Conformation and Internal Rotation of Nitroanilines Detected by Complete Nuclear Magnetic Resonance Line Shape Analysis. IV. Decreasing Barrier to Internal Rotation with Increasing Steric Effects[1]

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Abstract: The kinetic parameters of the restricted internal rotation about the amino nitrogen-ring carbon bond in *N*-R-2,4,6-trinitroanilines with R = CH_2CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$ were determined in liquid dichloromethane at temperatures between +30 and −80° by comparison of measured and calculated complete nmr line shape functions. It was found that the barrier E_a decreases and the frequency of jumping over the barrier strongly increases with increasing size of R, in concert with the results of HMO calculations based on a simplified model which, however, describes numerous experimental data on the conformation and internal rotation of nitroanilines. Nitroanilines appear to be the only planar, or effectively planar, anilines with detected internal rotation around the Ar–N bond.

Restricted rotation about the Ar–N bond in certain ortho-substituted aniline derivatives was recognized in studies of their optical activity by Mills in 1937 and Adams in 1940.[2] Later by nmr line shape methods restricted rotation about the Ar–N bond was observed, and rotational barriers E_a were measured in *N*-alkylnitroanilines[1,3] and *o*-toluidines.[4–6] Whereas the latter compounds, which have been extensively investigated,[7] have a nonplanar ground-state conformation of the aniline with one N substituent above and the other below the ring plane, the only anilines with an effectively planar aniline framework and detected internal rotation appear to be the *N*-alkylnitroanilines.

Apparently few systematic studies on internal rotations within a class of related compounds have been performed employing complete nmr line shape analysis. As part of a systematic study, the conformation and internal rotation about the Ar–N amino bond in *N*-R-2,4,6-trinitroanilines with R = CH_2CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$ were investigated using complete nmr line shape analysis.

Experimental Section

Materials. The compounds I–III were prepared by adding alcoholic solutions of picryl chloride and the corresponding amine and were purified by repeated crystallization in ethanol.

Table I. Data on Compounds

Compound no.		Mp, °C	—Analysis, %— N_{calcd}	N_{found}
I	*N*-Ethyl-2,4,6-trinitroaniline[a]	83.0	21.87	21.47
II	*N*-Isopropyl-2,4,6-trinitroaniline[b]	106.5	20.74	20.66
III	*N*-*tert*-Butyl-2,4,6-trinitroaniline[c]	94.5	19.71	19.82

[a] P. van Romburgh, *Recl. Trav. Chim. Pays-Bas*, **2**, 105 (1883). [b] A. Mulder, *ibid.*, **25**, 116 (1906). [c] P. van Romburgh, *ibid.*, **4**, 193 (1885).

To avoid complications from the overlapping nmr peaks of the ring protons and the proton at the amino site, the latter proton was substituted by a deuteron by shaking solutions of I–III in CCl_4 with an excess of D_2O at room temperature. The intensities of the nmr lines and the lack of spin-spin coupling proved that the deuteration was complete (>95%).

The solvent for the nmr samples was CH_2Cl_2 (Merck, Uvasol) which had been distilled twice over P_2O_5 and then twice over anhydrous K_2CO_3. It was chosen because it is relatively inert, has only one nmr peak, outside of the resonances of I–III, and grants a sufficient solubility of the compounds also at low temperatures. Above all, a direct comparison with previous nmr data on polynitroanilines[1,3] is possible. The solutions were prepared in nmr sample tubes, degassed thoroughly (six times at 10^{-5} Torr), and sealed *in vacuo*.

Apparatus and Measurement Technique. The 60-MHz pmr spectra were recorded with a Varian A-60 spectrometer equipped with a V-6031 variable-temperature probe and a V-6040 variable-temperature controller. A linear sweep rate of 0.1 Hz/sec both in upfield and downfield directions, a low amplitude of the rf field H_1, and the side-band technique were used to record and calibrate the spectra. Temperatures were obtained from the chemical shift of a standard methanol probe. The temperature dependence of the CH_3OH shift had been determined by a calibrated thermocouple. In view of the problems of measuring the temperature in the probe[8,9] it should be noted that the unchanged procedure of measuring and calibrating the sample temperature as well as all other unchanged experimental techniques provide that at least the relative order of activation energies and frequency factors including the approximate differences in these numbers are real within the whole

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(1) For part III, see J. v. Jouanne and J. Heidberg, *Ber. Bunsenges. Phys. Chem.*, **75**, 261 (1971).

(2) W. H. Mills and R. M. Kelham, *J. Chem. Soc.*, 274 (1937); R. Adams and L. J. Dankert, *J. Amer. Chem. Soc.*, **62**, 2191 (1940), and later papers.

(3) J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

(4) T. H. Siddall and C. A. Prohaska, *J. Amer. Chem. Soc.*, 88, 1172 (1966).

(5) B. J. Price, J. A. Eggleston, and I. O. Sutherland, *J. Chem. Soc. B*, 922 (1967).

(6) Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, **89**, 4910 (1967); A. Mannschreck and H. Muensch, *Tetrahedron Lett.*, 28, 3227 (1968).

(7) See, *e.g.*, L. W. Reeves, *Advan. Phys. Org. Chem.*, **3**, 187 (1965); G. Binsch, *Top. Stereochem.*, **3**, 97 (1968); T. H. Siddall and W. E. Stewart, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 33 (1969). H. Kessler, *Angew. Chem.*, **82**, 237 (1970); F. A. L. Anet and R. Anet in "Determination of Organic Structures by Physical Methods," Vol. 3, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, p 343; I. O, Sutherland, *Annu. Rep. Nucl. Magn. Resonance Spectrosc.*, **4**, 71 (1971).

