Conformational Analysis. 5. Molecular Structure, Composition, Trans-Gauche Energy and Entropy Differences, and Potential Hindering Internal Rotation of Gaseous Formaldazine as Determined by Electron Diffraction

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Abstract: Formaldazine (2,3-diaza-1,3-butadiene, H_2CNNCH_2) has been studied by electron diffraction from the gas at nozzle-tip temperatures of −30, 60, and 225 °C. As in the cases of oxalyl chloride and bromide reported earlier, the molecules exist as a mixture of s-trans and gauche conformers with the trans the more stable. The composition (mol fraction) of the vapor with uncertainties estimated at 2σ was found to be 0.911 (0.077), 0.785 (0.095), and 0.749 (0.108) at −30, 60, and 225 °C, respectively. These values correspond to an energy difference with estimated standard deviations $\Delta E° = E_g° - E_t° = 1.2 \pm 0.5$ kcal mol^{-1} and an entropy difference $\Delta S° = S_g° - S_t° = -0.9 \pm 1.5$ cal/mol^{-1} K^{-1}. Certain of the diffraction results permit the evaluation of an approximate torsional potential function of the form $2V = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi)$; the results are $V_1 = 1.10 \pm 0.19$, $V_2 = 0.50 \pm 0.31$, and $V_3 = 0.73 \pm 0.79$, all in kilocalories per mole. The barriers separating the conformers trans from gauche and gauche from gauche are respectively 1.50 ± 0.74 and 0.53 ± 0.83 kcal mol^{-1}. The results for the distance (r_a), angle, and rms amplitude (l) parameters obtained at the three temperatures are entirely consistent. At −30 °C the more important ones are, with estimated uncertainties of 2σ, r(N–N) = 1.418 (0.003) Å, r(C=N) = 1.277 (0.002) Å, r(C–H) = 1.094 (0.005) Å, ∠CNN = 111.4 (0.2°), ∠HCN = 120.7 (0.8°), δ (rms amplitude of torsional vibration of the trans conformer) = 15.8 (3.7°), l(N–N) = 0.0558 (0.0026) Å, l(C=N) = 0.0448 (0.0022) Å, l(C···N) = 0.0596 (0.0029) Å, l(C···C) = 0.0600 Å (assumed).

In earlier publications[1-3] in this series we have reported determinations of the structures and conformations of some simple conjugated molecules with the general formula $(COX)_2$, with X = Cl, Br, or CH_3. In such molecules different skeletal conformations are possible as a result of rotation around the single bond in the conjugated chain. For the oxalyl halides two different conformers were observed, a lower energy s-trans form ($\phi = 0°$) and higher energy gauche form ($\phi \simeq 120°$), but for 2,3-butanedione (X = CH_3) only the s-trans form was observed even at a temperature of 228 °C.

Formaldazine (2,3-diaza-1,3-butadiene, H_2CNNCH_2) is structurally similar to the molecules just described. The heavy-atom configuration is known to be chainlike[4] in a conformation at first thought to be s-cis from the appearance of the IR spectrum and the observation of a weak microwave spectrum[5] but later held to be s-trans from analysis of more extensive IR and Raman data.[6] This conclusion has been corroborated in the main by recent IR and Raman experiments,[7] but some features of the spectra were consistent with the presence of a second conformer at room temperature.

The conformation problem associated with formaldazine and the fact that no structure determination of it had been carried out impelled us to undertake an electron-diffraction study of the vapor. The results turned out to be similar to those found for the oxalyl halides: There are substantial amounts of two forms present in the vapor, a lower energy s-trans and a higher energy gauche (Figure 1). This article describes our results for the structures, the equilibrium between the two forms, and the rotational potential function.

Experimental Section

Materials. Polymeric formaldazine was prepared as described by Pulvermacher[8] by reaction of formaldehyde with hydrazine. The polymer was thermally decomposed under vacuum to give the monomer, which was purified by several distillations and stored at −78 °C.

Diffraction Data. The experiments were carried out at nozzle-tip temperatures of −30, 60, and 225 °C under conditions very similar to those described for oxalyl chloride.[1] Reduction of the data was done in the usual way[1] and a calculated background[9] was removed by subtraction from the data from each plate.[10] Composites of the resulting experimental intensity curves in the form sI_m are shown in Figure 2. Table I is a summary of information concerning the experiment and the reduction of data.

