# Structural and Conformational Studies of *N*,*N*-Dichloroethanamine and *N*,*N*-Dichloro-2-propanamine by Gas Electron Diffraction Combined with ab Initio Calculations

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The molecular structure and conformation of *N*,*N*-dichloroethanamine ($EtNCl_2$, NDCEA) and *N*,*N*-dichloro-2-propanamine (*i*-$PrNCl_2$, NDCPA) were studied by gas electron diffraction. The optimized structures and the force constants obtained by MP2/6-31G** ab initio calculations were used in the analyses. The force constants were scaled to reproduce the vibrational wavenumbers of the gas-phase infrared spectra measured in the present study. At room temperature, NDCEA exists in a conformational equilibrium of $C_1$ and $C_s$ forms and the abundance of the $C_1$ conformer is 79 ± 9%. The abundance of the $C_1$ for NDCPA is 88 ± 12%. The structural parameters ($r_g$ and $\angle_\alpha$) for the $C_1$ conformer of NDCEA are as follows: $r(\mathrm{N-C}) = 1.479(6)$ Å; $r(\mathrm{C-C}) = 1.542(7)$ Å; $\langle r(\mathrm{N-Cl})\rangle = 1.759(2)$ Å; $\langle r(\mathrm{C-H})\rangle = 1.107(8)$ Å; $\angle\mathrm{N-C-C} = 108.2(8)°$; $\langle\angle\mathrm{C-N-Cl}\rangle = 108.2(3)°$; $\angle\mathrm{Cl-N-Cl} = 106.9(2)°$; $\phi\ \mathrm{C-C-N-Cl_g} = -76(2)°$. Angle brackets denote averaged values and parenthesized values are the estimated limits of error ($3\sigma$) referring to the last significant digit. $Cl_g$ means the Cl atom gauche to the C−C bond. Those for the $C_1$ conformer of NDCPA are as follows: $r(\mathrm{N-C}) = 1.496(11)$ Å; $\langle r(\mathrm{C-C})\rangle = 1.531(6)$ Å; $\langle r(\mathrm{N-Cl})\rangle = 1.762(2)$ Å; $\langle r(\mathrm{C-H})\rangle = 1.119(5)$ Å; $\langle\angle\mathrm{N-C-C}\rangle = 112.4(8)°$; $\angle\mathrm{C-C-C} = 108.3(18)°$; $\langle\angle\mathrm{C-N-Cl}\rangle = 109.1(6)°$; $\angle\mathrm{Cl-N-Cl} = 106.7(4)°$; $\phi\ \mathrm{C_t-C-N-Cl_g} = 63(3)°$. $C_t$ means the C atom trans to the lone pair of the N atom, and $Cl_g$ means the Cl atom gauche to the C−H bond of the α carbon.

## Introduction

We have determined the geometrical structures of some monochloroamines, $Me_2NCl$,[1] $Et_2NCl$,[2] and $(CH_2)_3NCl$,[3] by means of gas electron diffraction method. Durig et al. pointed out that the N−Cl bond length is sensitive to the chemical environment of the nitrogen atom, that is, the substituent attached to it,[4] and our studies as well as the one for $NCl_3$[5] have confirmed that. However, structural data are still quite scarce for the compounds with the N−Cl bond. For further investigation, therefore, *N*,*N*-dichloroethanamine ($EtNCl_2$, NDCEA) and *N*,*N*-dichloro-2-propanamine (*i*-$PrNCl_2$, NDCPA), that are *N*,*N*-dichlorinated compounds of ethylamine and isopropylamine, respectively, are chosen as target molecules for the structural determination in the present study. Neither experimental nor theoretical study has been reported on the structures of these molecules. As shown in Figure 1, each of these molecules is expected to have two conformers, $C_1$ and $C_s$, and hence, another interest in these molecules is focused on the conformational stability.

In addition to electron diffraction experiments, the measurement of infrared spectra in the gas phase and ab initio calculations have been carried out in order to obtain supporting information. The results of the ab initio calculations have been used for the structural constraints and vibrational analyses as described later. The purpose of the measurement of infrared spectra is two-fold, that is, to monitor the progress of the dichlorination of the amines and to check the reliability of force constants.

## Experimental Section

**Samples.** The samples of dichloroamines were prepared by the dichlorination of ethylamine and isopropylamine by means of the direct contact with *N*-chlorosuccinimide (NCS). The sample of ethylamine was obtained by adding commercial sample of ethylamine hydrochloride (Nacalai Tesque Inc.) to an aqueous solution of NaOH followed by vacuum distillation. The obtained amine was further desiccated by using metallic sodium. The sample of isopropylamine was purchased from Nacalai Tesque Inc. and was used after vacuum distillation. *N*,*N*-dichlorinations of the amines were carried out by condensing them on an excess amount of the NCS powder. The reaction vessel was kept at room temperature while the reaction proceeded, and the obtained gaseous products were taken out from the vessel shortly before electron diffraction experiments.

**Infrared Spectra.** The vapor-phase infrared spectra of amines and *N*,*N*-dichloroamines were measured by using a BOMEM DA 3.16 Fourier-transform spectrometer with a resolution of 0.5 $cm^{-1}$. An absorption cell with a path length of 10 cm was used with KBr windows. Observed spectra are shown in Figures 2 and 3. The spectra measured shortly after the condensation

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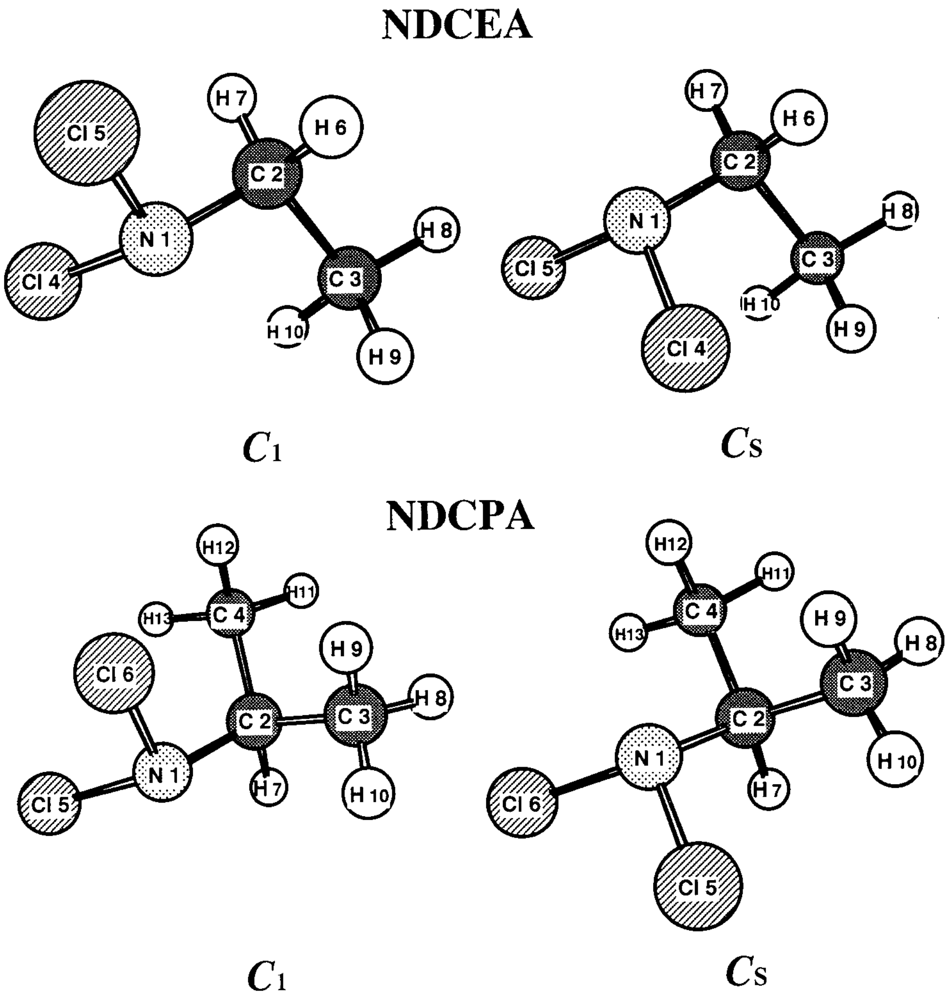

