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Molecular Structure of Piperazine as Studied by Gas Electron Diffraction

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A study of piperazine by means of gas electron diffraction has given the following structural parameters (the r_g distances and the angles based on the r_α structure) with estimated limits of error: C–C=1.540±0.008 Å, C–N=1.467±0.004 Å, ∠C–C–N=110.4 ±0.8°, ∠C–N–C=109.0 ±0.8°, C–H=1.110±0.008 Å and ∠H–C–H=$109._1 \pm 5°$; the molecule takes a chair conformation. The C–C distance is nearly equal to that in cyclohexane, and the C–N–C angle is slightly smaller than the C–C–N angle. These angles agree with those predicted by an SCF-CNDO/2 method.

In succession of the studies of triethylenediamine[1] and ethylenediamine,[2] the molecular structure of diethylenediamine (piperazine: Fig. 1) has now been investigated by means of gas electron diffraction. Previous studies of this molecule (electron diffraction,[3] infrared,[4,5] and Raman[6]) showed that this molecule had a chair conformation (C_{2h} symmetry) analogous to cyclohexane. Davis and Hassel[3] reported that the C–N and C–C bond distances were 1.471 and 1.527 Å, respectively, the latter being claimed to be equal to that of cyclohexane, which they studied at the same time, 1.528 Å. However, their C–C distances are found to be about 0.013 Å shorter than that determined by a recent study of cyclohexane.[7] Furthermore, in comparison with the C–C distance in ethylenediamine,[2] 1.545±0.008 Å, their C–C distance seems to be questionably short. Their C–N distance and the C–C–N bond angle, on the other hand, seem to agree with those in ethylenediamine. The present paper reports on a reinvestigation of the piperazine structure and a comparison with those of analogous molecules.

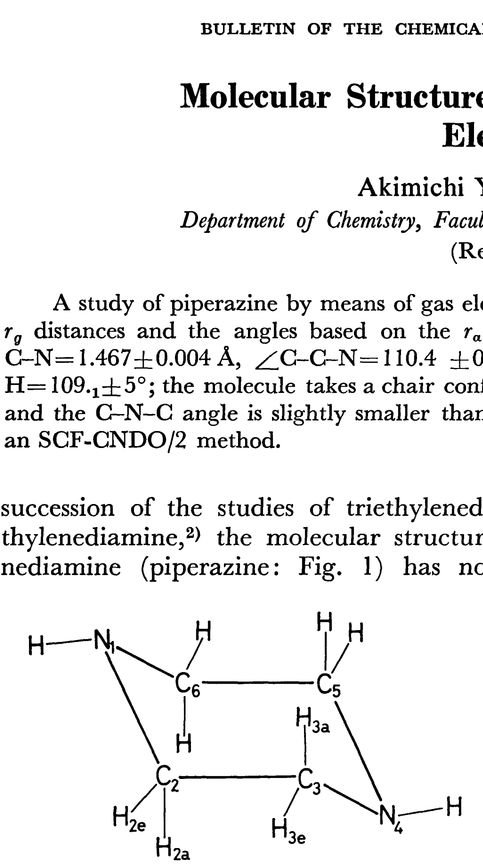

Fig. 1. The numbering of piperazine.

Experimental

Anhydrous piperazine (Guaranteed Reagent, above 99% pure) was purchased from the Tokyo Chemical Industry Co., Ltd. Diffraction photographs were taken on Fuji Process Hard plates at 130°C using a high-temperature nozzle assembly[1] with an apparatus equipped with an r^3-sector.[8] The accelerating voltage (stabilized to within 0.01%) and the beam current were about 40 kV and 0.44 μA, respectively.

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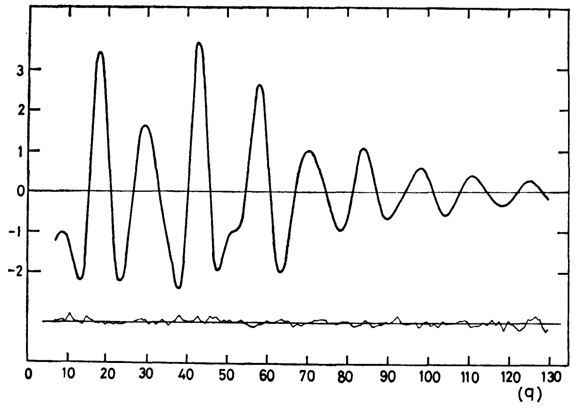

Fig. 2. Molecular intensity curve $qM(q)$ for piperazine. Upper curve: best-fit theoretical; lower curve: experimental minus theoretical.