(8) T. Drakenberg, K.-I. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, **24**, 694 (1970).

(9) A. L. Van Geet, *Anal. Chem.*, 40, 2227 (1968).

Table II. 60-MHz Pmr Spectra of *N*-Alkyl-2,4,6-trinitroanilines at 28.8 ± 0.5° [a]

Ia, *N*-Ethyl-2,4,6-trinitroaniline (concn 0.5 *M*)	
δ_{CH_3}	+237.03 ± 0.10
δ_{CH_2}	+130.18 ± 0.09
δ_{NH}	−220[b]
δ_{picryl}	−220.22 ± 0.03
$J_{CH_3-CH_2}$	7.05 ± 0.07
J_{NH-CH_2}	4.87 ± 0.06
Ib, *N*-Deuterio-*N*-ethyl-2,4,6-trinitroaniline (concn 0.36 *M*)	
δ_{CH_3}	+237.22 ± 0.04
δ_{CH_2}	+130.33 ± 0.18
δ_{picryl}	−220.55 ± 0.10
$J_{CH_3-CH_2}$	7.09 ± 0.04
IIa, *N*-Isopropyl-2,4,6-trinitroaniline (concn 0.57 *M*)	
$\delta_{(CH_3)_2}$	+242.01 ± 0.08
δ_{CH}	*c*
δ_{NH}	−219[b]
δ_{picryl}	−218.67 ± 0.17
$J_{(CH_3)_2-CH}$	6.37 ± 0.05
J_{NH-CH}	*c*
IIb, *N*-Deuterio-*N*-isopropyl-2,4,6-trinitroaniline (concn 0.39 *M*)	
$\delta_{(CH_3)_2}$	+242.44 ± 0.03
δ_{CH}	*c*
δ_{picryl}	−219.10 ± 0.04
$J_{(CH_3)_2-CH}$	6.20 ± 0.05
IIIa, *N*-*tert*-Butyl-2,4,6-trinitroaniline (concn 0.5 *M*)	
$\delta_{(CH_3)_3}$	+237.96 ± 0.06
δ_{NH}	−218[b]
δ_{picryl}	−217.93 ± 0.08
IIIb, *N*-Deuterio-*N*-*tert*-butyl-2,4,6-trinitroaniline (concn 0.15 *M*)	
$\delta_{(CH_3)_3}$	+237.99 ± 0.04
δ_{picryl}	−218.62 ± 0.15

[a] Chemical shifts, δ, and coupling constants, J_{ij}, are given in Hz and + and − refer to an upfield and downfield shift with respect to the CH_2Cl_2 solvent line. [b] The very broad and barely detectable NH peak and the A_2 spectrum of the picryl protons overlap. [c] The low concentration of the samples and the high splitting prevented detection of the peaks.

Table III. Line Widths (*W*), Relative Chemical Shifts (2δ), and Coupling Constants (*J*) of A_2 ($T \approx +30°$) and AB ($T \approx -80°$) Spectra of Picryl Protons

Compound no.		A_2	AB		
		W, Hz	2δ, Hz	*J*, Hz	*W*, Hz
I	*N*-Deuterio-*N*-ethyl-2,4,6-trinitroaniline	0.51 ± 0.03	27.22 ± 0.08	2.80 ± 0.04	0.50 ± 0.04
II	*N*-Deuterio-*N*-isopropyl-2,4,6-trinitroaniline	0.50 ± 0.04	30.80 ± 0.10	2.80 ± 0.06	0.8[a]
III	*N*-Deuterio-*N*-*tert*-butyl-2,4,6-trinitroaniline	0.76 ± 0.04	(32.2)[b]	*b*	*b*

[a] Still exchange broadening at the low-temperature limit of the apparatus (∼−85°). [b] The A_2 spectrum remained unchanged down to −70° even with a slight decrease of the line width of the single peak. 2δ is estimated from the A_2 peak position (see Discussion).

class of *N*-alkylpicramides with unbranched[1,3] and branched alkyl groups.

Analysis of Spectra. Besides the coalescing AB quartet of the picryl protons the pmr spectra could be analyzed on the basis of first-order theory. The theoretical complete line shape function for a coalescing AB quartet is given by the expression[3]

$$v(\omega,\tau) = C\left(\frac{r_+b_+ - sa_+}{a_+{}^2 + b_+{}^2} + \frac{r_-b_- - sa_-}{a_-{}^2 + b_-{}^2}\right) \qquad (1)$$

which is explained in detail in ref 3.

Determination of τ from Experimental Spectra. To determine the mean lifetime τ from the experimentally recorded line shapes the following procedure was chosen. By removing the electronic noise in the measured spectra by hand an idealized curve was obtained, from which in constant steps on the frequency scale the corresponding values of amplitudes were read. This set $\{a_i\}$ of amplitudes together with the frequencies were used as input parameters in a Fortran IV program. In this program the theoretical line-shape equation $v(\omega,\tau)$ was coded allowing variations of τ while treating δ, *J*, and T_2 as (constant) input parameters. For comparison of $v(\omega,\tau)$ and $\{a_i\}$ the parameter *C* was chosen to fit *v* and $\{a_i\}$ at the point of maximal experimental amplitude. While varying τ the function $F = \Sigma_i|v(\tau,\omega_i) - a_i|$ was minimized yielding the best τ value to fit the experimental and theoretical spectrum. It may be worthwhile to note that the usual manner to define *F* in quadratic terms was abandoned because in the case of relatively sharp peaks small errors in frequencies of the few points near the top of the peak may give an overwhelming contribution to the total value of *F*.