**Figure 1.** Molecular models and atom numbering for the $C_1$ and $C_s$ conformers of NDCEA and NDCPA.

of the amines on the NCS (Figures 2b and 3b) show new peaks at about 700 and 600 cm$^{-1}$, which were assigned to the $NCl_2$ antisymmetric and symmetric stretching modes, respectively, and the rapid decreases in the strong peaks of $NH_2$ bending (about 800 cm$^{-1}$). In these spectra, some peaks that do not appear in the spectra of amines (Figures 2a and 3a) or the final products (Figures 2c and 3c) are also observed (the peaks marked with asterisk in the figures). The asterisked peaks in Figure 2b were identified as those of monochloroamine, EtNHCl, by referring to the literature.[6] Accordingly, the asterisked peaks in Figure 3b, that are similar in the time evolution to those in Figure 2b, were also assigned to the monochloroamine, *i*-PrNHCl. Therefore, it is concluded that neither amines nor monochloroamines are present in the final products and hence that the dichlorination reactions have proceeded completely. The observed vibrational wavenumbers of the final products are listed in Table 1.

**Gas Electron Diffraction.** Electron diffraction patterns of NDCEA and NDCPA were recorded on 8 × 8 in. Kodak projector slide plates with an apparatus equipped with an $r^3$-sector[7] at room temperature. The accelerating voltage of incident electrons was about 37 kV. The diffraction patterns of $CS_2$ were recorded in the same sequence of exposures as the samples. The photographic plates were developed for 4.5 min in Dektol developer diluted 1:1. The photometry process was the same as that described elsewhere in details.[8] The experimental intensities and backgrounds are available as Supporting Information (Table S1). The electron wavelength was calibrated to the known $r_a$(C=S) distance of $CS_2$ (1.5570 Å).[9] Other experimental conditions are summarized in Table 2.

Elastic atomic scattering factors were calculated as described in ref 10, and inelastic ones were taken from ref 11. The experimental molecular scattering intensities are shown in Figure 4 along with the calculated ones in the final data analysis.

## Ab Initio Calculations

Structure optimizations and vibrational frequency calculations for the $C_1$ and $C_s$ conformers of NDCEA and NDCPA were carried out with the program GAUSSIAN 94.[12] The level of theory applied was MP2 (frozen core)[13] with the 6-31G** basis set. The obtained structural parameters and conformational energies are listed in Table 3.

As shown in Table 3, there are significant differences between the theoretical geometries of NDCEA and NDCPA and between the geometries of the $C_1$ and $C_s$ conformers of each species. The followings are remarkable features. (1) The N−C distance of NDCPA is about 0.01 Å longer than that of NDCEA. (2) The N−C−C angle of the $C_s$ conformer of NDCEA is about 8.6° larger than that of the $C_1$ conformer. Similarly, the $N_1-C_2-C_4$ angle of the $C_1$ conformer of NDCPA is much larger than the other N−C−C angles of this molecule ($N_1-C_2-C_3$ of the $C_1$, and $N_1-C_2-C_{3,4}$ of the $C_s$). (3) The $C_1$ conformers of NDCEA and NDCPA have almost the same Cl−N−Cl angle (107.6° and 107.9°, respectively). However, the $C_s$ conformer of NDCEA has larger, and the $C_s$ conformer of NDCPA has much smaller, Cl−N−Cl angles. (4) The C−C−C angle for the $C_1$ conformer of NDCPA is 2.7° larger than that for the $C_s$

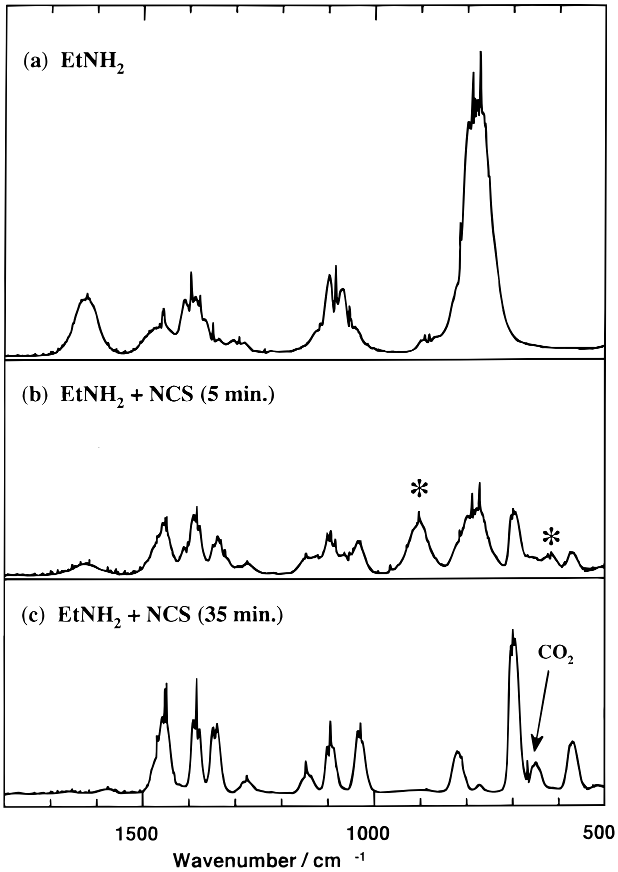

**Figure 2.** Infrared spectra of the reaction product of ethylamine with NCS: (a) ethylamine; (b) reaction product sampled 5 min after the condensation of ethylamine on NCS (see Experimental Section for the asterisked peaks); (c) reaction product sampled 35 min after the condensation. The R- and Q-branches of contaminate $CO_2$ are marked.

conformer. Most of these features can be accounted for qualitatively in terms of the Cl···$CH_3$ steric repulsion. For example, the methyl group of the $C_s$ conformer of NDCEA has repulsive interactions with both $Cl_4$ and $Cl_5$ in contrast to the methyl group of the $C_1$ conformer for which only $Cl_4$ atom is in the position to have the repulsion (see Figure 1). This can explain the N−C−C angle difference between the $C_s$ and $C_1$ conformers of NDCEA (feature (2) above). These features were included in the analyses of the gas electron diffraction data (see the following section).

For both NDCEA and NDCPA, the $C_1$ conformer is slightly more stable than the $C_s$ one, and hence, the former is expected to have more than twice the abundance of the latter because its statistical weight is 2.