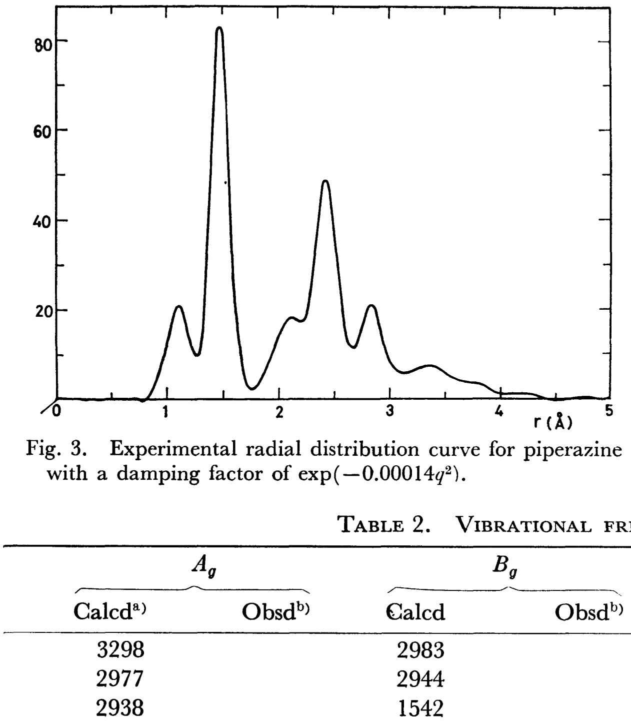

Fig. 3. Experimental radial distribution curve for piperazine with a damping factor of $\exp(-0.00014q^2)$.

The exposure times were about 150 and 60 sec for camera lengths of 113.69 and 249.06 mm. The vapor pressure of the sample at 130°C was estimated to be 70±30 Torr. The vacuum in the diffraction chamber was about 6×10^{-5} Torr during the exposure. In order to obtain correct scales of the diffraction patterns, photographs of reference gases (N_2 and CO_2 for the long and short camera lengths, respectively) were taken in experimental conditions similar to those for the sample, and the scale factors were calibrated to within 0.07% with reference to the r_a(C=O), 1.1646 Å,[8] and r_a(N–N), 1.1007 Å.[9] The photographic densities (0.19 to 0.57) of four plates for each camera length were measured at the intervals of integral q values with a digital microphotometer.[10] Experimental and theoretical molecular intensities and radial distribution function[11] are shown in Figs. 2 and 3, respectively.[12] Most of the calculations were performed by the use of a HITAC-5020E computer in the Computer Centre of the University of Tokyo.

Analysis

Mean Amplitudes of Vibration. The root-mean-square amplitudes and shrinkage corrections for thermal vibration[13] (at 130°C) were obtained from a normal-coordinate analysis by the use of the Urey-Bradley force constants estimated from those for cyclohexane[14]

TABLE 1. ESTIMATED FORCE CONSTANTS FOR PIPERAZINE[a]

K(C–C)	2.3	H(C–C–N)	0.30	F(C–C–N)	0.70
K(K–N)	5.5	H(C–N–C)	0.35	F(C–N–C)	0.30
K(C–H)	4.3	H(C–C–H)	0.25	F(C–C–H)	0.47
K(N–H)	5.6	H(N–C–H)	0.28	F(N–C–H)	0.52
Y(C–C)	0.11	H(C–N–H)	0.32	F(C–N–H)	0.46
Y(C–N)	0.11	H(H–C–H)	0.42	F(H–C–H)	0.07

a) The Urey-Bradley force constants for piperazine estimated from those for cyclohexane[14] and several amides.[15] In md/Å units (except for Y in md·Å).

TABLE 2. VIBRATIONAL FREQUENCIES FOR PIPERAZINE (cm^{-1})

A_g		B_g		A_u		B_u	
Calcd[a]	Obsd[b]	Calcd	Obsd[b]	Calcd	Obsd[c]	Calcd	Obsd[c]
3298		2983		2976	2944	3298	3328
2977		2944		2929		2984	
2938		1542		1539		2944	2941
1441	1431	1484	1451	1445	1444	1506	1458
1318		1320		1309	1320	1336	1382
1297	1279	1277	1279	1293	1271	1307	1323
1190	1109	1261	1184	1231	1197	1079	1076
1086	1023	848	836	1011	1138	992	977
926		514	515	941	983	900	839
803				254		613	633
503	448					248	
390	404						

a) Calculated by the use of the Urey-Bradley force constants listed in Table 1.
b) Observed by Raman spectra (Ref. 6).
c) Observed by infrared spectra (Refs. 4 and 5).

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

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[12] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7111). 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.