Results

The nmr line positions, chemical shifts, and spin-spin coupling constants of the compounds investigated are summarized in Table II.

At room temperature the line positions were nearly independent of the concentration (0.1–1 *M*) of the compounds. Lowering the temperature, slight but regular variations of the chemical shifts were observed. At −80° the picryl protons spectrum of all compounds is shifted downfield by *ca.* 3 Hz, while all alkyl peaks are shifted upfield where a maximal effect is observed for the α CH protons (*ca.* 8 Hz). At low temperatures the peaks of the alkyl protons broadened noticeably (by a factor of 2–3), whereas the coupling constants remained unchanged within experimental error.

The characteristics of the limiting A_2 and AB spectral types of the picryl protons are given in Table III. The AB spectrum of I could be observed from −60° down to −80° and within these limits no change of 2δ and/or *J* nor a change of *W* was found. The same was true for the low-temperature picryl protons AB spectra of various other N-substituted 2,4,6-trinitroanilines (see Table IV). Therefore it appears to be justified to use constant parameters 2δ, *J*, and *W* (T_2) in the evaluation of the mean lifetime τ from eq 1.

In Table V the τ values near the limiting A_2 and AB cases were omitted, because in these cases the line shapes become very insensitive to changes in τ, so that these values are not very reliable. It was found that in the region of coalescence the line shapes were independent of the concentration (0.1–0.6 *M*) of the compounds (Figure 1).

From the first-order rate constants $k = 1/\tau$ the Arrhenius parameters, $1/\tau = k = A\exp(-E_a/RT)$,

Table IV. Low-Temperature AB Spectra of Picryl Protons of *N*-R-2,4,6-Trinitroanilines Dissolved in CH_2Cl_2 Relative Chemical Shifts 2δ and Coupling Constants *J*

R	2δ, Hz	*J*, Hz
CH_3[a]	26.7	2.7
n-C_3H_7[b]	27.05 ± 0.10	2.80 ± 0.03
n-C_4H_9[b]	26.95 ± 0.06	2.80 ± 0.05
n-C_5H_{11}	26.94 ± 0.15	2.77 ± 0.08
n-C_6H_{13}[b]	27.00 ± 0.05	2.80 ± 0.04
n-C_8H_{17}[b]	26.98 ± 0.08	2.80 ± 0.06
n-$C_{12}H_{25}$	27.10 ± 0.15	2.79 ± 0.05
n-$C_{13}H_{27}$	27.10 ± 0.10	2.80 ± 0.05
n-$C_{15}H_{31}$[c]	27.15	2.80
n-$C_{18}H_{37}$[c]	27.15	2.80
$CH(CH_3)CH_2CH_3$[d]	32.35 ± 0.12	2.82 ± 0.02
$CH(CH_3)(CH_2)_5CH_3$[d]	32.85	2.80
$C(CH_3)_2(CH_2)_2CH(CH_3)_2$[e]		
c-C_6H_{11}	31.87 ± 0.15	2.79 ± 0.03
$CH_2C_6H_5$	26.02 ± 0.07	2.79 ± 0.06
CH_2CH_2COOH	25.16 ± 0.10	2.78 ± 0.03
$N(C_6H_5)_2$[a]	40.86	2.75

[a] For a detailed discussion see paper I.[3] [b] For a detailed discussion see paper III.[1] [c] Low solubility at −60 to −80° prevented very accurate measurements. [d] Still exchange broadening at −80°. [e] Single peak at −80°.

were calculated by the method of least squares. From the rate constants at 298.2 and 193.2°K, calculated from the Arrhenius equation, the thermodynamic quantities of activation at standard temperature and at the low-temperature limit of measurements were obtained by the Eyring equations.

Because for *N*-deuterio-*N*-*tert*-butyl-2,4,6-trinitroaniline the line shape of the picryl protons did not change upon lowering the temperature to the limit of measurements, one may assume from the single narrow peak that $\tau \leq 10^{-5}$ sec at −65°, yielding $E_a \leq 10$ kcal/mol if $\log A = 15.5$ (Figure 2).

Discussion

Data on the Conformation. While in the aniline molecule (in the gaseous state) the amino nitrogen has a pyramidal structure analogoes to NH_3, as derived from uv[10] and microwave[11] spectra, nitrobenzene is planar in the crystal.[12] The crystal data on 1,3-diamino- and 1,3,5-triamino-2,4,6-trinitrobenzene[13,14] show that the molecule is approximately planar with strong hydrogen bonds between adjacent NH_2 and NO_2 groups and that the benzene ring is distorted such as to relieve the overcrowding of the planar configuration. This supports the assumption that, partly due to hydrogen bonding, picramide is a planar molecule also. In more seriously overcrowded trinitroanilines, however, the nitro groups are twisted.[15,16] Thus, variations

Table V. Temperature Dependence of Mean Lifetimes (τ) between Exchanges of Picryl Protons