## Analyses

**Normal Vibration Analyses.** The Cartesian force constants obtained from the MP2/6-31G** calculations were transformed into the symmetrized internal force constants, $F_{ij}$, which were then modified by the scaling method in order to reproduce the observed vibrational wavenumbers. The linear scaling formula[14]

$$F_{ij}\,(\text{scaled}) = (c_i c_j)^{1/2} F_{ij}\,(\text{unscaled})$$

was adopted, where $c_i$ is the scale factor. After some trials of the normal vibration calculations for the $C_1$ conformers, the $c_i$ was chosen to be 0.85 for CH, $CH_2$ and $CH_3$ stretching modes and to be 0.90 for the other vibrational modes. Resultant vibrational wavenumbers are listed in Table 1. The agreement between the observations and calculations is better than 1% for most of the values of both NDCEA and NDCPA as shown in the Table. The definitions of internal coordinates and the corresponding scaled force constants are listed in Tables S2 and S3 of the Supporting Information, respectively.

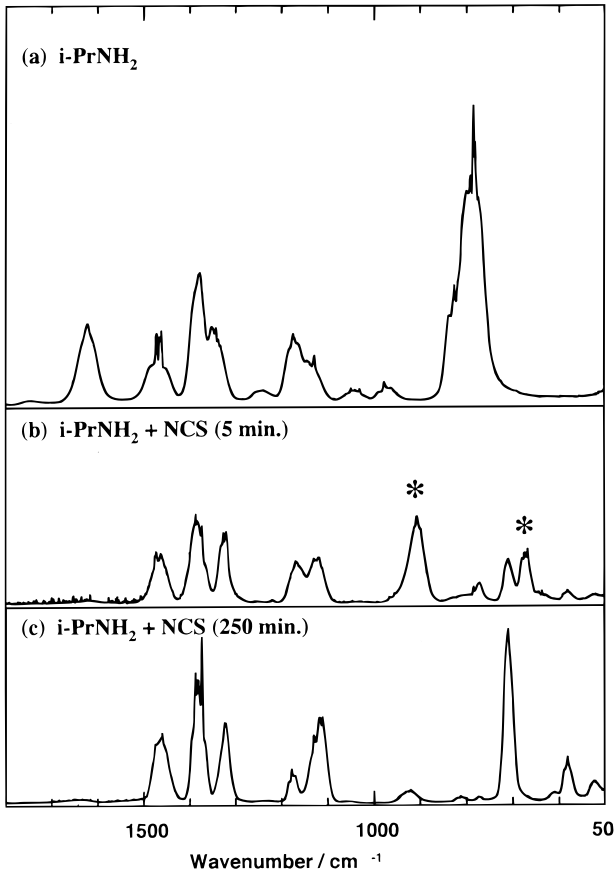

**Figure 3.** Infrared spectra of the reaction product of isopropylamine with NCS: (a) isopropylamine; (b) reaction product sampled 5 min after the condensation of isopropylamine on NCS (see Experimental Section for the asterisked peaks); (c) reaction product sampled 250 min after the condensation.

**Analyses of Electron Diffraction Data.** In the analyses of the gas electron diffraction data, the $C_1$ and $C_s$ conformers were assumed to coexist and the abundance of the former was varied as an independent parameter. Similar geometrical parameters were bound together and were refined as groups in order to reduce the number of adjustable variables. The differences among the bound parameters were fixed at the MP2/6-31G** values. The independent parameters and the constraints are summerized in Table 4.

Mean amplitudes, $l$, and shrinkage corrections,[15] $r_a - r_\alpha$, were calculated from the above-mentioned scaled force constants. The small-amplitude vibrational model was adopted. The mean amplitudes were adjusted in groups. The groups were separated according to the distances of the atomic pairs at $r_a = 1.30$, 2.00, and 3.05 (3.00 for NDCPA) Å. The differences among mean amplitudes in each group were fixed at the calculated values. The first group ($r_a = 0.0-1.30$ Å) corresponds to the C−H bonds, the second group ($r_a = 1.30-2.00$ Å) to the C−C, C−N and N−Cl bonds, and the third group ($r_a = 2.00-3.05$ Å) to the nonbonded N···C, C···C, and C···H, etc. The mean amplitudes with the corresponding $r_a$ distances and the grouping are listed in Table 5. The anharmonicity parameters,[16] $\kappa$, for bonded atom pairs were estimated in a diatomic approximation,[17] $\kappa = (a/6)l^4$, where the Morse parameter, $a$, was assumed to