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Table 3. Calculated mean amplitudes and shrinkage corrections for piperazine[a)]

i—j	l_{ij}	d_{ij}	i—j	l_{ij}	d_{ij}
N_1—C_2	451	31	$N_1\cdots H_4$	1033	21
$N_1\cdots C_3$	657	4	C_2—H_2	787	120
C_2—C_3	520	23	$C_2\cdots H_1$	1021	74
$C_2\cdots C_6$	711	0	$C_2\cdots H_3$	1010	74
$C_3\cdots C_6$	715	−10	$C_2\cdots H_4$	988	43
$N_1\cdots N_4$	694	−9	$C_6\cdots H_{2a}$	1638	−22
N_1—H_1	738	148	$C_6\cdots H_{3a}$	1596	−35
$N_1\cdots H_2$	1057	78	$C_6\cdots H_{2e}$	1013	41
$N_1\cdots H_{3a}$	1561	−12	$C_6\cdots H_{3e}$	1080	17
$N_1\cdots H_{3e}$	1000	43			

a) Mean amplitudes (l_{ij}) and shrinkage corrections (d_{ij}) calculated for 130°C by the use of the force constants in Table 1. In 10^{-4} Å units. The hydrogen-hydrogen pairs are not listed.

and amides[15)] (Table 1). The calculation was based on a C_{2h} structure with an equatorial N–H bond (see next subsection). The vibrational frequencies of piperazine calculated in this way are compared in Table 2 with observed infrared and Raman frequencies,[4,6)] to which a tentative assignment, similar to that of Hendra and Powell,[5)] was made. The mean amplitudes and vibrational corrections obtained here are listed in Table 3. The vibrational corrections and some of the mean amplitudes were used as fixed constants in the least-squares analysis.

Determination of Molecular Structure. The radial distribution curve has confirmed a chair (C_{2h}) conformation of the piperazine skeleton but has given no evidence as to the orientation of the N–H bonds (equatorial and/or axial). In this connection, Katritzky *et al.*[16,17)] reported from the measurements of the dipole moments and the infrared NH-overtone spectra of piperidine that the N-hydrogen atom prefers the equatorial position in the gas phase and in non-interacting solvents with the ΔG^0 of 0.4—0.5 kcal/mol.

In order to determine the structural parameters, the following assumptions about the hydrogen positions were made for the r_α structure[18)] of C_{2h} symmetry.

Table 5. Structural parameters for piperazine

	Present study[a)]	Davis & Hassel[b)]
C——C	1.540±0.008	1.527±0.005
C——N	1.467±0.004	1.471±0.005
∠C–C–N	110.4±0.8°	109.8±0.5°
∠C–N–C	109.0±0.8°	112.6±0.5°
C——H	1.110±0.008	1.11$_2$±0.01
∠H–C–H	109.$_1$±5°	——
k	0.97±0.06	——

a) The r_g distances (Å) and the angles based on the r_α structure determined in the present study with estimated limits of error. The index of resolution k is dimensionless.

b) Ref. 3, where the physical significance of the parameters and their errors is not specified.

Table 6. Mean amplitudes for piperazine (in Å units)

Atom pair	Obsd[a)]	Calcd[b)]
N_1——C_2	0.048±0.005	0.045$_1$
$N_1\cdots\cdots C_3$	0.069±0.006	0.065$_7$
C_2——C_3	0.053±0.02$_2$	0.052$_0$
$C_2\cdots\cdots C_6$	0.065±0.02$_0$	0.071$_1$
$C_3\cdots\cdots C_6$	0.069±0.01$_7$	0.071$_5$
C_2——H_2	0.072±0.007	0.078$_7$
$C_2\cdots\cdots H_3$	0.110±0.07	0.101$_0$
$N_1\cdots\cdots H_2$	0.115±0.08	0.105$_7$

a) Determined by a least-squares analysis with estimated limits of error.

b) Calculated values in Table 3.

Table 4. Error matrix for piperazine[a)]

	X_1	X_2	X_3	X_4	X_5	X_6	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8	k
X_1	32	−17	8	−36	2	44	12	−20	−45	−25	−17	−5	82	−79	−63
X_2		16	−2	16	−8	13	−8	12	29	16	10	6	−48	45	42
X_3			32	−8	−8	40	5	7	14	9	7	10	6	−12	40
X_4				56	−40	−108	4	8	13	−49	−44	−8	25	24	16
X_5					59	67	4	20	−25	34	47	−14	−61	58	−51
X_6						331	−22	38	76	99	72	25	−216	183	134
l_1							21	−6	−22	−9	−4	5	28	−26	−16
l_2								20	28	−6	18	11	−60	55	51
l_3									75	40	28	24	−97	88	120
l_4										65	47	15	31	−41	72
l_5											56	13	−32	21	56
l_6												22	−16	4	59
l_7													275	242	−143
l_8														282	122
k															246

a) Error matrix for the independent parameters (X_i) and mean amplitudes (l_i): X_1=C–C, X_2=C–N, X_3=C–H, X_4=∠C–C–N, X_5=∠C–N–C, X_6=∠H–C–H, $l_1=N_1$–C_2, $l_2=N_1$–C_3, $l_3=C_2$–C_3, $l_4=C_2$–C_6, $l_5=C_3$–C_6, $l_6=C_2$–H_2, $l_7=C_2$–H_3, $l_8=N_1$–H_2. Units ($\times 10^{-4}$) for the distances are Å, those for the angles are rad., and the index of resolution k is dimensionless.