T, °K	τ, sec			
	N-Deuterio-*N*-ethyl-2,4,6-trinitroaniline			
249.1	0.118×10^{-2}	0.111×10^{-2}		
241.7	0.207×10^{-2}	0.292×10^{-2}	0.255×10^{-2}	
236.2	0.406×10^{-2}	0.490×10^{-2}	0.540×10^{-2}	
233.5	0.630×10^{-2}	0.720×10^{-2}	0.660×10^{-2}	
227.5	0.126×10^{-1}	0.133×10^{-1}		
224.5	0.272×10^{-1}	0.302×10^{-1}	0.179×10^{-1}	0.230×10^{-1}
219.0	0.470×10^{-1}	0.550×10^{-1}	0.430×10^{-1}	0.470×10^{-1}
213.4	0.114	0.157	0.128	0.157
208.4	0.348	0.340	0.369	0.318
	N-Deuterio-*N*-isopropyl-2,4,6-trinitroaniline			
250.4	0.490×10^{-4}	0.530×10^{-4}		
242.3	0.141×10^{-3}	0.185×10^{-3}	0.137×10^{-3}	
236.4	0.414×10^{-3}	0.312×10^{-3}	0.262×10^{-3}	
233.3	0.560×10^{-3}	0.460×10^{-3}	0.530×10^{-3}	
227.8	0.860×10^{-3}	0.850×10^{-3}	0.820×10^{-3}	
218.9	0.300×10^{-2}	0.270×10^{-2}	0.300×10^{-2}	0.325×10^{-2}
214.4	0.505×10^{-2}	0.485×10^{-2}		
209.0	0.740×10^{-2}	0.780×10^{-2}	0.820×10^{-2}	0.108×10^{-1}
202.8	0.286×10^{-1}	0.295×10^{-1}		
199.1	0.480×10^{-1}	0.560×10^{-1}		
193.3	0.148	0.168	0.126	0.172
188.8	0.340	0.400	0.355	0.370

Table VI. Hindered Internal Rotation of *N*-Deuterio-*N*-R-2,4,6-trinitroanilines, Arrhenius Parameters and Thermodynamic Quantities of Activation

R	E_a, kcal/mol	Log *A*, A in sec^{-1}	$\Delta G^{\ddagger}$, kcal/mol		$\Delta H^{\ddagger}$, kcal/mol		$\Delta S^{\ddagger}$, cal/(deg mol)	
			298.2°K	193.2°K	298.2°K	193.2°K	298.2°K	193.2°K
CH_2CH_3	14.53 ± 0.24	15.76 ± 0.23	10.5	11.7	13.9	14.2	11.6	12.5
$CH(CH_3)_2$	13.08 ± 0.14	15.63 ± 0.14	9.2	10.4	12.5	12.7	11.0	11.9
$C(CH_3)_3$	(≤ 10)[a]	(15.5)[a]						

[a] E_a is estimated from the sharp A_2 spectrum at −65° of the picryl protons and a frequency factor $A = 3 \times 10^{15}$ sec^{-1}, which, in comparison with the frequency factor of the *n*-butyl compound,[1] is supposed to be an upper limit.

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(10) J. C. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectrosc.*, 20, 196 (1966).

(11) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).

(12) J. Trotter, *Acta Crystallogr.*, **12**, 884 (1959).

(13) J. R. Holden, *ibid.*, **22**, 545 (1967).

(14) H. H. Cady and A. C. Larson, *ibid.*, **18**, 485 (1965).

