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Structure and Rotational Isomerism of Ethylenediamine as Studied by Gas Electron Diffraction

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The structure and the rotational isomerism of ethylenediamine have been investigated by means of gas electron diffraction. Evidence has been given for the presence of one conformer (*gauche*) in the vapor phase (at 50—120°C); the N-C-C-N dihedral angle measured from the *cis* position is $64._0 \pm 4°$, and the fraction of any other isomer, if present, is estimated to be less than 5%. A theoretical prediction based on the SCF-CNDO/2 method has essentially accounted for this finding. The r_g distances and the angles based on the r_α structure determined by a least-squares analysis on molecular intensities, with estimated limits of error, are as follows: C–C=1.545 ± 0.008 Å, C–N=1.469 ± 0.004 Å, ∠C–C–N=$110.2 \pm 0.7°$, C–H=$1.10_9 \pm 0.01$ Å, ∠C–C–H=$111._9 \pm 5°$, and ∠H–C–H=$112._7 \pm 8°$.

A previous paper[1] has reported on the molecular structure of triethylenediamine. One of the characteristic aspects is that this molecule has a twisting motion around the N···N axis, where the ethylenediamine bridges have a large-amplitude torsion about the *cis* conformation. Moreover, the C–C distance in the bridge is longer than those in normal alkanes by more than 0.02 Å.

On the other hand, the structure of free ethylenediamine has not been studied in detail, in contrast with extensive studies of its complexes by X-ray crystallography,[2] and the existing assignment of the vibrational data (infrared and Raman) to a single (*cis*) conformer was only tentative[3] (see Fig. 1). Under these circumstances, an electron-diffraction study was initiated in order to elucidate the structure and rotational isomerism of ethylenediamine in the gas phase. A preliminary result[4] has given evidence for a dominant *gauche* conformer. In the present paper a further analysis has been made in consideration of the hydrogen positions of the amino groups.

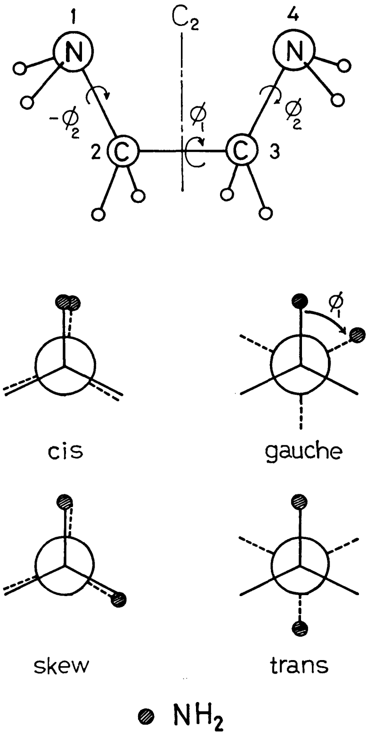

Fig. 1. Rotational isomerism for ethylenediamine. (See text).

Experimental

Anhydrous ethylenediamine (Guaranteed Reagent) obtained from the Tokyo Chemical Industry Co., Ltd. was used in this work. Diffraction photographs were taken on Fuji Process Hard plates at 55, 65, 90, and 118°C using an apparatus equipped with an r^3 rotating sector.[5] The sample was introduced into the diffraction chamber through a heated nozzle assembly,[1] and the above-mentioned temperatures were kept within ±1°C at the nozzle tip and in the sample flask during the experiment. The accelerating voltage was about 40 kV and was stabilized to within 1×10^{-4}. Two camera lengths of 114 and 249 mm were used, and the scale factors of the diffraction patterns were calibrated with reference to the r_a(C–O) distance of carbon dioxide (1.1646 Å)[5] for the shorter camera length and to the r_a(N–N) distance of nitrogen (1.1007 Å)[6] for the longer camera length. Four plates taken at each camera length with photographic densities ranging from 0.19 to 0.57 were used for the analysis. A typical experimental