Structure Analysis.[11] Radial Distribution Curves. Radial distribution curves are shown in Figure 3. That the gaseous sample contains more than one conformer is revealed by the temperature dependence of the 2.5–4.2 Å area in the experimental curves. The areas of the strong peak at 3.3 Å and the weak one at 4.2 Å are seen to decrease as the temperature increases while the area of the feature in the region 2.5–3.0 Å increases. Theoretical radial distribution curves were calculated for a number of models comprising mixtures of cis-trans and gauche (ϕ = 120°)-trans conformers using approximate bond distances and bond angles deduced from the experimental curves. Good agreement with experiment was obtained from the latter when the amounts of the gauche form were rather small, i.e., about 25% at the highest temperature. The cis-trans mixtures gave much poorer agreement.

Structure Refinement. The structure refinements were carried out by the method of least squares, adjusting a single theoretical intensity curve to the seven sets of data simultaneously, using a unit weight matrix. With the usual assumption that the two conformers have the same geometrical structure except for the CNNC torsion angle ϕ in the gauche form, it was found that the structure of formaldazine could be adequately described by a composition parameter, six geometrical parameters (r_{N-N}, $r_{C=N}$, r_{C-H}, ∠CCN, ∠HCN, and ϕ), and seven amplitude parameters ($l_{N-N} = l_{C=N} + \Delta$, l_{C-H}, $l_{13} = l_{18} = l_{25} + \Delta'$, l_{26}, $l_{28} = l_{27} = l_{17}$, $l_{28'} = l_{27'} = l_{26'} + \Delta''$, and δ, the root-mean-square amplitude for the torsional vibration in the trans conformer; the Δ's are assumed constants.) The composition parameter, all of the geometrical parameters except ϕ, and three of the amplitude parameters (l_{N-N}, l_{13}, and δ) could be refined simultaneously for all three temperatures. The parameter ϕ was refinable with the others for the high-temperature experiment, but at −30 °C the small amount of gauche form present required an assumption about its value; the high-temperature result was chosen. For the 60 °C experiment it was necessary to refine ϕ separately rather than simultaneously with the other parameters. Values of the parameter δ were obtained in the way previously described[1] by representing the continuous distribution of near-trans rotational conformers by nine distinct, appropriately weighted species. Aside from l_{N-N} and l_{13}, the amplitude parameters

Table I. Data Concerning the Experiments

	−30 °C		60 °C		225 °C	
Nozzle-to-plate distance, mm	749.77	299.93	749.68	299.71	749.84	299.85
Electron wavelength, Å	0.057 10	0.057 09	0.057 12	0.057 13	0.057 11	0.057 10
Exposure times, s	45-90	180-210	45-60	150-210	105-135	180-240
Electron beam current, μA	0.48-0.50	0.48	0.54	0.60	0.46-0.50	0.50
No. of plates used[a]	3	4	3	4	3	4
Range of data in s,[b] Å^{-1}	1.00-12.75	7.00-31.25	1.00-13.00	7.50-31.75	1.00-12.75	7.50-31.25
Data interval in s,[b] Å^{-1}	0.25	0.25	0.25	0.25	0.25	0.25
Apparatus pressure during admission of sample, Torr × 10^6	6	6-8	4-6	8	6	5

[a] Plates were Kodak lantern slide, medium contrast, 8 × 10 in., developed in D-19 diluted 1:1 for 10 min at 20 °C. [b] $s = 4\pi\lambda^{-1} \sin \theta/2$, θ is the scattering angle.

Table II. Final Structural Results[a,b] for Formaldazine at Different Temperatures