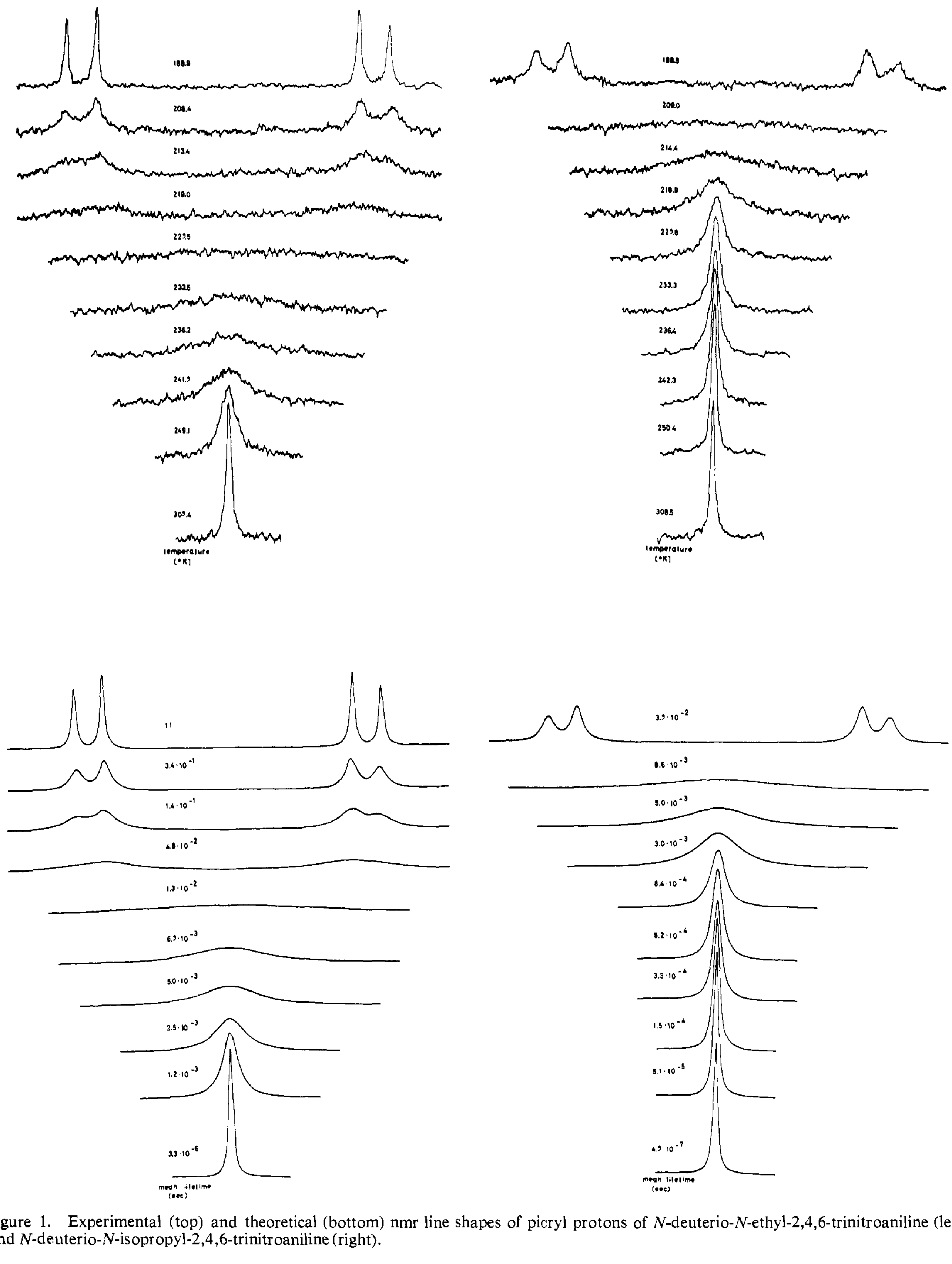

Figure 1. Experimental (top) and theoretical (bottom) nmr line shapes of picryl protons of *N*-deuterio-*N*-ethyl-2,4,6-trinitroaniline (left) and *N*-deuterio-*N*-isopropyl-2,4,6-trinitroaniline (right).

in the uv intensities of *N*-alkyl-2,4-6-trinitroanilines[17] are correlated to the rotation of one nitro group (2 or 6) out of coplanarity to the ring, yielding rotational angles of 66, 70, and 90° in the series of the *N*-methyl, *N*-ethyl, and *N*-isopropyl compounds, respectively. One may keep in mind, however, that especially for the *N*-isopropyl and *N*-*tert*-butyl compounds, a dis-

(15) C. Dickinson, J. M. Stewart, and J. R. Holden, *Acta Crystallogr.*, **21**, 663 (1966).

(16) M. J. Kamlet, R. R. Minesinger, J. C. Hoffsommer, J. C. Dacons, and H. G. Adolph, *J. Chem. Soc. B*, 1147 (1968).

(17) M. J. Kamlet, J. C. Hoffsommer, R. R. Minesinger, and H. G. Adolph, *J. Org. Chem.*, **33**, 3070 (1968).

tortion of the benzene ring[13,14] and perhaps a slight twist and subsequent pyramidal structure of the amino group are not out of question.

Chemical Shifts and Coupling Constants. In general chemical shifts and coupling constants, measured at room temperature, agree well with those reported for the same and related molecules.[2,3,18–20] An *ab initio* interpretation of these quantities will not be attempted here, but regularities and semiquantitive relations can be established.

Chemical Shifts of Ring Protons. For geometrical and symmetry reasons no direct effects of the *N*-alkyl groups can be responsible for the fact that the 3,5 ring protons in the *N*-alkylpicramides become inequivalent at low temperatures. Therefore it is suggested that in accordance with the above mentioned data, the inequivalence is caused by different orientations of the 2- and 6-nitro groups. Strong evidence for this comes from the correlation between the size of the alkyl group and the relative chemical shift 2δ of the ring protons. It is expected that the bulkier the alkyl group is the more the neighboring NO_2 group is rotated and consequently the larger 2δ is due to increasing differences in π-electron density and the effect of the magnetic anisotropy of the NO_2 groups on the 3,5 positions. Looking at Table IV an exact agreement between the sequence of increasing bulkiness of the alkyl groups and the sequence of increasing 2δ values is found while a remarkable constancy is observed for the *n*-alkyl compounds (n-C_xH_{2x+1}, $x = 3, \ldots, 18$), where a constant molecular overcrowding is expected. Consistent with this model is that at *ca.* −80° the low-field part of the picryl protons AB spectra of all branched and unbranched alkyl compounds (including the cyclohexyl and propionic and with slight variations the benzyl and diphenylamino compounds) is within the limits of ±0.5 Hz located at −239.5 and −236.7 Hz and only the high-field lines are shifted upfield with increasing bulkiness of the substituents. On this basis the relative AB shift of the *tert*-butyl compound may be estimated from the position of the unchanged A_2 spectrum, yielding a value of approximately 32.2 Hz.