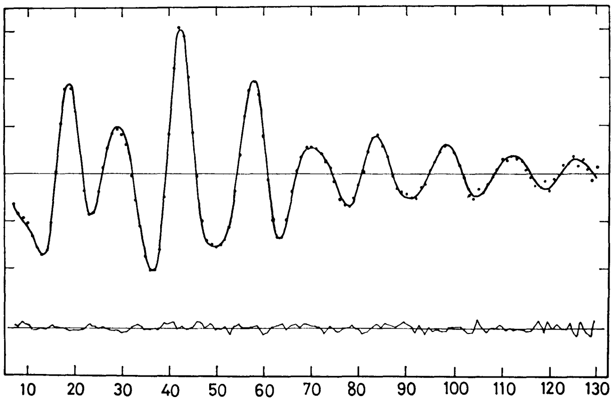

Fig. 2. Molecular intensity $qM(q)$ curve for ethylenediamine. Upper solid curve: best-fit theoretical; dots: experimental; lower curve: experimental minus theoretical.

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[1] A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 72 (1971).

[2] For example, M. Iwata, K. Nakatzu, and Y. Saito, *Acta Crystallogr.*, **B25**, 2562 (1969).

[3] A. Sabatini and S. Califano, *Spectrochim. Acta*, **16**, 677 (1960).

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[6] K. Kuchitsu, This Bulletin, **40**, 498 (1967).

molecular intensity $qM(q)$ ($q=7-130$ Å^{-1}) is illustrated in Fig. 2.[7] The intensity curves[8] derived from plates taken at different temperatures were not distinguishable from one another beyond the uncertainties in the measurement. Most of the calculations were carried out by the HITAC-5020E in the Computer Centre of the University of Tokyo.

Analysis

Ethylenediamine has two axes of internal rotation (C–C and C–N) as illustrated in Fig. 1. The parameters ϕ_1 and ϕ_2 represent, respectively, the dihedral angle between the N_1–C_2–C_3 and C_2–C_3–N_4 planes measured from the *cis* position and that between the planes which bisect the H–N_1–H and the H–C_2–H angles measured from the eclipse position.

In order to make the analysis tractable, the following assumptions were made.

1) The bond lengths and bond angles are independent of internal rotation.

2) The C–C–N plane is perpendicular to the H–C–H plane and bisects the H–C–H angle.

3) The C–N–H and H–N–H angles are equal to those in methylamine:[9] ∠C–N–H=112.1° and ∠H–N–H=105.9°.

4) The N–H bond distance is equal to that in ammonia,[10] r_g (N–H)=1.0302 Å.

5) The molecule has C_2 symmetry; *i.e.*, the ϕ_2 angles for the amino groups have equal values with opposite signs (Fig. 1).

On the above assumptions, seven parameters were chosen for the subsequent analysis: the C–C, C–N, and C–H bond distances, the C–C–N and H–C–H bond angles, and the ϕ_1 and ϕ_2 dihedral angles.

In addition, the mean amplitudes of vibration and shrinkage corrections[1] for all the atom pairs were calculated by a normal-coordinate analysis based on the force constants listed in Table 1, where the torsional force constants Y(C–C) (0.16 md·Å) and Y(C–N) (0.12 md·Å) were estimated so as to roughly reproduce the observed torsional frequencies[3] of 186 cm^{-1} for the C–C axis and 327 cm^{-1} for the C–N axis. The estimated value of Y(C–C) is justified in a later section. The calculated vibrational frequencies based on a staggered conformation ($\phi_1=\phi_2=60°$) by the use of the above force constants are given in Table 2. No refine-

TABLE 1. ESTIMATED FORCE CONSTANTS FOR ETHYLENEDIAMINE[a]

K(C–C)	2.3	H(C–C–N)	0.30	F(C–C–N)	0.70
K(C–H)	4.3	H(C–C–H)	0.25	F(C–C–H)	0.47
K(C–N)	5.5	H(N–C–H)	0.28	F(N–C–H)	0.52
K(N–H)	5.6	H(C–N–H)	0.32	F(C–N–H)	0.46
Y(C–C)[b]	(0.16)	H(H–N–H)	0.40	F(H–N–H)	0.00
Y(C–N)[b]	(0.12)				

a) Force constants for ethylenediamine estimated from those for normal alkanes and amides (See Ref. 1). Y's in units of md·Å and others in md/Å.

b) See text.