Parameters[c]	−30 °C			60 °C			225 °C		
	r_a	l^d		r_a	l^d		r_a	l^d	
N—N	1.418 (0.003)	0.0558	(0.0026)	1.418 (0.003)	0.0559	(0.0027)	1.416 (0.003)	0.0559	(0.0027)
C=N	1.277 (0.002)	0.0448	(0.0022)	1.278 (0.002)	0.0449	(0.0023)	1.280 (0.002)	0.0449	(0.0024)
C—H	1.094 (0.005)	[0.0770]		1.097 (0.005)	[0.0770]		1.096 (0.005)	[0.0770]	
$C_2\cdots N_5$	2.229 (0.003)	0.0596	(0.0029)	2.225 (0.003)	0.0635	(0.0032)	2.233 (0.003)	0.0673	(0.0034)
$N_1\cdots H_3$	2.062 (0.008)	0.0896	(0.0040)	2.037 (0.010)	0.0935	(0.0042)	2.039 (0.011)	0.0973	(0.0044)
$N_1\cdots H_8$	2.384 (0.015)	0.0896	(0.0040)	2.331 (0.019)	0.0935	(0.0042)	2.344 (0.021)	0.0973	(0.0044)
$N_1\cdots H_7$	3.264 (0.006)	[0.0900]		3.249 (0.008)	[0.0900]		3.254 (0.008)	[0.0900]	
$C_2\cdots C_6$	3.335 (0.004)	[0.0600]		3.321 (0.004)	[0.0600]		3.324 (0.004)	[0.0600]	
$C_2\cdots H_8$	3.641 (0.015)	[0.0900]		3.580 (0.018)	[0.0900]		3.585 (0.021)	[0.0900]	
$C_2\cdots H_7$	4.268 (0.009)	[0.0900]		4.232 (0.011)	[0.0900]		4.232 (0.012)	[0.0900]	
$C_2\cdots C_6'$	2.654 (0.006)	[0.1200]		2.625 (0.177)	[0.1400]		2.665 (0.128)	[0.1600]	
$C_2\cdots H_8'$	2.485 (0.017)	[0.1800]		2.392 (0.346)	[0.2000]		2.452 (0.244)	[0.2200]	
$C_2\cdots H_7'$	3.677 (0.008)	[0.1800]		3.653 (0.141)	[0.2000]		3.688 (0.102)	[0.2200]	
∠CNN'	111.4 (0.2)			111.2 (0.2)			111.7 (0.2)		
∠HCN	120.7 (0.8)			118.0 (1.0)			118.0 (1.1)		
$\angle\phi^e$	[117.7]			120.2 (22.7)			117.7 (15.4)		
δ^f	15.8 (3.7)			20.3 (4.8)			32.8 (5.7)		
% trans	91.1 (7.0)			78.5 (9.5)			74.9 (10.8)		
R^g	0.105			0.085			0.084		

[a] Distances (r) and root-mean-square amplitudes (l) in angströms; angles in degrees. [b] Parenthesized values are 2σ and include estimates of systematic error. Values in square brackets were assumed. [c] Unprimed items refer either to nontorsion-sensitive distances or to torsion-sensitive distances in the trans conformer. Primed items refer to torsion-sensitive distances in the gauche conformer. [d] Quantities in curly brackets were refined with constant differences as a group. [e] Average torsion angle in the gauche form relative to 0° for the trans conformer. [f] Root-mean-square amplitude of torsional motion in the trans conformer. [g] $R = [\Sigma w_i \Delta_i^2/(w_i I_i^2(\text{obsd})]^{1/2}$, where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$.

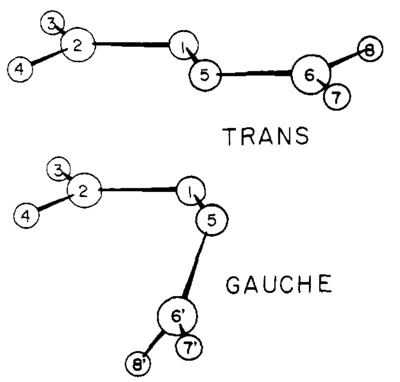

Figure 1. Diagrams of the trans and gauche forms of formaldazine with atom numbering.

could not be refined and were given assumed values estimated partly from results for related molecules[12] and partly by observing changes in the R factor and radial distribution curves as the amplitude values were changed. "Shrinkage" corrections[13] of 0.01-0.02 Å were applied to the C ··· C and the long C ··· H distances in the trans form.

The final results are given in Table II and the theoretical intensity and radial distribution curves corresponding to them are shown in Figures 2 and 3 together with curves of differences. The correlation matrix for the results from the lowest temperature data is given in Table III; the other two correlation matrices are similar and will appear in the microfilm edition of this journal.

Discussion

Molecular Structure and Bonding. Our structure analysis draws on the assumption that the geometries of the two conformers are identical except for the CNNC torsion angle. To the extent that this assumption is poor the parameter values given in Table II are really averages for the two forms. However, there is evidence that the assumption is a good one. For example, if the corresponding bond lengths and bond angles in the two forms were substantially different, changes in the measured values consistent with changing composition (temperature) should be present but are not. Further, substantially different bond distances would be reflected with our assumption in larger than normal vibrational amplitude values. However, the measured values are about as would be expected for a single conformer. We conclude that the bond distances and bond angles are nearly the same in the two conformers.