With the assumption that in all picramides considered only the NO_2 group adjacent to the *N*-alkyl group is rotated while the 4 and 6 nitro groups and the amino group are coplanar to the ring, one may calculate 2δ using simple HMO theory and Yamaguchi's theory on the effect of the magnetic anisotropy of a nitro group.[21] Taking an angle of rotation $\vartheta_2 = 65$, 75, and 90° in the ethyl, isopropyl, and *tert*-butyl compounds, respectively, shifts of 4.6, 5.2, and 5.6 Hz and 18.7, 21.3, and 22.8 Hz[22] are found due to π-electron density and magnetic anisotropy effects. The total values of 23.3, 26.5, and 28.4 Hz agree quite well with the observed ones (27.2, 30.8, and 32.2? Hz), and the small difference of about 4 Hz may arise from local electrical field gradients.[23] The predicted angles of rotation, which are close to those obtained from uv spectra,[17] may be checked by comparison of the experimental barriers to internal rotation about the amino nitrogen–ring carbon bond to those obtained from HMO theory (see below). Assuming a transition state where the amino group is rotated by 90° and both ortho nitro groups (2 and 6) are coplanar to the ring[3] and subtracting from the experimental barriers 5 kcal/mol for breaking the intramolecular hydrogen bond, one gets $\vartheta_2 = 30$, 45, and ≥65° for the ethyl, isopropyl, and *tert*-butyl compounds, respectively. Because of the assumptions and the limitations of the model these latter values are not very reliable (*e.g.*, taking 7 kcal/mol for the hydrogen bond values of 45, 60, and 90° are obtained), but the relative and absolute orders of magnitude are predicted correctly.

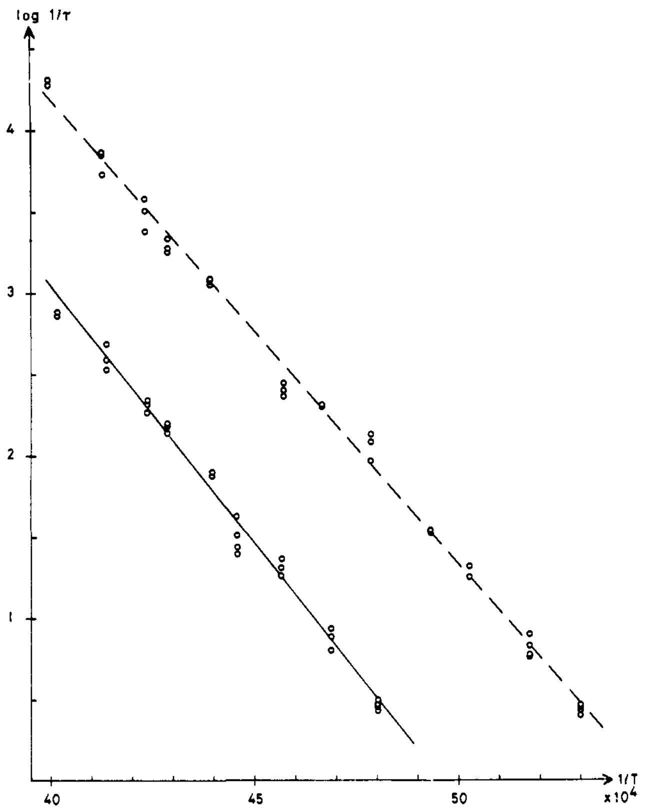

Figure 2. Arrhenius plots for *N*-deuterio-*N*-ethyl-2,4,6-trinitroaniline (———) and *N*-deuterio-*N*-isopropyl-2,4,6-trinitroaniline (- - - -).

NH and Alkyl Chemical Shifts, Coupling Constants. The large downfield shift of the NH proton of all *N*-alkylpicramides indicates in agreement with the ir spectra of these compounds[24] a strong hydrogen bond between the amino proton and the ortho nitro group. It is known from *N*-methyl-3,5-dimethyl-2,4,6-trinitroaniline[20] that the NH shift sensitively reflects changes in the strength of this hydrogen bond and/or conformation of the H–N alkyl group with respect to the aromatic ring. From the almost equal (within 3 Hz) NH shift of all *N*-alkyl-2,4,6-trinitroanilines it is therefore concluded that neither the strength of the hydrogen bond nor the conformation of the H–N-alkyl group is changed significantly with different alkyl groups.

Owing to the conjugation of the amino group with

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(18) I. D. Rae, *Aust. J. Chem.*, **18**, 1807 (1965); **19**, 409 (1966); **20**, 1173 (1967).

(19) B. Lamm, *Acta Chem. Scand.*, **19**, 2316 (1965).

(20) B. Lamm and K. Nordfält, *ibid.*, **20**, 1208, 1221 (1966); **24**, 1597 (1970).

(21) I. Yamaguchi, *Mol. Phys.*, **6**, 105 (1963).

(22) Formulas are given in ref 3.

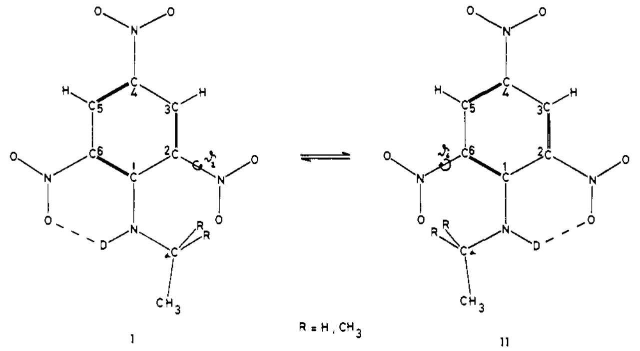
(23) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(24) L. K. Dyall, *Aust. J. Chem.*, **14**, 493 (1961).