TABLE 2. VIBRATIONAL FREQUENCIES OF ETHYLENEDIAMINE (cm^{-1})

	Calcd[a]	Obsd[b]	Calcd	Obsd	Calcd	Obsd
A	3259	3246	1367	—	904	761
	3200	—	1299	1298	383	468
	2977	2891	1236	—	331	—
	2936	2858	1196	1104	167	186
	1486	1597	1065	980		
	1401	1469	973	920		
B	3259	3335	1459	1456	1041	951
	3201	3171	1369	1360	877	775
	2983	2930	1299	1305	590	510
	2951	2917	1207	1249	309	327
	1493	1608	1166	1065		

a) Frequencies for a *gauche* conformation (C_2) calculated by the use of the force constants given in Table 1. (See text).

b) Observed values by infrared and Raman spectra listed in Ref. 3, where a tentative assignment for a *cis* conformer (C_{2v}) was made. The correspondence of the observed and calculated frequencies is, therefore, mostly ambiguous.

TABLE 3. CALCULATED MEAN AMPLITUDES FOR ETHYLENEDIAMINE[a]

C—N	0.0451	$C_2 \cdots H_1$[b]	0.1057
C—C	0.0517	$C_2 \cdots H_3$	0.1053
C···N	0.0686	$N_1 \cdots H_2$	0.1018
C—H	0.0784	$C_2 \cdots H_4$(S)[c]	0.1676
N—H	0.0746	$C_2 \cdots H_4$(L)	0.1019
$l(\phi_1)$[d]	0°	60°	180°
N···N	0.1795	0.1471	0.0677
$N_1 \cdots H_3$(S)	0.1408	0.1582	0.1570
$N_1 \cdots H_3$(L)	0.1408	0.1003	0.1570
$N_1 \cdots H_4$(S)	0.2942	0.2578	0.1173
$N_1 \cdots H_4$(L)	0.1375	0.1577	0.1850
$l(\phi_2)$[e]	a_i	b_i	c_i
$C_2 \cdots H_4$(S)	0.0170	−0.0166	0.1248
$C_2 \cdots H_4$(L)	−0.0170	−0.0162	0.1248
$N_1 \cdots H_4$(S)	0.0409	−0.0373	0.2055
$N_1 \cdots H_4$(L)	−0.0436	−0.0269	0.2055

a) Mean amplitudes calculated for 90°C by the use of the force constants given in Table 1 (in Å units). Those for the H···H pairs are not listed. Values listed in the first section are independent of the N_1–C_2–C_3–N_4 dihedral angle ϕ_1 (for $\phi_2=60°$).

b) Subscript of the hydrogen atom denotes the number of the atom to which the hydrogen atom is bonded.

c) Atom pairs denoted as S and L have shorter and longer distances, respectively.

d) Mean amplitudes calculated for three conformers (for $\phi_2=60°$) (See Fig. 1).

e) Parameters of the mean amplitudes dependent on ϕ_2 (for $\phi_1=60°$), given in Eq. (1).

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[7] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7117). A copy may be secured by citing the document number and by remitting, in advance, ¥200 for photoprints. Payment by check or money order payable to: the Chemical Society of Japan, 5, 1-Chome, Kanda-Surugadai, Chiyodaku, Tokyo.

[8] Y. Morino, K. Kuchitsu, and T. Fukuyama, This Bulletin, **40**, 423 (1967).

[9] D. R. Lide, Jr., *J. Chem. Phys.*, **27**, 343 (1957).

[10] K. Kuchitsu, J. P. Guillory, and L. S. Bartell, *ibid.*, **49**, 2488 (1968).