The nitrogen-nitrogen bond is, as expected, shorter in formaldazine than in hydrazine (1.449 ± 0.004 Å[14]) or in 1,2-dimethylhydrazine (1.45 ± 0.03 Å[15]) which have bond lengths about equal to the sum of the covalent radii corrected for electronegativity difference. However, the amount of the shortening (0.03 Å) is substantially less than that found for

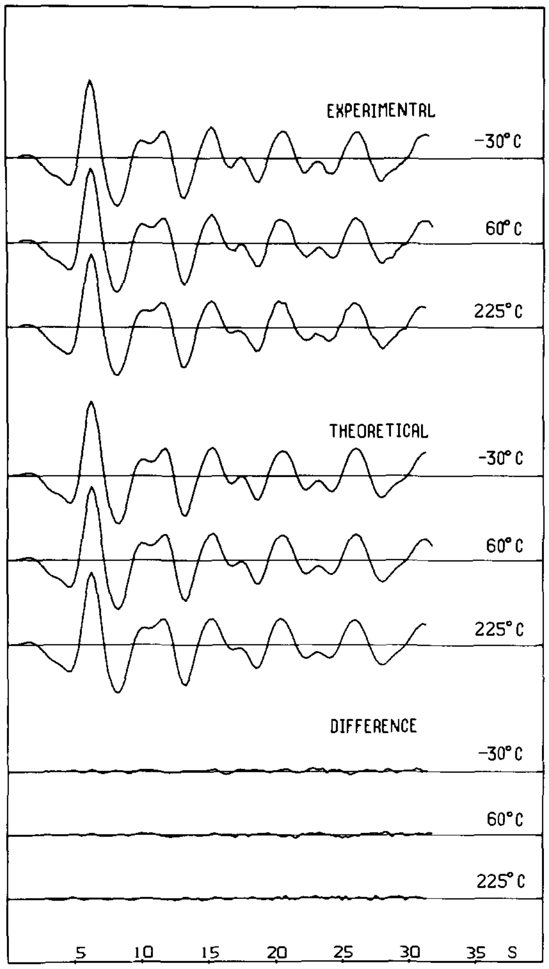

Figure 2. Intensity curves for formaldazine. The experimental curves are composites from several experiments; the theoretical curves were calculated from the parameter values of Table 1. All curves are on the same scale and are in the form $sI_m(s)$ (see ref 1).

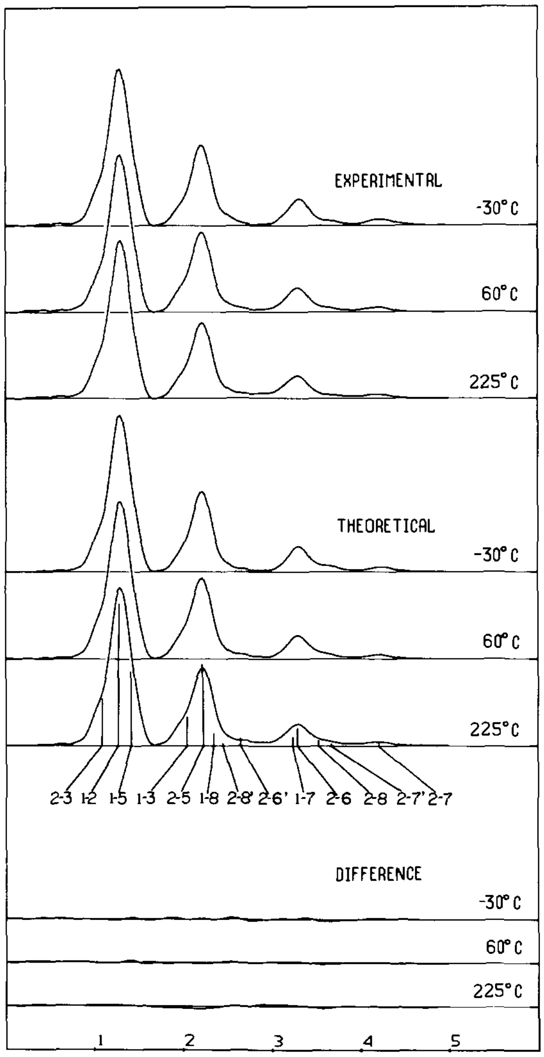

Figure 3. Radial distribution curves for formaldazine. The curves were calculated from the intensity curves of Figure 2 with $B = 0.0020$. Unobserved or uncertain experimental intensity data for the region $0 < s < 1.75$ were taken from theoretical curves. The vertical lines indicate the interatomic distances in the final models; the lengths of the lines are proportional to the weights of the distances. All curves are on the same scale.

