. They suggest this may depend on an increase in dihedral angle between the aromatic ring and the carbonyl group that takes place on substitution.

BARRIERS AND HAMMETT CORRELATIONS

The rate constants and free energies of activation for the rotations are given in Table 4.

Table 4. Coalescence data for compounds I, II, III and IV in 10 % solutions in ODC.

Compound	$\Delta\nu_0$ Hz	T_c K	$\Delta G^{\ddagger}_{T_c}$ kcal/mol	$\Delta G^{\ddagger}_{300\ K}$	log k^a
Ia	10.4	293.2	15.3	15.3	1.64
b	10.2	295.2	15.4	15.4	1.57
c	12.4	312.1	16.3	16.2	0.986
IIa	22.2	329.4	16.8	16.6	0.695
b	24.4	336.9	17.1	16.9	0.476
c	23.6	339.2	17.3	17.0	0.403
d	24.8	341.6	17.4	17.1	0.330
e	26.4	346.8	17.6	17.3	0.184
f	29.4	370.3	18.8	18.3	−0.545
g	29.4	389.6	19.8	19.2	−1.20
III	36.6	437.0	22.1	21.2	−2.66
IV	18.5	340.6	17.5	17.2	0.257

[a] Recalculated to 300 K using the Eyring equation and $\Delta S^{\ddagger} = -6.5$ e.u.

Table 5. Results from a complete lineshape treatment of I d in a 10 % solution in ODC.

T K	$\Delta\nu_0$ Hz	T_2 sec	τ sec	$\Delta G^{\ddagger}$ kcal/mol
315.5	25.2	0.374	0.0624	17.2
318.2	25.3	0.354	0.0547	17.3
322.6	25.2	0.374	0.0393	17.3
326.7	24.9	0.354	0.0302	17.4
329.1	25.1	0.354	0.0247	17.4
332.4	25.1	0.354	0.0191	17.4
335.3	25.0	0.374	0.0156	17.4
338.2	25.0	0.354	0.0123	17.4
341.4	24.9	0.374	0.00974	17.4
343.4	24.9	0.354	0.00831	17.4
346.8	24.8	0.374	0.00683	17.4
350.2	24.8	0.374	0.00537	17.4
352.9	24.8	0.374	0.00456	17.5
355.9	24.7	0.374	0.00381	17.5
359.3	24.7	0.374	0.00300	17.5

$\Delta H^{\ddagger} = 15.2 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -6.5 \pm 0.7$ e.u. The errors are standard deviations from the least-squares plot.

The Hammett equation has been used with varying success in relating and systematising side-chain reactivities of heterocyclic compounds.[23–24] Hüttel and Kratzer [25] obtained good linear relations between the logarithms of the rate constants for the hydrolysis of 1-acylpyrazoles and σ_p values for substituents in position 4. Carlsson and Sandström [11] used Hammett's σ values to choose between two possible mechanisms for the ethanolysis of 1,1′-thiocarbonyl-bis-pyrazoles.

The rate constants for compounds II a – g at 300 K have been calculated from $\Delta G^{\ddagger}$ values at the coalescence temperature, and the $\Delta S^{\ddagger}$ value determined

for II d using the Eyring eqn. (3). A linear correlation was obtained between log k and σ_p with a correlation coefficient of 0.96 and the reaction constant $\varrho = -1.98$. The σ_p values were taken from Jaffé.[26]

The Hammett relation can be used as the two methyl groups in positions 3 and 5 are constant in the series. An optimistic calculation on I a–c gives $\varrho = -0.88$, with the correlation coefficient 0.98. From the data by Jackman *et al.*,[22] Korver *et al.*[27] calculate a reaction constant $\varrho = -1.15$ (298.2 K) for *p*-substituted dimethylbenzamides. Rotation in the benzene series is consequently less susceptible to substituent influence than in the pyrazole series.