[11] K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

ment of the force constants was made, since only a provisional assignment of the observed frequencies[3] was available. The mean amplitudes calculated for a number of conformers are given in Table 3. They were treated as constants until the final stage of the conformational analysis.

Conformational Analysis (I). The structural parameters were first estimated from a preliminary analysis of the molecular intensity on the assumption that the ϕ_2 angle was 60°. As a result of a least-squares analysis,[4] the following parameters were derived: C–C=1.55 Å, C–N=1.47 Å, and $\angle$C–C–N=110°. This analysis also gave the ϕ_1 angle of about 60°, *i.e.*, the "*gauche*" conformation about the skeleton.

This conformation was also evidenced in the radial distribution (RD) curve for $r \gtrsim 2.5$ Å. For the calculation of the RD curve with a damping factor of exp $(-0.00014q^2)$, a small-angle region (q=0—7 Å^{-1}) of the molecular intensity curve was spliced by a set of theoretical intensity curves computed for different ϕ_1 angles: 0° (*cis*), 60° (*gauche*), 120° (*skew*), and 180° (*trans*). As for the hydrogen positions in the NH_2 groups, contributions from three staggered positions were averaged. The experimental and theoretical RD curves for *cis*, *gauche*, *skew*, and *trans* forms are compared in Fig. 3. The N···N peak shown by vertical lines shows that the *gauche* form is dominant in the vapor phase. A further conformational analysis is made in later sections.

Refinements of Structural Parameters. In the preceding section, the skeletal parameters were determined on the basis of the ϕ_2 angle fixed to 60°. This parameter was now treated as an additional variable. When the analysis was started from 60, 180, and 300° (three staggered positions), it converged to 81, 200, and 308° with standard deviations of about 9°, and hence, the equilibrium hydrogen positions of the amino groups about the C–N axes seem to be staggered.

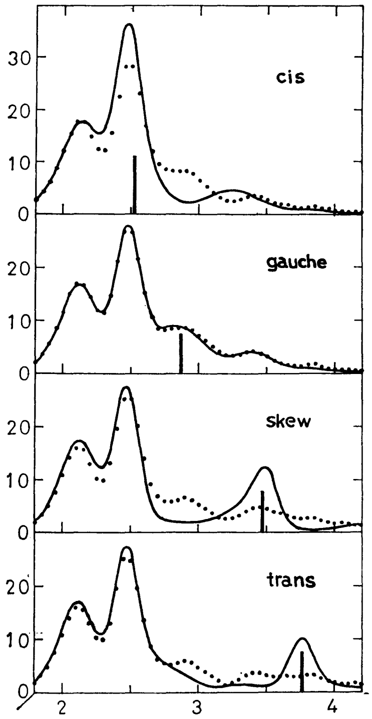

Fig. 3. Radial distribution curves for ethylenediamine. Dots: experimental; solid lines: corresponding theoretical curves for *cis*, *gauche*, *skew*, and *trans* conformers about the C–C axis with the index of resolution of 100%. Vertical line indicates the nonbonded N···N distance for each conformer.

In order to refine the structural parameters, the contribution to the scattering intensity from the atom pairs dependent on the internal rotation about the C–N axis was calculated by taking a weighted average of the intensity at every position of the ϕ_2 angle.[12,13] The weight was given by the Boltzmann distribution with a three-fold potential, $V(\phi_2)={}^1/_2H_3(1+\cos3\phi_2)$, where the barrier height H_3 was assumed to be 3.8 kcal/mol from the torsional force constant Y(C–N) of 0.12 md·Å mentioned above. In this treatment a rotation-inversion coupling was ignored, since the frequency of the NH_2 wagging motion is much higher than that of the torsion about the C–N axis.[3] Contributions from the skeletal vibrations to the mean amplitudes, $l(\phi_2)$, were obtained as a function,

$$l_i = a_i \sin\phi_2 + b_i \cos\phi_2 + c_i, \qquad (1)$$

and the three parameters given in Table 3 were determined so as to reproduce the mean amplitudes calculated for several ϕ_2 angles.[12,13]

On the above-mentioned assumptions, the independent parameters and some of the mean amplitudes were determined by a least-squares analysis on the molecular intensity curves. The error matrix[14] derived from the analysis is given in Table 4. The results are listed in Tables 5 and 6 with the estimated limits of error including possible systematic errors. The experimental systematic errors primarily depend on the uncertainty in the electron wavelength (0.07%) and sector imperfection (0.05%),[15] whereas the systematic errors due to the assumptions made in the above analysis were estimated by the method described elsewhere[16] with moderate changes in the assumed values to be of the order of the corresponding random standard errors.