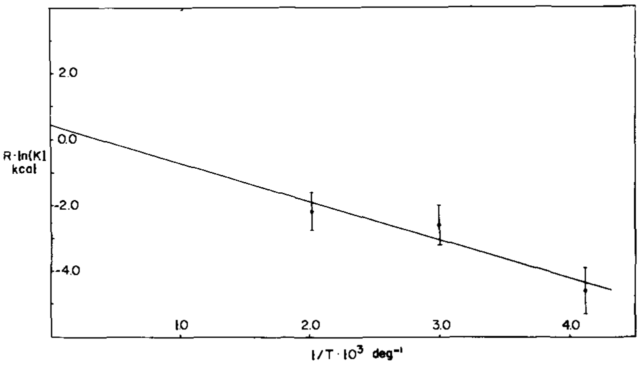

Figure 4. van't Hoff plot of composition data. $K = N_g/N_t$. The half-lengths of the vertical bars indicate 1σ. Least-squares straight line.

comparable hydrocarbons; butadiene-1,3, for example, has $r_{C-C} = 1.467 \pm 0.003$ Å,[16] some 0.07 Å shorter than the normal value. These shortenings are suggestive of substantially more double-bond character in conjugated carbon compounds than in similar nitrogen compounds and are consistent with the assignment of a greater torsional frequency in butadiene (163 cm^{-1}) than in formaldazine (115 cm^{-1}).

The absence of the cis ($\phi = 180°$) and skew ($\phi \simeq 60°$) forms in detectable amounts and the presence of the gauche ($\phi \simeq 120°$) has been discussed in the cases of the oxalyl halides in terms of the double bonds viewed as "bent" single bonds.[1] When the molecule is viewed along the conjugated single bond, this simple valence-bond picture has the cis and skew forms with eclipsed bonds much as in the eclipsed form of ethane. Entirely analogous arguments may be applied to formaldazine.

Energy and Entropy Differences of the Conformers. From the measured variation of sample composition with temperature, it is possible to determine the energy and entropy differences between the trans and the gauche conformers by use of the formula

$$N_g/N_t = 2e^{\Delta S°/R}e^{-\Delta E°/RT} \qquad (1)$$

where N_g and N_t are the fractions of gauche and trans molecules and the factor 2 is the ratio of the statistical weights of the two forms. Figure 4 shows the usual plot of the data in the form of the van't Hoff equation, where $K_p = N_g/N_t$. The best-fit (least squares) line leads to the values with estimated standard deviations $\Delta E° = E_g° - E_t° = 1.2 \pm 0.5$ kcal mol^{-1} and $\Delta S° = S_g° - S_t° = -0.9 \pm 1.5$ cal mol^{-1} K^{-1}. The value for $\Delta E°$ lies between those found for oxalyl halides (1.38 ± 0.35 kcal mol^{-1} for oxalyl chloride and 0.63 kcal mol^{-1} for oxalyl bromide) and that for $\Delta S°$ is lower than either (2.3 ±

Table III. Correlation Matrix for Parameters of Formaldazine at −30 °C[a]

	$r_{N\text{-}N}$	$r_{C=C}$	$r_{C\text{-}H}$	∠CNN	∠HCN	δ^b	$l_{N\text{-}N}$	l_{25}	Mol fraction trans
σ^c	0.0007	0.0003	0.0016	0.07	0.27	1.32	0.0005	0.0006	0.025
	1.000	0.524	0.078	−0.712	−0.078	−0.040	0.242	−0.182	−0.184
		1.000	0.515	−0.564	−0.208	−0.071	−0.228	−0.072	−0.053
			1.000	−0.205	−0.347	−0.128	−0.587	−0.261	−0.060
				1.000	0.443	0.232	−0.006	−0.095	−0.172
					1.000	0.208	0.210	0.083	0.114
						1.000	−0.069	−0.047	0.301
							1.000	0.412	−0.165
								1.000	−0.072
									1.000

[a] Distances (r) and root-mean-square amplitudes (l) in angströms; angles in degrees. [b] Root-mean-square amplitude of the torsional vibration. [c] Standard deviations from least squares.