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(1) The N–H bonds are equatorial, and the C–N–H angle is equal to that in dimethylamine, 108.8°.[19]

(2) The N–H bond distance is equal to that in ammonia, r_g (N–H) = 1.0302 Å.[20]

(3) The C–C–N plane is perpendicular to the H–C–H plane and bisects the H–C–H bond angle, and *vice versa*.

By taking into account the above geometrical constraints, the total number of the independent parameters was reduced to six: the C–N, C–C and C–H distances, and the C–C–N, C–N–C and H–C–H angles. They were determined, together with an index of resolution and several mean amplitudes, by a least-squares analysis on the molecular intensity curves. The error matrix[21] is listed in Table 4, and the most probable values of the structural parameters and the mean amplitudes are given in Tables 5 and 6 with estimated limits of error including random and systematic errors. The experimental systematic uncertainties in the scale factor and sector imperfection[18] were estimated to be 0.08% in total, while those due to the geometrical constraints mentioned above were estimated to be of the order of random standard errors, since moderate changes in the assumed values had no effect on the most probable values beyond their random standard deviations. The systematic errors in the mean amplitudes were estimated to be 5%,[18] within which the observed mean amplitudes agree with the calculated values. This justifies the above estimation of the force constants; in addition, the systematic errors caused by the use of constant parameters for some of the mean amplitudes seem to have little effect.

Discussion

The structural parameters determined in the present study are compared in Table 7 with those of related compounds studied by gas electron diffraction. The C–C distance, 1.540±0.008 Å, is significantly longer than that reported previously by Davis and Hassel,[3] 1.527±0.005 Å, and is essentially equal to that in cyclohexane,[7] 1.540 Å, and in ethylenediamine,[2] 1.545±0.008 Å, whereas that in triethylenediamine[1] is about 0.02 Å longer, as has been discussed in Ref. 2. The C–N distances in the three molecules are essentially equal to one another and are similar to that in methylamine, 1.467±0.002 Å.[22] In this connection, the C–N distance in dimethylamine is measured to be $r_g = 1.455 \pm 0.002$ Å,[23] $r_s = 1.466 \pm 0.005$ Å,[19] while that in trimethylamine is $r_g = 1.454 \pm 0.002$ Å,[23] $r_s = 1.451 \pm 0.003$ Å.[24] As for bond angles, piperazine, ethylenediamine and triethylenediamine have nearly equal C–C–N angles of about 110°. They are slightly smaller than the C–C–C angles observed in cyclohexane (111.4°)[7] and in normal alkanes (*e.g.*, butane, 112.2°).[25] The C–N–C bond angle, 109.0°±0.8°, supersedes that reported in Ref. 3, 112.6°±0.5°. The hydrogen parameters (C–H and ∠H–C–H) determined in the present study seem to be compatible with those in cyclohexane.[7]

TABLE 7. STRUCTURES OF PIPERAZINE AND RELATED COMPOUNDS

	DED[a]	TED[b]	EDA[c]
C——C	1.540±0.008	1.562±0.009	1.545±0.008
C——N	1.467±0.004	1.472±0.007	1.469±0.004
∠C–C–N	110.4±0.8°	110.2±0.4°	110.2±0.7°
∠C–N–C	109.0±0.8°	108.7±0.4°	——
C——H	1.110±0.008	$1.11_0 \pm 0.01_2$	1.109±0.008
∠H–C–H	$109._1 \pm 5$	$111._5 \pm 5._6$°	$112._7 \pm 8._5$°

DED: piperazine, TED: triethylenediamine, EDA: ethylenediamine. a—c): r_g distances (Å) and r_α angles with estimated limts of error.

a) Present study.

b) Ref. 1.

c) Ref. 2.

A conformational analysis[2] by the use of a CNDO/2 program[26] written by Segal[27] was made with the C–C–N and C–N–C angles varied from 100° to 120° in step of 0.5°. Other structural parameters were set equal to the values determined above. A set of ∠C–C–N = 110.5° and ∠C–N–C = 109.5° gave the minimum energy, and hence, the calculation is in agreement with the present experiment.

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