**TABLE 1: Observed and Calculated Vibrational Wavenumbers (in cm$^{-1}$) and Assignment of NDCEA and NDCPA**

| mode | $\nu_{obs}$[a] | | $\nu_{calc}$[b] | assignments |
|---|---|---|---|---|
| | | | | (a)NDCEA |
| $\nu_1$ | 3003 | s | 3005.2 | $CH_3$ a.sym. stretch |
| $\nu_2$ | 2991 | vs | 2986.7 | $CH_3$ a.sym. stretch |
| $\nu_3$ | 2935 | s | 2955.9 | $CH_2$ a.sym. stretch |
| $\nu_4$ | 2886 | w | 2899.5 | $CH_3$ sym. stretch |
| $\nu_5$ | 2874 | w | 2883.4 | $CH_2$ sym. stretch |
| $\nu_6$ | 1470 | m | 1485.4 | $CH_3$ a.sym. deform |
| $\nu_7$ | 1452 | s | 1466.6 | $CH_3$ a.sym. deform |
| $\nu_8$ | 1449 | s | 1462.5 | $CH_2$ scissor |
| $\nu_9$ | 1384 | s | 1390.1 | $CH_3$ sym. deform |
| $\nu_{10}$ | 1345 | m | 1343.2 | $CH_2$ wag |
| $\nu_{11}$ | 1276 | vw | 1269.6 | $CH_2$ twist |
| $\nu_{12}$ | 1148 | w | 1145.2 | $CH_2$ rock + $CH_3$ rock |
| $\nu_{13}$ | 1096 | m | 1092.6 | $CH_3$ rock |
| $\nu_{14}$ | 1031 | m | 1036.4 | C−C stretch + N−C stretch |
| $\nu_{15}$ | 888 | vw | 882.4 | N−C stretch + $CH_3$ rock |
| $\nu_{16}$ | 820 | w | 807.6 | $CH_2$ rock + $CH_3$ rock |
| | 774 | vw | 796.1 | $CH_3$ rock + $CH_2$ rock of the $C_s$ |
| $\nu_{17}$ | 701 | vs | 702.1 | N−Cl a.sym. stretch |
| $\nu_{18}$ | 570 | w | 569.4 | N−Cl sym. stretch |
| $\nu_{19}$ | | | 384.8 | $NCl_2$ sym. deform |
| $\nu_{20}$ | | | 380.0 | $NCl_2$ sym. deform + N-C−C bend |
| $\nu_{21}$ | | | 280.1 | Cl−N−Cl bend |
| $\nu_{22}$ | | | 232.4 | C−C torsion |
| $\nu_{23}$ | | | 225.3 | N−C−C bend + C−N−Cl bend |
| $\nu_{24}$ | | | 122.4 | N−C torsion |
| | | | | (b) NDCPA |
| $\nu_1$ | 2995 | vs | 2998.0 | $CH_3$ a.sym. stretch |
| $\nu_2$ | | | 2995.6 | $CH_3$ a.sym. stretch |
| $\nu_3$ | 2987 | vs | 2983.8 | $CH_3$ a.sym. stretch |
| $\nu_4$ | | | 2980.6 | $CH_3$ a.sym. stretch |
| $\nu_5$ | | | 2901.9 | CH stretch |
| $\nu_6$ | | | 2896.4 | $CH_3$ sym. stretch |
| $\nu_7$ | 2948 | m | 2892.8 | $CH_3$ sym. stretch |
| | 2906 | w | 2873.4 | CH stretch of the $C_s$ |
| $\nu_8$ | 1475 | m | 1488.8 | $CH_3$ a.sym. deform |
| $\nu_9$ | 1460 | m | 1474.6 | $CH_3$ a.sym. deform |
| $\nu_{10}$ | | | 1468.0 | $CH_3$ a.sym. deform |
| $\nu_{11}$ | | | 1462.2 | $CH_3$ a.sym. deform |
| $\nu_{12}$ | 1388 | s | 1390.7 | $CH_3$ sym. deform |
| $\nu_{13}$ | 1374 | vs | 1375.3 | $CH_3$ sym. deform |
| $\nu_{14}$ | 1324 | m | 1324.4 | CH rock |
| $\nu_{15}$ | | | 1317.1 | CH rock |
| $\nu_{16}$ | 1179 | w | 1179.6 | $CH_3$ rock |
| $\nu_{17}$ | 1131 | m | 1133.2 | C−C a.sym. stretch |
| $\nu_{18}$ | 1112 | m | 1112.8 | $CH_3$ rock |
| $\nu_{19}$ | | | 933.4 | $CH_3$ rock |
| $\nu_{20}$ | | | 931.2 | N−C stretch + C−C sym. stretch |
| $\nu_{21}$ | 922 | vw | 915.9 | $CH_3$ rock |
| $\nu_{22}$ | 814 | vw | 806.9 | C−C sym. stretch + N−C stretch |
| $\nu_{23}$ | 711 | vs | 714.2 | N−Cl a.sym. stretch |
| | 612 | vw | 604.9 | N−Cl sym. stretch + $NCl_2$ sym. deform of the $C_s$ |
| $\nu_{24}$ | 582 | w | 577.2 | $NCl_2$ sym. deform + N−Cl sym. stretch + N-C−C bend |
| $\nu_{25}$ | 524 | vw | 514.4 | skeletal deform |
| $\nu_{26}$ | | | 425.9 | C−C−C bend + skeletal deform |
| $\nu_{27}$ | | | 337.9 | C−C−C bend |
| $\nu_{28}$ | | | 281.6 | Cl−N−Cl bend + $NCl_2$ sym. deform |
| $\nu_{29}$ | | | 243.4 | C−C torsion |
| $\nu_{30}$ | | | 238.3 | Cl−N−Cl bend |
| $\nu_{31}$ | | | 226.0 | C−N−Cl bend + C−C torsion |
| $\nu_{32}$ | | | 212.2 | C−C torsion + C−N−Cl bend |
| $\nu_{33}$ | | | 94.8 | N−C torsion |

[a] Abbreviations used: a.sym., anti symmetric; vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [b] Calculated for the $C_1$ conformers.

**TABLE 2: Experimental Conditions for Gas Electron Diffraction Experiments of NDCEA and NDCPA**

| | NDCEA | NDCPA |
|---|---|---|
| camera distance/mm | 244.4 | 244.4 |
| room temperature/K | 296.4 | 290.3 |
| electron wavelength/Å | 0.06348 | 0.06330 |
| uncertainty of the scale factor/% | 0.14 | 0.03 |
| sample pressure/Torr | 20 | 12 |
| background pressure during exposure/$10^{-6}$ Torr | 2 | 7 |
| beam current/$\mu$A | 2.64 | 1.53 |
| exposure time/s | 38−40 | 87−97 |
| number of plates used | 4 | 4 |
| range of $s$ value/Å$^{-1}$ | 4.2−33.0 | 4.5−33.8 |

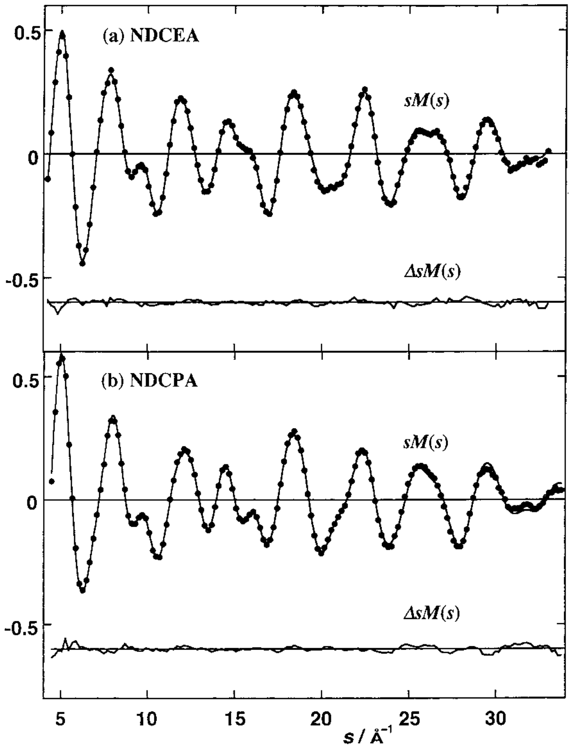

**Figure 4.** Experimental (dots) and theoretical (solid curves) molecular scattering intensities of (a) NDCEA and (b) NDCPA; $\Delta sM(s) = sM(s)^{obs} - sM(s)^{calc}$. The theoretical curves were calculated from the best-fit parameters.

be 2.0 Å$^{-1}$. Those for nonbonded atom pairs were assumed to be zero.

## Results and Discussion

In Table 6, the obtained structural and conformational parameters are listed along with those for amines.[18,19] Radial distribution curves are shown in Figure 5. The $R$-factors[20] for NDCEA and NDCPA are 0.064 and 0.070, respectively. The correlation matrices in the least-squares calculations are given in Table S4 of the Supporting Information. None of their off-diagonal elements exceeded ±0.85.

It is clear that the $r$(N−C) of NDCPA is significantly longer than that of NDCEA as qualitatively predicted by the MP2/6-31G** calculations. On the other hand, those of the unchlorinated amines are the same as that of NDCEA within the error limits. This shows the steric repulsion between the isopropyl group and the $NCl_2$ part is stronger than those of the other combinations of ethyl, isopropyl, amino, and $NCl_2$ groups. Our systematic investigation of the steric repulsion of the alkyl groups has revealed that there is a significant change in the

**TABLE 3: Geometrical Parameters and Relative Energies for the $C_1$ and $C_s$ Conformers of NDCEA and NDCPA Obtained from the MP2(frozen core)/6-31G** ab Initio Calculations**