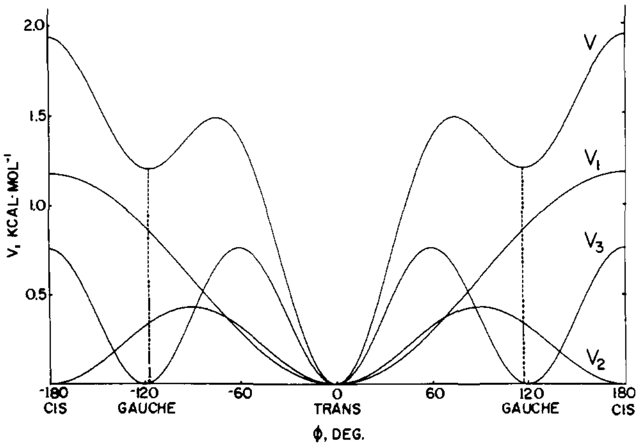

Figure 5. Form of hindering potential. The dashed lines indicate the measured gauche torsion angle.

1.0 and 1.1 ± 0.9 cal mol^{-1} K^{-1} for the chloride and bromide, respectively).

Rotational Potential Function. For the oxalyl halides it was found possible to evaluate a rough rotational potential function of the form

$$2V(\phi) = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos\phi) \quad (2)$$

from the diffraction data alone. A similar calculation may be carried out for formaldazine. Assuming that the harmonic approximation $V(\phi) = V^*\phi^2/4$ with $V^* = V_1 + 4V_2 + 9V_3$ (obtained by expansion of eq 2) may be applied to the trans conformer, the values of $V^* = 2RT/\delta^2$ from the three experiments are found to be 12.7, 10.5, and 6.0 kcal mol^{-1}. The average of these values ($V^* = 9.7 \pm 2.8$ kcal mol^{-1}), the value for the gauche torsion angle at which $V(\phi)$ has a minimum (119°), and the value of $V(\phi)$ at the gauche angle ($V(\phi) = \Delta E° = 1.2$ kcal mol^{-1}) lead to the equations

$$V_1 + 4V_2 + 9V_3 = 9.7 \quad (3)$$

$$V_1 - 1.696V_2 - 0.157V_3 = 0 \quad (4)$$

$$0.742V_1 + 0.765V_2 + 0.0007V_3 = 1.2 \quad (5)$$

The solution of these equations with standard deviations estimated from the errors in V, $\Delta E°$, and ϕ gives $V_1 = 1.10 \pm 0.19$, $V_2 = 0.50 \pm 0.31$, and $V_3 = 0.73 \pm 0.79$, all in kilocalories per mole. The potential function and its three components are shown in Figure 5. The barrier separating the trans from the gauche conformer is calculated to be 1.50 ± 0.74 kcal mol^{-1} and that separating the two gauche forms 0.53 ± 0.83 kcal mol^{-1}.

Torsional Frequencies. If the torsional motion about the nitrogen-nitrogen bond is assumed to be harmonic, the value of the torsional force constant may be estimated from the measurement of δ, the rms amplitude of the torsional motion. The result with estimated standard deviation is k_ϕ (equal to $V^*/2 = RT/\delta^2$) = 0.034 ± 0.019 mdyn Å rad^{-1}. If one now assumes that the low-frequency torsional mode is largely unaffected by the other vibrations, one may estimate its frequency by well-known methods.[17] The result is 100 ± 35 cm^{-1}, in good agreement with the experimental value of 115 cm^{-1} assigned from observation of combination bands.[6] The torsional frequency for the gauche conformer cannot be obtained in the same way because the torsional amplitude was not measured. However, it may be estimated from the relationship $k_\phi = (\delta^2 V/\delta\phi^2)_{119°}$ and is found to be 0.018 ± 0.002 mdyn Å rad^{-2}. The corresponding frequency is calculated to be 90 ± 8 cm^{-1}. There is no report of an observed value, which may be attributed in part to the small amount of the gauche conformer present at room temperature.

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Supplementary Material Available. Tables IV and V containing molecular intensity data in the form $sI_m(s)$ from each plate and the correlation matrices for the 60 and 225 °C results (15 pages). Ordering information is given on any current masthead page.

References and Notes

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(11) Details of the procedures including formulas are to be found in ref 1 and in references cited therein.
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(17) For example, the torsion is of symmetry species A_u and is of a form that may be regarded as the motion of the N_2 group against the two CH_2 groups. These masses together with a force constant equal to $4(0.034)/(r_{cm}{}^2 \sin 111.4°)$ *mdyn*·Å^{-1}, where r_{cm} is the distance from a nitrogen atom to the center mass of the CH_2 group bound to it, give the same frequency as does a calculation such as that described by W. D. Gwinn [*J. Chem. Phys.* **55**, 477 (1971)] based on a much more general force field.