the aromatic ring, resulting in a N–C(ring) partial double bond, the alkyl chemical shifts of the picramides, especially the αCH and less the βCH shift, are lowered when compared to those of the corresponding amines.[25] The observation that the αCH chemical shift shows the most marked temperature dependence of all chemical shifts gains in significance from the fact that a large effect of opposite sign has been observed for the CH_3 resonance of *N*-methyl-2,4-dinitroaniline.[3] In this compound the mean lifetime of the methyl group in a position trans to the 2 nitro group is expected to increase with decreasing temperature. Therefore one may suggest for the *N*-alkyl-2,4,6-trinitroanilines that an increasing lifetime of the αCH protons adjacent to a magnetic anisotropic NO_2 group (2 or 6) causes the observed temperature dependence. Denoting the mean lifetime in a state with the αCH protons not in contact with the ortho nitro groups, *i.e.*, in the transition state for the internal rotation about the amino N–ring C bond by τ_{TS} and the mean lifetime in the ground state for the latter rotation by τ_{GS}, the above explanation can only be true if the ratio τ_{TS}/τ_{GS} is markedly different from zero and decreases with decreasing temperatures.

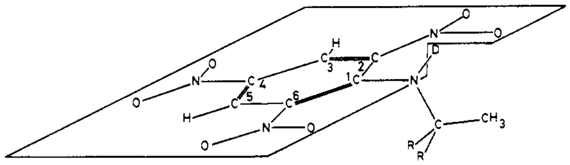
The observed coupling between the amino proton and the alkyl group proves that the amino proton is not involved in an (rapid) exchange process in CH_2Cl_2 solutions.[18] From the fact that only for the compounds not deuterated at the amino site the two high-field lines of the AB spectra of the ring protons were found to have a slightly larger line width (W = 0.8 Hz) than the two low-field lines (W = 0.5 Hz), one may derive that a small long range coupling ($J < 0.3$ Hz) exists between the amino proton and one of the ring protons.

Internal Rotation. Ground State. Summarizing the numerous data on *N*-alkyl-2,4,6-trinitroanilines collected from nmr spectra and other spectroscopic measurements these compounds have most likely the following conformation in common. The 4- and 6-nitro groups (I) are approximately coplanar with the aromatic ring, and the amino group which has valence angles of *ca.* 120° is coplanar to the ring too, implying that the α carbon also lies in the same plane. Between the 6-NO_2 and the amino group exists a strong hydrogen bond. The only marked difference in this series of compounds is the orientation of the 2-NO_2 group which is rotated out of the plane of the ring in order to relieve the steric strain caused by the molecular overcrowding between the amino group and the adjacent NO_2 group. In the series of *n*-alkyl (n-C_xH_{2x+1}, x = 1, 2, ..., 18) N substituted trinitroanilines, the angle of rotation ϑ amounts to *ca.* 60°, while in the case of bulkier substituents, *e.g.*, isopropyl and *tert*-butyl the angle is raised up to *ca.* 75 and 90°, respectively.



Slight deviations of the 6-NO_2 group and the amino group from coplanarity can not be excluded and are consistent with the experimental data. However, more serious deviations can be excluded on the basis of the chemical shifts of the picryl protons, especially when these data are compared to those of other di- and trinitroanilines.[3] But one may keep in mind that the vibrating molecule may reach high torsional (vibrational) states of short lifetimes that differ from the conformation of the ground state.

Transition State. According to HMO calculations[3] the transition state for the internal rotation about the amino nitrogen–ring carbon bond in the *N*-alkyl-2,4,6-trinitroanilines is characterized as follows. The amino group is rotated by 90° so that the N–αC bond lies in a plane perpendicular to that of the ring and possibly the amino nitrogen gains a more pyramidal structure. Both ortho nitro groups are coplanar to the aromatic ring. This molecular arrangement implies at least two consequences. First, the intramolecular hydrogen bond important for fixing the ground-state geometry should be broken in the transition state. Second, the molecular overcrowding in the ground state between the N alkyl and the adjacent NO_2 group is reduced to zero in the transition state. Therefore at least the internal rotation about the amino N–αC (alkyl) bond which is seriously hindered in the ground state is sterically no longer affected in the transition state. One may speculate that possible distortions of the aromatic ring of the seriously overcrowded ground state in the *N*-isopropyl- and *N*-*tert*-butylpicramide are reduced in the transition state. This detailed description of the transition state has only some physical sense if the lifetime of that state is long enough. The fact, however, that the ground state of the closely related anilides[26] is approximately equal to this transition state of the anilines and the conclusions drawn from the temperature dependence of the αCH shifts and from the activation entropies of the anilines indicate that this basic requirement is fulfilled (see below).



One may imagine that by inversion at the amino nitrogen a transition state of reduced overcrowding is reached in which the amino group has a pyramidal structure and both ortho nitro groups are coplanar to the aromatic ring. Such an in- and out-of-plane movement of one ortho NO_2 group,[27] however, cannot be the reason for the observed A_2–AB conversion of the picryl protons spectra because this (symmetric)

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[25] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

[26] J. A. Weil, A. Blum, A. H. Heiss, and J. K. Kinnaird, *ibid.*, **46**, 3132 (1967).