(a) NDCEA

| parameters[a] | $C_1$ conformer | $C_s$ conformer |
|---|---|---|
| Bond Lengths (in Å) | | |
| $N_1-C_2$ | 1.483 | 1.484 |
| $N_1-Cl_4$ | 1.771 | 1.770 |
| $N_1-Cl_5$ | 1.772 | 1.770 |
| $C_2-C_3$ | 1.516 | 1.518 |
| $C_2-H_6$ | 1.089 | 1.090 |
| $C_2-H_7$ | 1.093 | 1.090 |
| $C_3-H_8$ | 1.089 | 1.089 |
| $C_3-H_9$ | 1.088 | 1.087 |
| $C_3-H_{10}$ | 1.087 | 1.087 |
| Bond Angles (in degree) | | |
| $C_2-N_1-Cl_4$ | 108.3 | 108.9 |
| $C_2-N_1-Cl_5$ | 107.3 | 108.9 |
| $Cl_4-N_1-Cl_5$ | 107.6 | 108.7 |
| $N_1-C_2-C_3$ | 109.9 | 118.4 |
| $N_1-C_2-H_6$ | 104.2 | 103.6 |
| $N_1-C_2-H_7$ | 111.5 | 103.6 |
| $C_3-C_2-H_6$ | 110.3 | 111.1 |
| $C_3-C_2-H_7$ | 112.1 | 111.1 |
| $H_6-C_2-H_7$ | 108.5 | 108.2 |
| $C_2-C_3-H_8$ | 109.0 | 108.9 |
| $C_2-C_3-H_9$ | 110.2 | 111.2 |
| $C_2-C_3-H_{10}$ | 111.7 | 111.2 |
| $H_8-C_3-H_9$ | 108.6 | 108.2 |
| $H_8-C_3-H_{10}$ | 108.3 | 108.2 |
| $H_9-C_3-H_{10}$ | 108.9 | 108.2 |
| Dihedral Angles (in degree) | | |
| $Cl_4-N_1-C_2-C_3$ | −70.6 | 59.2 |
| $Cl_4-N_1-C_2-H_6$ | 171.3 | −64.4 |
| $Cl_4-N_1-C_2-H_7$ | 54.4 | −177.3 |
| $Cl_5-N_1-C_2-C_3$ | 173.5 | −59.2 |
| $Cl_5-N_1-C_2-H_6$ | 55.4 | 177.3 |
| $Cl_5-N_1-C_2-H_7$ | −61.5 | 64.4 |
| $N_1-C_2-C_3-H_8$ | −171.1 | 180.0 |
| $N_1-C_2-C_3-H_9$ | −52.0 | −60.8 |
| $N_1-C_2-C_3-H_{10}$ | 69.2 | 60.8 |
| $\Delta E$/kcal mol$^{-1}$ | 0.000[b] | 0.715 |
| $\Delta G$ (at 300 K)/kcal mol$^{-1}$ [c] | 0.000 | 0.768 |
| abundance (at 300 K)/%[d] | 87.9 | 12.1 |

(b) NDCPA

| parameters[a] | $C_1$ conformer | $C_s$ conformer |
|---|---|---|
| Bond Lengths (in Å) | | |
| $N_1-C_2$ | 1.493 | 1.494 |
| $N_1-Cl_5$ | 1.773 | 1.776 |
| $N_1-Cl_6$ | 1.773 | 1.776 |
| $C_2-C_3$ | 1.521 | 1.523 |
| $C_2-C_4$ | 1.520 | 1.523 |
| $C_2-H_7$ | 1.093 | 1.095 |
| $C_3-H_8$ | 1.089 | 1.089 |
| $C_3-H_9$ | 1.088 | 1.089 |
| $C_3-H_{10}$ | 1.088 | 1.085 |
| $C_4-H_{11}$ | 1.089 | 1.089 |
| $C_4-H_{12}$ | 1.088 | 1.089 |
| $C_4-H_{13}$ | 1.087 | 1.085 |
| Bond Angles (in degree) | | |
| $C_2-N_1-Cl_5$ | 108.7 | 108.9 |
| $C_2-N_1-Cl_6$ | 110.0 | 108.9 |
| $Cl_5-N_1-Cl_6$ | 107.9 | 106.0 |
| $N_1-C_2-C_3$ | 107.1 | 107.9 |
| $N_1-C_2-C_4$ | 116.6 | 107.9 |
| $N_1-C_2-H_7$ | 101.5 | 110.2 |
| $C_3-C_2-C_4$ | 112.7 | 110.1 |
| $C_3-C_2-H_7$ | 108.7 | 110.4 |
| $C_4-C_2-H_7$ | 109.4 | 110.4 |
| $C_2-C_3-H_8$ | 109.0 | 108.8 |
| $C_2-C_3-H_9$ | 111.1 | 109.7 |
| $C_2-C_3-H_{10}$ | 110.6 | 112.5 |
| $H_8-C_3-H_9$ | 108.3 | 108.6 |
| $H_8-C_3-H_{10}$ | 108.8 | 108.3 |
| $H_9-C_3-H_{10}$ | 109.0 | 108.9 |
| $C_2-C_4-H_{11}$ | 109.0 | 108.8 |
| $C_2-C_4-H_{12}$ | 110.8 | 109.7 |
| $C_2-C_4-H_{13}$ | 111.5 | 112.5 |
| $H_{11}-C_4-H_{12}$ | 108.2 | 108.6 |
| $H_{11}-C_4-H_{13}$ | 108.2 | 108.3 |
| $H_{12}-C_4-H_{13}$ | 109.0 | 108.9 |
| Dihedral Angles (in degree) | | |
| $Cl_5-N_1-C_2-C_3$ | −170.3 | −63.0 |
| $Cl_6-N_1-C_2-C_3$ | 71.7 | −178.2 |
| $Cl_5-N_1-C_2-C_4$ | 62.4 | 178.2 |
| $Cl_6-N_1-C_2-C_4$ | −55.6 | 63.0 |
| $Cl_5-N_1-C_2-H_7$ | −56.4 | 57.6 |
| $Cl_6-N_1-C_2-H_7$ | −174.4 | −57.6 |
| $N_1-C_2-C_3-H_8$ | 167.4 | −171.5 |
| $N_1-C_2-C_3-H_9$ | −73.3 | −52.9 |
| $N_1-C_2-C_3-H_{10}$ | 47.8 | 68.6 |
| $N_1-C_2-C_4-H_{11}$ | −174.0 | 171.5 |
| $N_1-C_2-C_4-H_{12}$ | 67.0 | 52.9 |
| $N_1-C_2-C_4-H_{13}$ | −54.6 | −68.6 |
| $\Delta E$/kcal mol$^{-1}$ | 0.000[b] | 0.666 |
| $\Delta G$ (at 290 K)/kcal mol$^{-1}$ [c] | 0.000 | 0.509 |
| abundance (at 290 K)/%[d] | 82.9 | 17.1 |

[a] See Figure 1 for the atom numberings. [b] Absolute values of the energies are $-1052.697864E_h$ for NDCEA and $-1091.884281E_h$ for NDCPA. [c] Estimated from the energy difference, $\Delta E$, theoretical vibrational wavenumbers and theoretical rotational constants. [d] Estimated from the theoretical $\Delta G$ value.

magnitude of the steric repulsion when the ethyl group is replaced with the isopropyl group.[21] The present result is in accordance with this observation. The N−Cl distances and the Cl−N−Cl angles were determined with good precision because of the high scattering power of Cl atoms. These values of NDCEA agree with those of NDCPA. This tendency is also seen in the results of the MP2/6-31G** calculations although the theoretical Cl−N−Cl angles are about 1° larger than the observed values. The N−C−C angles of ethylamine and isopropylamine are found to decrease by the *N*, *N*-dichlorination and the magnitudes of the changes are almost the same for these molecules (1.5 and 1.3°).