Conformational Analysis (II). For a quantitative examination of the fractions of the *gauche* conformer and other possible candidates, a background analysis[17] was undertaken by the use of the scattering intensity observed in a small-angle region (q=7—20 Å^{-1}). The background function $I_b(q)$ is given by $I_b(q)=I_0(q)/[1+kM_c(q)]f(q)$. "Smoothness" of the $I_b(q)$ function, which should have no systematic fluctuation with a period similar to that of the molecular intensity, was taken as a criterion for the choice of a correct structural model. The index of resolution k was assumed to be unity, and an empirical quartic function $f(q)$ was used

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[17] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958); M. Abe, K. Kuchitsu, and T. Shimanouchi, *J. Mol. Structure*, **4**, 245 (1969).

TABLE 4. ERROR MATRIX[a)]

	x_1	x_2	x_3	x_4	x_5	x_6	x_7	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8	k
x_1	30	−6	−7	−30	37	25	61	−10	11	−17	19	−17	−24	−16	−11	30
x_2		13	8	−12	−11	31	50	15	10	25	17	17	14	4	16	39
x_3			31	4	−32	18	64	10	7	17	7	25	9	9	11	44
x_4				48	−78	−63	−108	−13	−11	−22	−27	16	54	53	106	−53
x_5					265	190	−174	18	−36	12	39	−127	−120	−146	−204	−34
x_6						302	−130	48	−32	72	64	−150	−176	−69	−201	131
x_7							553	56	76	97	78	216	−123	46	226	207
l_1								23	15	35	28	16	−21	−14	−24	59
l_2									22	22	21	32	21	25	66	45
l_3										56	39	33	−33	−16	−23	90
l_4											46	9	−32	−24	−37	79
l_5												137	89	34	125	79
l_6													137	45	122	−65
l_7														150	253	−31
l_8															333	−44
k																199

a) x_1=C-C, x_2=C-N, x_3=C-H, x_4=∠C-C-N, $x_5=\phi_1$, x_6=∠C-C-H, and x_7=∠H-C-H. The mean amplitudes l_1—l_8 follow the order listed in Table 6. Units ($\times 10^{-4}$) for the distances are Å, those for the angles are rad., and the index of resolution k is dimensionless.

TABLE 5. STRUCTURAL PARAMETERS FOR ETHYLENEDIAMINE[a)]

C—C	1.545 ± 0.008
C—N	1.469 ± 0.004
∠C-C-N	$110.2 \pm 0.7°$
ϕ_1[b)]	$64._0 \pm 4._5°$
C—H	$1.10_9 \pm 0.01$
∠C-C-H	$111._9 \pm 4._6°$
∠H-C-H	$112._7 \pm 8._5°$
k[c)]	1.02 ± 0.05

a) Experimental r_g distances in Å units and r_α angles determined in the present study with estimated limits of error (See text).

b) The N-C-C-N dihedral angle measured from the *cis* position (See Fig. 1).

c) Index of resolution (dimensionless).