[27] This "vibration" of the NO_2 group would only contribute to the absolute chemical shifts of the 3,5 ring protons; see *e.g.*, G. E. Maciel, P. D. Ellis, and D. C. Hofer, *J. Phys. Chem.*, **71**, 2160 (1967).

conversion only takes place if the chemical shifts of protons A and B are mutually exchanged. It can be also excluded that the picramides have two interchanging ground-state conformations which correspond to the ground state M and to the transition state N (one may imagine a pyramidal amino group or a conformation of the amino group normal to the ring; both are expected to have A_2 ring protons spectra) described above. Even if in the slow exchange limit state N cannot be observed, for a low abundance according to thermodynamic quantities, in the intermediate and fast exchange regions at least an asymmetry and/or a pronounced variation of the chemical shift of the center of the picryl protons spectrum should be observed.

Barrier. The barrier to internal rotation in all *N*-alkyl-2,4,6-trinitroanilines is symmetrical and in a first approximation twofold as concluded from the AB spectra of the ring protons. The height of the barrier which is close to the measured Arrhenius activation energies contains mainly two terms. First, the strength of the strong hydrogen bond between the amino group and the adjacent ortho nitro group which is approximately given by the standard enthalpy ΔH. The almost constant NH chemical shifts in all *N*-alkyl-2,4,6-trinitroanilines as well as the measured Arrhenius activation energies for the internal rotation in *N*-*n*-alkyl-2,4,6-trinitroanilines[3] indicate that the strength of the hydrogen bond is almost equal for all picramides with branched and unbranched alkyl substituents. From the comparison of measured and calculated (HMO) barriers and from data on other hydrogen bonded systems, the enthalpy for the hydrogen bond may be estimated to be in the range of 5–7 kcal/mol. The second important contribution to the barrier is within the Hückel MO model determined by the bond order of the amino nitrogen–ring carbon bond. From these calculations[3] it turns out that an increasing angle of rotation of the 2 (or 6) nitro group, due to alkyl substituents becoming more bulky, causes a decreasing amino N–ring C bond order. On this basis it is obvious that the decreasing of Arrhenius activation energies experimentally found in the series *N*-ethyl-, *N*-isopropyl-, and *N*-*tert*-butyl-2,4,6-trinitroaniline has its origin mainly in the decreasing of the bond orders. In this context it is interesting to note that for the internal rotation about the *tert*-butyl carbon–nitrogen single bond in *tert*-butyldimethylamine, an activation energy $E_a = 6.4 \pm 0.2$ kcal/mol has been measured.[28]

From the observed activation entropies, the temperature dependence of the αCH shift as well as from the fact that the ground state of the anilides is equal to the transition state of the anilines, it had been concluded that the lifetime of the transition state is relatively large. Therefore one may speculate that on the top of the barrier is a small potential well, implying that the barrier may be really fourfold. To account for the observed phenomena a rough calculation on the depth of well yields a minimum value of *ca.* 3 kcal/mol and a maximum value which is at least *ca.* 3 kcal/mol above the ground state (see below).

Motion Over the Barrier. According to the line shape analysis of the picryl protons the mean lifetimes of the ground state for the internal rotation of the picramides are at +25°: 7.7×10^{-6}, 9.1×10^{-7}, $\leqslant 6 \times 10^{-10}$ sec, and at −80°: 5, 0.15, $\leqslant 0.001$ sec for the ethyl, isopropyl, and *tert*-butyl compounds, respectively. The classical torsional frequency ω_t is governed in the harmonic oscillator approximation by the height U of the barrier and the moments of inertia I_1 and I_2 with respect to the amino N–ring C bond[29]

$$\omega_t = 2\sqrt{UA_1A_2A^{-1}}$$

where the factor 2 refers to the twofold barrier and the rotational constants are given by $A_i = h/(8\pi^2 cI_i)$ and $A = h/(8\pi^2 c(I_1 + I_2))$. Taking the bond lengths and angles given in ref 1, the moments of inertia can be calculated, yielding 1.45×10^{-37}, 8.0×10^{-39}, 1.97×10^{-38}, and 3.93×10^{-38} gcm^2 for the picryl, ethyl, isopropyl, and *tert*-butyl parts, respectively. From these data and barrier heights of 14.0, 12.6, and $\leqslant 9.5$ kcal/mol the fundamental torsional frequencies ω_t are expected to be 85.1, 53.3, and $\leqslant 34.7$ cm^{-1} in the series of the ethyl, isopropyl, and *tert*-butyl compounds. In this context it should be mentioned that the corresponding zero point energies are much too low to be responsible for the differences in the measured Arrhenius activation energies.

From the low torsional states the motion over the barrier takes place according to a first-order rate process where both an internal and external mechanism may contribute to the activation of the critical oscillator. The upper and lower limits of the mean lifetime of the oscillator in the transition state can be estimated. First, as the theoretical line shapes are calculated on the basis of the jump model and the experimental line shapes show no significant deviations from the calculated ones (nor weak peaks of other molecular species are to be seen) the lifetime in the transition state should be shorter at least by a factor of 10^3 than that in the ground state. Second, the observation of high activation entropies which are attributed to the breaking of the intramolecular hydrogen bond (contribution to $\Delta S^{\ddagger} \sim 6$ eu) and to a less hindered internal rotation about the N–C bond (contribution to $\Delta S^{\ddagger} \sim 3$ eu/degree of freedom) indicates that the lifetime in the transition state is at least equal to the reciprocal frequency (approximately 10^{12} sec^{-1}) of that latter rotation.

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(28) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **92**, 6349 (1970).

(29) G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, New York, N. Y., 1951.