The abundances of the $C_1$ conformers of NDCEA and NDCPA agree with each other within the error limits, and it is found that the $C_1$ conformer is dominant at room temperature. The abundance is also consistent with the theoretical values. The error limit for NDCPA contains the case of 100% $C_1$ form. However, a weak peak observed at 612 cm$^{-1}$ in the infrared spectrum was assigned to the N−Cl stretching mode of the $C_s$ conformer. Therefore, the existence of the $C_s$ conformer cannot be ruled out. The free energy difference, $\Delta G(C_s - C_1)$, of NDCEA calculated from the observed abundance was $0.44 \pm 0.34$ kcal/mol. The lower limit of the $\Delta G(C_s - C_1)$ of NDCPA was 0.29 kcal/mol. In the case of ethylamine, the $C_s$ conformer (trans) was found to be slightly more stable than the $C_1$ (gauche)[18] contrary to the dichlorinated species. On the other hand, conformational analysis was not carried out for isopropylamine, where only the $C_s$ conformer was assumed.[19] As

**TABLE 4: Structural Parameters and Constraints for the $C_1$ and $C_s$ Conformers of NDCEA and NDCPA**

| parameter[a] | $C_1$ conformer | $C_s$ conformer |
|---|---|---|
| (a) NDCEA | | |
| Bond Lengths (in Å) | | |
| $\mathrm{N_1-C_2}$ | $r_1$ | $r_1 + 0.001$ |
| $\mathrm{C_2-C_3}$ | $r_2$ | $r_2 + 0.001$ |
| $\mathrm{N_1-Cl_4}$ | $r_3$ | $r_3 - 0.001$ |
| $\mathrm{N_1-Cl_5}$ | $r_3 + 0.001$ | $r_3 - 0.001$ |
| $\mathrm{C_2-H_6}$ | $r_4$ | $r_4 + 0.001$ |
| $\mathrm{C_2-H_7}$ | $r_4 + 0.004$ | $r_4 + 0.001$ |
| $\mathrm{C_3-H_8}$ | $r_4 - 0.000$ | $r_4 - 0.000$ |
| $\mathrm{C_3-H_9}$ | $r_4 - 0.002$ | $r_4 - 0.002$ |
| $\mathrm{C_3-H_{10}}$ | $r_4 - 0.003$ | $r_4 - 0.002$ |
| Bond Angles (in degree) | | |
| $\mathrm{N_1-C_2-C_3}$ | $\theta_1$ | $\theta_1 + 8.6$ |
| $\mathrm{C_2-N_1-Cl_4}$ | $\theta_2$ | $\theta_2 + 0.6$ |
| $\mathrm{C_2-N_1-Cl_5}$ | $\theta_2 - 0.9$ | $\theta_2 + 0.6$ |
| $\mathrm{Cl_4-N_1-Cl_5}$ | $\theta_3$ | $\theta_3 + 1.1$ |
| $\mathrm{N_1-C_2-H_6}$ | 104.2 | 103.6 |
| $\mathrm{N_1-C_2-H_7}$ | 111.5 | 103.6 |
| $\mathrm{H_6-C_2-H_7}$ | 108.5 | 108.2 |
| $\mathrm{C_2-C_3-H_8}$ | 109.0 | 108.9 |
| $\mathrm{C_2-C_3-H_9}$ | 110.2 | 111.3 |
| $\mathrm{C_2-C_3-H_{10}}$ | 111.7 | 111.3 |
| $\mathrm{H_8-C_3-H_9}$ | 108.6 | 108.2 |
| $\mathrm{H_8-C_3-H_{10}}$ | 108.3 | 108.2 |
| Dihedral Angles (in degree) | | |
| $\mathrm{Cl_4-N_1-C_2-C_3}$ | $\phi_1$ | dependent |
| $\mathrm{N_1-C_2-C_3-H_8}$ | −171.1 | 180.0 |
| abundance of $C_1$ conformer | $x$ | $1 - x$ |
| (b) NDCPA | | |
| Bond Lengths (in Å) | | |
| $\mathrm{N_1-C_2}$ | $r_1$ | $r_1 + 0.000$ |
| $\mathrm{C_2-C_3}$ | $r_2$ | $r_2 + 0.002$ |
| $\mathrm{C_2-C_4}$ | $r_2 - 0.001$ | $r_2 + 0.002$ |
| $\mathrm{N_1-Cl_5}$ | $r_3$ | $r_3 + 0.003$ |
| $\mathrm{N_1-Cl_6}$ | $r_3 - 0.001$ | $r_3 + 0.003$ |
| $\mathrm{C_2-H_7}$ | $r_4$ | $r_4 + 0.003$ |
| $\mathrm{C_3-H_8}$ | $r_4 - 0.003$ | $r_4 - 0.004$ |
| $\mathrm{C_3-H_9}$ | $r_4 - 0.005$ | $r_4 - 0.004$ |
| $\mathrm{C_3-H_{10}}$ | $r_4 - 0.005$ | $r_4 - 0.007$ |
| $\mathrm{C_4-H_{11}}$ | $r_4 - 0.003$ | $r_4 - 0.004$ |
| $\mathrm{C_4-H_{12}}$ | $r_4 - 0.005$ | $r_4 - 0.004$ |
| $\mathrm{C_4-H_{13}}$ | $r_4 - 0.005$ | $r_4 - 0.007$ |
| Bond Angles (in degree) | | |
| $\mathrm{N_1-C_2-C_3}$ | $\theta_1$ | $\theta_1 + 0.8$ |
| $\mathrm{N_1-C_2-C_4}$ | $\theta_1 + 9.6$ | $\theta_1 + 0.8$ |
| $\mathrm{C_3-C_2-C_4}$ | $\theta_2$ | $\theta_2 - 2.7$ |
| $\mathrm{C_2-N_1-Cl_5}$ | $\theta_3$ | $\theta_3 + 0.2$ |
| $\mathrm{C_2-N_1-Cl_6}$ | $\theta_3 + 1.2$ | $\theta_3 + 0.2$ |
| $\mathrm{Cl_5-N_1-Cl_6}$ | $\theta_4$ | $\theta_4 - 1.9$ |
| $\mathrm{N_1-C_2-H_7}$ | 101.5 | 110.2 |
| $\mathrm{C_2-C_3-H_8}$ | 109.0 | 108.8 |
| $\mathrm{C_2-C_3-H_9}$ | 111.1 | 109.7 |
| $\mathrm{C_2-C_3-H_{10}}$ | 110.6 | 112.5 |
| $\mathrm{H_8-C_3-H_9}$ | 108.3 | 108.6 |
| $\mathrm{H_8-C_3-H_{10}}$ | 108.8 | 108.3 |
| $\mathrm{C_2-C_4-H_{11}}$ | 109.0 | 108.8 |
| $\mathrm{C_2-C_4-H_{12}}$ | 110.8 | 109.7 |
| $\mathrm{C_2-C_4-H_{13}}$ | 111.5 | 112.5 |
| $\mathrm{H_{11}-C_4-H_{12}}$ | 108.2 | 108.6 |
| $\mathrm{H_{11}-C_4-H_{13}}$ | 108.2 | 108.3 |
| Dihedral Angles (in degree) | | |
| $\mathrm{Cl_5-N_1-C_2-C_4}$ | $\phi_1$ | dependent |
| $\mathrm{Cl_5-N_1-C_2-H_7}$ | −56.4 | dependent |
| $\mathrm{N_1-C_2-C_3-H_8}$ | 167.4 | −171.5 |
| $\mathrm{N_1-C_2-C_4-H_{11}}$ | −174.0 | 171.5 |
| abundance of $C_1$ conformer | x | $1 - x$ |

[a] See Figure 1 for the atom numberings.