TABLE 6. MEAN AMPLITUDES IN ETHYLENEDIAMINE (Å)

Atom Pair	Obsd[a)]	Calcd[b)]
C—N	$0.046_1 \pm 0.006$	0.045_1
C···N	$0.074_7 \pm 0.006$	0.069_2
C—C	$0.05_3 \pm 0.01_4$	0.051_7
C—H	$0.08_2 \pm 0.01_1$	0.078_4
$C_2 \cdots H_1$	$0.11_1 \pm 0.03_4$	0.106
$C_2 \cdots H_3$	$0.10_2 \pm 0.03_4$	0.105
N···N	$0.14_5 \pm 0.03_7$	0.147
$N_1 \cdots H_3$(S)	$0.14_8 \pm 0.08$	0.158

a) Experimental root-mean-square amplitudes of vibration determined in the present study with estimated limits of error (See text). Subscripts of the atom pairs follow those listed in Table 3.

b) Theoretical mean amplitudes for the *gauche* conformer given in Table 3.

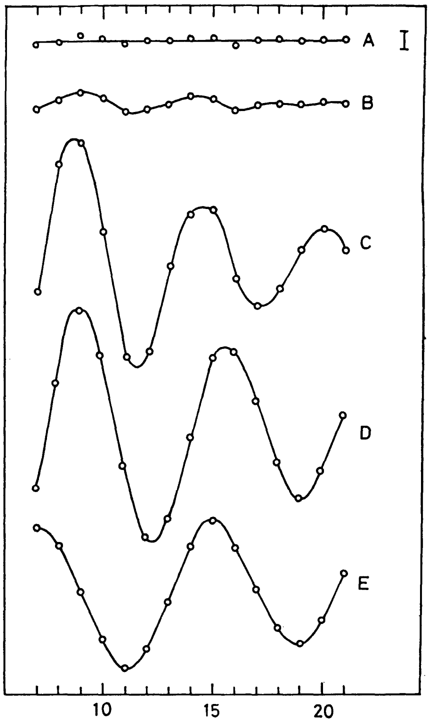

Fig. 4. Background functions I_b for different compositions of the *gauche* and other conformers. (See text).
(A) *gauche* (100%); (B) *gauche-trans* (95%: 5%);
(C) *trans* (100%); (D) *skew* (100%); (E) *cis* (100%).
The vertical bar represents the magnitude of 0.5% of I_b.

for leveling the total intensity $I_0(q)$. Theoretical molecular intensities $qM_c(q)$ were based on the structural parameters determined above, except that the ϕ_1 parameter was taken to be 0, 60, 120, and 180°. Typical I_b curves are illustrated in Fig. 4. The I_b curve corresponding to 100% *gauche* population is flat to within 0.5% of I_b, while other models are definitely unacceptable because of the systematic oscillations in the I_b curves.

The limit of uncertainty in the above results was estimated from two principal sources of errors:[17)] (A) random errors in the intensity measurement and (B) uncertainties in the structural parameters assumed in the analysis. The noise levels in I_b due to (A) was estimated to be 0.2% from the reproducibility of photographic measurements. Furthermore, the I_b function of nitrogen obtained by the same procedure had no fluctuation exceeding 0.2%. On the other hand, the uncertainties due to (B) originated principally from the assumption of the ϕ_2 parameter. In this analysis, the amino-hydrogen positions were averaged with a threefold potential $V(\phi_2)$ as mentioned in the preceding section. The systematic error due to this assumption was estimated to be 0.3% of I_b from similar analyses using the ϕ_2 parameter fixed to the staggered positions.

Therefore, the total uncertainty level of I_b was estimated to be 0.4%, corresponding to the limit of uncertainty in the concentration of 5%. Hence, in the temperature range from 50 to 120°C at least 95% of the molecule takes the *gauche* conformation in the gas phase.