As can be seen in Table 4, the barrier to rotation is 15.3 kcal/mol for I a, 16.9 kcal/mol for II b and 21.2 kcal/mol for III. (These values may be compared to the $\Delta G^{\ddagger}$ value for dimethylthioformamide in ODC, which is 24.1 kcal/mol.[28]) The difference between the three $\Delta G^{\ddagger}$ values can be understood as follows. In the initial state there is some resonance interaction between the pyrazole ring and the thiocarbamoyl group, stronger for I a than for II b and III, as the dihedral angle between the pyrazole ring and the thiocarbamoyl group increases in this order. This is supported by the changes in *N*-methyl shifts discussed above. In the transition state for the rotation, however, there is increased conjugation between pyrazole ring and thiocarbonyl group compared to the initial state, since the competing dimethylamino group is turned out of conjugation. This increase is larger for compound I a than for II b and III, since the angle dependence of the resonance stabilisation is assumed to be greater in the transition state than in the initial state.

CHEMICAL SHIFTS OF THE *N*-METHYL GROUPS

The difference in chemical shifts between the *N*-methyl hydrogens changes 2 Hz for compounds I but 7 Hz for compounds II on changing the 4-substituent from H to NO_2. Furthermore the $\Delta G^{\ddagger}$ values for internal rotation changes more in the series II than in the series I. The difference in chemical shift between the *N*-methyl hydrogens for compounds II a–g correlates with σ_p ($r = 0.92$) and log k ($r = 0.93$). This reflects the dependence of the $\Delta G^{\ddagger}$ values and the shift differences on the dihedral angle, a dependence which seems to be greater for compounds II than I. It is possible that the dihedral angle in compounds II increases with the –M effect of the substituent in position 4, since the interaction between the ring and the dimethylthiocarbamoyl group, which tends to restrict the dihedral angle, will decrease in the same direction. The angle dependence of the interaction energy is probably also in these molecules greater in the transition state than in the initial state, which should explain why $\Delta G^{\ddagger}$ increases more rapidly with increasing –M effect of the 4-substituent in compounds II than in compounds I, and it also explains the relations between chemical shifts and 4-substituents.

ENTROPY OF ACTIVATION

The entropy of activation for II d was determined to be -6.5 ± 0.7 e.u. by the complete lineshape method. The error is the standard deviation from a least-squares plot. Small positive entropies of activation are generally found

for the rotation around the carbon-to-nitrogen bond in amides and thioamides.[1,29,30] This is as expected, since the rotation results in a small decrease in polarity and thus in decreased order in the solvent, which should give a positive contribution to $\Delta S^{\ddagger}$.

A comparison of the NMR spectrum of an *N*,*N*-dimethylamide or thioamide in an aromatic solvent with that in a nonaromatic solvent usually shows that one of the *N*-methyl group resonances exhibits a greater upfield shift than the other. This has been explained by a specific interaction between the amide nitrogen and the π-electron system of the aromatic ring with the carbonyl oxygen or thiocarbonyl sulphur as far away from the aromatic ring as possible.[21] As can be seen from Table 3, a change in solvent from deuterochloroform to benzene or ODC results in an upfield shift of the same magnitude for both *N*-methyl signals. This probably indicates that the solvation is centered at the pyrazole ring, not at the thioamide group. In the transition state for the rotation, there is an increased interaction between the pyrazole ring and the thiocarbamoyl group, and this results in an increase in the dipole moment of the pyrazole ring, which is directed from N_1 towards N_2 and nearly parallell with the N–N bond.[31] This leads to an increase in dipole-induced dipole interactions, and thus in the order in the solvent cage on going to the transition state, which is reflected in a negative $\Delta S^{\ddagger}$ for the rotation.

Stilbs [32] determined the activation entropy for the dimethylaminorotation in 1,1-dimethyl-3-isopropylurea in equal volumes of dichlorofluoromethane and 3-fluorotoluene. The negative activation entropy obtained (-4.4 ± 1.0 e.u.) can be understood as the result of a solvation which is stronger in the transition state than in the initial state. This is the case if the solvation is centered at the $(CH_3)_2CHNH$ group, which acquires an increased positive charge in the transition state.

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