**TABLE 5: Mean Amplitudes, *l*, $r_a$ Distances, Shrinkage Corrections, $r_\alpha - r_a$, and Anharmonicity Parameters, $\kappa$, for the $C_1$ Conformer of NDCEA and NDCPA (in Å)**

| atom pair[a] | $l_{\mathrm{calc}}$[b] | $l_{\mathrm{obs}}$[c] | $r_a$ | group | $r_\alpha - r_a$ | $\kappa$[d] |
|---|---|---|---|---|---|---|
| (a) NDCEA | | | | | | |
| $\mathrm{N_1-C_2}$ | 0.052 | 0.045(2) | 1.478 | 2 | −0.0020 | 24 |
| $\mathrm{N_1\cdots C_3}$ | 0.073 | 0.068(2) | 2.439 | 3 | −0.0040 | 0 |
| $\mathrm{N_1-Cl_4}$ | 0.054 | 0.047 | 1.757 | 2 | −0.0017 | 29 |
| $\mathrm{N_1-Cl_5}$ | 0.054 | 0.047 | 1.758 | 2 | −0.0025 | 29 |
| $\mathrm{C_2-C_3}$ | 0.051 | 0.044 | 1.540 | 2 | −0.0107 | 22 |
| $\mathrm{C_2\cdots Cl_4}$ | 0.071 | 0.066 | 2.631 | 3 | −0.0011 | 0 |
| $\mathrm{C_2\cdots Cl_5}$ | 0.071 | 0.066 | 2.617 | 3 | −0.0020 | 0 |
| $\mathrm{C_2-H_6}$ | 0.079 | 0.074(8) | 1.102 | 1 | −0.0178 | 127 |
| $\mathrm{C_2-H_7}$ | 0.079 | 0.075 | 1.106 | 1 | −0.0177 | 130 |
| $\mathrm{C_3\cdots Cl_4}$ | 0.121 | 0.109(8) | 3.166 | 4 | −0.0002 | 0 |
| $\mathrm{C_3\cdots Cl_5}$ | 0.071 | 0.060 | 3.984 | 4 | −0.0009 | 0 |
| $\mathrm{C_3-H_8}$ | 0.078 | 0.074 | 1.102 | 1 | −0.0376 | 126 |
| $\mathrm{C_3-H_9}$ | 0.078 | 0.074 | 1.101 | 1 | −0.0465 | 125 |
| $\mathrm{C_3-H_{10}}$ | 0.078 | 0.074 | 1.099 | 1 | −0.0443 | 124 |
| $\mathrm{Cl_4\cdots Cl_5}$ | 0.070 | 0.065 | 2.822 | 3 | −0.0009 | 0 |
| (b) NDCPA | | | | | | |
| $\mathrm{N_1-C_2}$ | 0.053 | 0.051(2) | 1.494 | 2 | −0.0010 | 26 |
| $\mathrm{N_1\cdots C_3}$ | 0.070 | 0.068(3) | 2.438 | 3 | −0.0041 | 0 |
| $\mathrm{N_1\cdots C_4}$ | 0.067 | 0.065 | 2.577 | 3 | −0.0030 | 0 |
| $\mathrm{N_1-Cl_5}$ | 0.054 | 0.052 | 1.761 | 2 | −0.0027 | 29 |
| $\mathrm{N_1-Cl_6}$ | 0.054 | 0.052 | 1.760 | 2 | −0.0022 | 29 |
| $\mathrm{C_2-C_3}$ | 0.051 | 0.049 | 1.530 | 2 | −0.0072 | 23 |
| $\mathrm{C_2-C_4}$ | 0.051 | 0.049 | 1.529 | 2 | −0.0059 | 23 |
| $\mathrm{C_2\cdots Cl_5}$ | 0.068 | 0.066 | 2.644 | 3 | −0.0014 | 0 |
| $\mathrm{C_2\cdots Cl_6}$ | 0.069 | 0.066 | 2.663 | 3 | −0.0007 | 0 |
| $\mathrm{C_2-H_7}$ | 0.079 | 0.067(5) | 1.118 | 1 | −0.0120 | 130 |
| $\mathrm{C_3\cdots C_4}$ | 0.074 | 0.071 | 2.479 | 3 | −0.0098 | 0 |
| $\mathrm{C_3\cdots Cl_5}$ | 0.072 | 0.067(8) | 4.002 | 4 | −0.0010 | 0 |
| $\mathrm{C_3\cdots Cl_6}$ | 0.124 | 0.119 | 3.102 | 4 | −0.0002 | 0 |
| $\mathrm{C_3-H_8}$ | 0.079 | 0.066 | 1.115 | 1 | −0.0321 | 127 |
| $\mathrm{C_3-H_9}$ | 0.078 | 0.066 | 1.114 | 1 | −0.0353 | 125 |
| $\mathrm{C_3-H_{10}}$ | 0.078 | 0.066 | 1.114 | 1 | −0.0358 | 125 |
| $\mathrm{C_4\cdots Cl_5}$ | 0.119 | 0.114 | 3.181 | 4 | −0.0009 | 0 |
| $\mathrm{C_4\cdots Cl_6}$ | 0.125 | 0.119 | 3.099 | 4 | 0.0008 | 0 |
| $\mathrm{C_4-H_{11}}$ | 0.079 | 0.066 | 1.115 | 1 | −0.0356 | 127 |
| $\mathrm{C_4-H_{12}}$ | 0.078 | 0.066 | 1.114 | 1 | −0.0387 | 125 |
| $\mathrm{C_4-H_{13}}$ | 0.078 | 0.066 | 1.113 | 1 | −0.0391 | 125 |
| $\mathrm{Cl_5\cdots Cl_6}$ | 0.070 | 0.068 | 2.824 | 3 | −0.0022 | 0 |

[a] See Figure 1 for the atom numberings. Nonbonded atom pairs containing H atom are not listed for the simplicity although they are included in the analyses. [b] Calculated at 296.4 K for NDCEA and 290.3 K for NDCPA. [c] Numbers in parentheses are estimated error limits ($3\sigma$) referring to the last significant digit. [d] In $10^{-7}$ Å$^3$.

shown in the Newman projections (see Figure 6), the methyl group and the hydrogen atoms of NDCEA are replaced by the hydrogen atom and the methyl groups in NDCPA, respectively. Therefore, they would have opposite signs of $\Delta G(C_s - C_1)$, if the conformational stability were to be ruled only by the repulsion between the Cl atom and the methyl group and that between the Cl and H atoms. The present results (experimental and theoretical) show that such a simple picture is not appropriate to explain the conformation of these molecules even qualitatively.

In Table 7, the N−Cl distances and the Cl−N−Cl angles are compared with those of related molecules. For monochloroamines, R−NCl−R, the $r$(N−Cl) significantly depends on the substituent, R. On the other hand, the $r$(N−Cl) of dichloroamines, $\mathrm{R-NCl_2}$, is not dependent on R and agrees with that of $\mathrm{NCl_3}$.[5] In addition, the Cl−N−Cl angles of dichloroamines are almost equal to that of $\mathrm{NCl_3}$. Therefore, it can be concluded that the N−Cl bond properties of the *N*, *N*-dichloroamines, $\mathrm{R-NCl_2}$, are not sensitive to the substituent, R, in contrast to those of *N*-chloroamines, R−NCl−R.