Discussion

Structural Parameters. The C–C bond distance, 1.545 Å, seems to be about 0.01 Å longer than that in ethane, 1.534 Å,[18] while the C–N bond distance, 1.469 Å, is similar to that in methylamine, 1.467 Å.[19] The C–C–N bond angle, 110.2°, is nearly equal to the tetrahedral angle and is smaller than the C–C–C angles in normal alkanes (*e.g.*, 112° for butane).[20] The azimuthal angle ϕ_1, found to be 64°, is similar to that in butane[20] and is about 10° smaller than those in 1, 2-dichloroethane[21] and ethylene glycol.[22]

A related bicyclic compound, triethylenediamine,[1] has analogous C–C–N angle and C–N distance, whereas the C–C distance in triethylenediamine, 1.562 Å, is significantly longer than that in ethylenediamine. A similar lengthening in the C–C bond in a bicyclic compound as compared with normal alkanes has also been suggested for bicyclo[2.2.2]octane.[12]

The observed mean amplitudes, listed in Table 6, agree with the calculated values, which have comparable uncertainties. The calculated N···N amplitude is sensitive to the choice of Y(C–C): *e.g.*, 0.1641 Å for $Y=0.11$ md·Å and 0.1805 Å for $Y=0.083$ md·Å[23] (corresponding to that in ethane). Therefore, from the observed N···N amplitude of $0.145_4 \pm 0.037$ Å one can estimate Y(C–C) to be 0.16_7 md·Å. The Y value determined in this way[24] is about twice as large as that for ethane and is nearly equal to that for the *gauche* form of 1,2-dichloroethane, 0.16 md·Å.[25]

Rotational Isomerism. The *gauche* conformer is found to be by far the most stable in the gas phase; the fractions of any other conformers, if present, should not exceed 5%. This is analogous to the case of ethylene glycol[22] and contrasts with that in 1,2-dichloroethane,[21,26] where the *trans* form is about 1.14 kcal/mol more stable than the *gauche* form.

In order to examine the rotational isomerism in this molecule, a conformational analysis was carried out by a SCF-MO (CNDO/2) method[27] by the use of a program written by Segal.[28] The azimuthal angles ϕ_1 and ϕ_2 were varied systematically in all directions. Other structural parameters were fixed to the values determined in the present study. The results are illustrated in Fig. 5 as a contour map. The areas where the energies are less than 1 kcal/mol above the deepest minimum, enclosed in solid lines, are located in the neighborhood of $\phi_1=60°$ (*gauche*) and 180° (*trans*), with $\phi_2=60°$ or 300° (staggered). The cross sections of the energy surface at $\phi_2=60°$ or 300° show that the *gauche* form ($\phi_1=60°$) is about 0.9 kcal/mol more stable than the *trans* form (corresponding to the equilibrium fraction of about 10% around 100°C) and that the barrier heights at $\phi_1=0°$ and 120° are about 1.5 and 2.8 kcal/mol, respectively. The theoretical prediction about the *gauche*-minimum agrees with the present experiment, whereas the predicted energy difference between the *trans* and *gauche* forms is much too small. This discrepancy seems to be due to the fault in the theory, since the CNDO/2 method often gives proper estimates of molecular geometry but fails to predict correct energies.[29] More reliable information on the potential function should await future spectroscopic measurements.

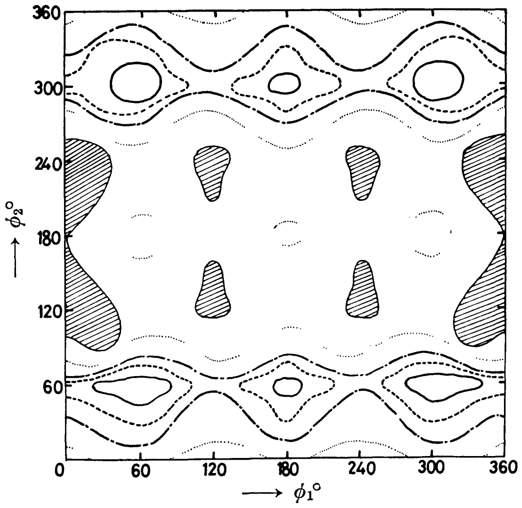

Fig. 5. Contour map for the potential energy of internal rotation of ethylenediamine calculated by the SCF–CNDO/2 method. (See text).

——: limits within 1 kcal/mol above the deepest minimum; ------: 2 kcal/mol; —·—: 3 kcal/mol; ······: 5 kcal/mol. Shaded regions indicate local maxima 10 kcal/mol above the minimum.

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