**TABLE 6: Molecular Structures of NDCEA, NDCPA, and Related Amines Determined by Gas Electron Diffraction ($r_g$ and $\angle_\alpha$)[a]**

| parameters[b] | NDCEA[c] | ethylamine[d] | | NDCPA[c] | isopropylamine[e] |
|---|---|---|---|---|---|
| | | Bond Lengths (in Å) | | | |
| $N_1-C_2$ | 1.479(6) | 1.475(10) | $N_1-C_2$ | 1.496(11) | 1.469(13) |
| $C_2-C_3$ | 1.542(7) | 1.524(6) | $C_2-C_3$ | 1.532 }(6) | 1.529 }(5) |
| | | | $C_2-C_4$ | 1.530 | 1.529 |
| $N_1-Cl_4$ | 1.759 }(2) | | $N_1-Cl_5$ | 1.762 }(2) | |
| $N_1-Cl_5$ | 1.760 | | $N_1-Cl_6$ | 1.762 | |
| ⟨C−H⟩[f] | 1.107(8) | 1.107(6) | ⟨C−H⟩[f] | 1.119(5) | 1.105(15) |
| | | Bond Angles (in degree) | | | |
| $N_1-C_2-C_3$ | 108.2(8) | 109.7(3) | $N_1-C_2-C_3$ | 107.6 }(8) | 108.9 }(9) |
| | | | $N_1-C_2-C_4$ | 117.1 | 108.9 |
| | | | $C_2-C_3-C_4$ | 108.3(18) | 114.4(16) |
| $C_2-N_1-Cl_4$ | 108.7 }(3) | | $C_2-N_1-Cl_5$ | 108.5 }(6) | |
| $C_2-N_1-Cl_5$ | 107.7 | | $C_2-N_1-Cl_6$ | 109.7 | |
| $Cl_4-N_1-Cl_5$ | 106.9(2) | | $Cl_5-N_1-Cl_6$ | 106.7(4) | |
| | | Dihedral Angles (in degree) | | | |
| $Cl_4-N_1-C_2-C_3$ | −76(2) | | $Cl_5-N_1-C_2-C_4$ | 63(3) | |
| | | Abundance (in %) | | | |
| $C_1$ | 79(9) | 54(10) | | 88(12) | 0[g] |
| | | Indices of Resolution | | | |
| $k^h$ | 0.81(2) | | | 0.88(3) | |

[a] Numbers in parentheses are the estimated limits of error (3$\sigma$) referring to the last significant digit. [b] See Figure 1 for the atom numbering. [c] Present work. The $C_1$ conformer. [d] Reference 18. The $C_1$ conformer. [e] Reference 19. Only the $C_s$ conformer was assumed. [f] Average values. [g] Assumed. [h] $k$ is defined as $sM(s)^{obs} = ksM(s)^{calc}$.

**TABLE 7: N−Cl Distances and the Cl−N−Cl Angles of Chlorinated Amines[a]**

| | $Me_2NCl$[b] | $Et_2NCl$[c] | $(CH_2)_3NCl$[d] | NDCEA[e] | NDCPA[e] | $NCl_3$[f] |
|---|---|---|---|---|---|---|
| $r_g$(N−Cl)/Å | 1.759(2) | 1.765(2) | 1.745(2) | 1.759(2)[g] | 1.762(2)[g] | 1.759(2) |
| $\angle_\alpha$(Cl−N−Cl)/deg | | | | 106.9(2) | 106.7(4) | 107.1(5)[h] |

[a] Numbers in parentheses are the estimated limits of error (3$\sigma$) referring to the last significant digit. [b] Reference 1. [c] Reference 2. The trans−trans conformer. [d] Reference 3. [e] This work. The $C_1$ conformer. [f] Reference 5. Error limits are 1$\sigma$. [g] Average value. [h] Shrinkage effect was not corrected.

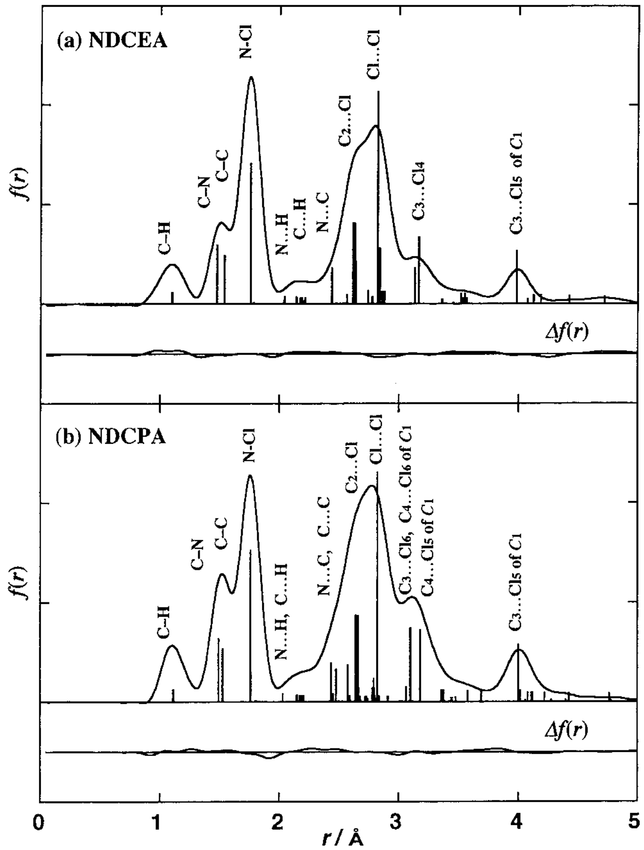

**Figure 5.** Experimental radial distribution curves of (a) NDCEA and (b) NDCPA; $\Delta f(r) = f(r)^{obs} - f(r)^{calc}$. Distance distributions are shown by vertical bars.

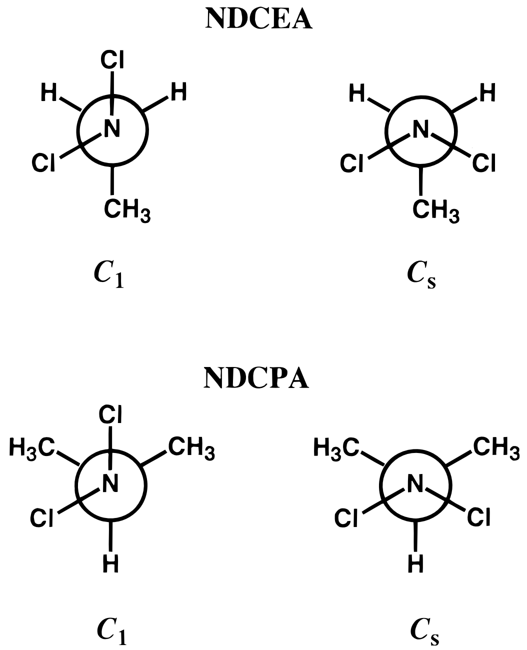

**Figure 6.** Schematic Newman projections for the $C_1$ and $C_s$ conformers of NDCEA and NDCPA.

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**Supporting Information Available:** Tables of the leveled total intensities and the backgrounds, definitions of the internal coordinates, the scaled harmonic force constants, and the correlation matrices. This material is available free of charge via the Internet at http://pubs.acs.org.

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