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THEORETICAL PREDICTION OF VIBRATIONAL INFRARED FREQUENCIES OF TERTIARY AMINES

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This report computes the vibrational frequencies of seven amines. Experimental data are available for four of these molecules: trimethylamine, diethylmethylamine, bis(2-chloroethyl)methylamine, and triethylamine. The ratios are determined between the experimental and the computed frequencies of these molecules. The ratios are then used to derive a set of effective correction factors for the various vibrational modes. The vibrational frequencies are computed for three other tertiary amines: tris(chloromethyl)amine, tris(2-chloroethyl)amine (HN3), and bis(2-chloroethyl) ethylamine (HN1). The computed frequencies, the corresponding intensities, and the corrected frequencies are reported here. The authors emphasize that the correction factors are valid only for 3-21G computations.

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PREFACE

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1. Introduction

We present theoretical predictions of the frequencies and intensities of the infrared absorption spectra of the three molecules bis(2-chloroethyl)ethylamine, bis(2-chloroethyl)methylamine and tris(2-chloroethyl)amine. These molecules are popularly known as the three nitrogen mustards HN1, HN2 and HN3, respectively. Our first step is the computation of the optimized geometries and the corresponding vibrational modes and frequencies with the Gaussian 88 Program Package[1]. We base the computations on the consistent use of the 3-21G basis set. The presently available computing facilities permit the use of this basis set for all molecules we are interested in. It is possible that the use of larger basis sets, such as 6-31G*, may lead to more accurate frequency results. We plan to investigate this as soon as improvements in the computing facilities permit the the use of larger basis sets for all molecules of interest.

In previous work on a group of mercaptans and sulfides[2] and on a group of alcohols and ethers[3] we found that the differences between 3-21G computed frequencies and the corresponding experimental values vary between 1% and 15%. The accuracy of theoretical frequency predictions may be improved by combining computations with available experimental information. This is accomplished by selecting a group of similar molecules. The group contains the molecules we are interested in and also some molecules for which experimental IR and Raman spectra are available. In the present case we consider a group of seven tertiary amines. Both the IR spectrum[4] and the Raman spectrum[5] of trimethylamine have been measured. The IR spectra of three additional tertiary amines, triethylamine, diethylmethylamine and HN2 are listed in the Aldrich Atlas[6]. We have computed the 3-21G optimized geometries and the corresponding vibrational modes and frequencies of the above four amines. We then assigned the computed frequencies to the corresponding experimental values and we determined the ratio between each experimental frequency and the corresponding computed value.

Our procedure is based on the assumption that the ratios between experimental and computed frequancies are fairly constant for each type of characteristic frequency such as C-H stretch, C-Cl stretch, C-N symmetric stretch, etc. It is then possible to derive a correction factor for each characteristic frequency by taking the average of the ratios between the experimental and computed frequencies. We derived all these correction factors for tertiary amines by analyzing the frequency data of the four molecules mentioned above.

Finally, we compute the vibrational frequencies of the remaining molecules, HN1, HN3 and tris(chloromethylamine, and we correct the computed frequencies by multplying by our correction factors of Table V. The computed IR intensity values are also listed, these are relative intensities and their values are not particularly accurate. Nevertheless they offer useful guidelines for deciding which IR lines are predominant in the spectra and which lines are not. For good measure we also report the corrected frequencies and intensities for HN2, these values may then be compared with the experimental data of Table IV.

2. Computational Methods

These calculations were run using GAUSSIAN88 as implemented on the Stardent Titan superworkstation in CBM Branch. All geometries were optimized using the 3-21G basis set.[1] Frequencies were calculated using the coupled-perturbed Hartree-Fock equations. Intensities were evaluated by calculating the dipole derivatives of the displacements. Computed spectra were compared to known experimental spectra in cases were the experimental spectra was available.

3. Results

Four of the seven molecules that we studied have c_{3v} symmetry or they almost have c_{3v} symmetry. For example, the nitrogen-carbon skeletons of the trimethylamine and trichloromethylamine molecules have c_{3v} symmetry but the rotation of the CH_3 or the CH_2Cl groups may cause a slight distortion of the c_{3v} pattern. For practical purposes we may assume c_{3v} symmetry since those distortions are small and they have little effect. Consequently there are two groups of vibrational modes, the symmetric nondegenerate A modes and the nonsymmetric two-fold degenerate E modes.

3.1 Trimethyl and tris(chloromethyl) Amine

In order to analyze the vibrational spectra of the seven molecules that we have studied we first consider the above mentioned two molecules trimethylamine and tris(chloromethyl)amine since they have the simplest spectra. The results for trimethylamine are listed in Table I and the results for tris(chloromethyl)amine are listed in Table VI. The characteristic frequencies are the three C-N stretch modes and the three C-N bend modes for both molecules, in addition there are three C-Cl stretch modes for the $(CH_2Cl)_3N$ molecule. These modes are easily identified by a simple inspection of the nuclear motions of the vibrational modes. It should be noted also that the frequencies of the C-N stretch modes for the two molecules are not that far apart, the A frequencies are at 840 and at 770 cm^{-1} and the E frequencies are at 1125 and at 1240 cm^{-1}.

The other vibrational modes of the two molecules are not all that important because they are not unique for tertiary amines. For example, trimethylamine has 9 C-H stretch modes between 3150 and 3250 cm^{-1} and tris(chloromethyl)amine has six C-H stretch modes between 3300 and 3400 cm^{-1}. However, the majority of organic molecules have C-H stretch modes in the same frequency range and these frequencies are not of much help for identification purposes. The CH_2Cl group exhibits a H-C-H scissor motion, which we have identified. In addition there are CH_3 and CH_2 rocking motions. There are some additional C-H bend modes and we list them as a group.

3.2 Triethyl and tris(chloroethyl) Amine

Next we consider the other two molecules with c_{3v} (or "almost c_{3v}") symmetry, triethylamine and tris(2-chloroethyl)amine. We present the results for these two molecules in Table II and in Table VII. Some of the characteristic frequencies are identical with those of the trimethyl molecules, the three C-N stretch modes, the three C-N bend modes, the three C-Cl stretch modes and the group of C-H stretch modes. In addition the triethyl molecules exhibit three C-C stretch modes in the vicinty of 1000 cm^{-1} and six N-C-C bend modes. The latter bear some resemblance to the C-N bend modes and the difference between those two types of motion is not always obvious. We decided to use the name C-N bend for the vibrational mode where the two carbons move in the same direction and to use the name N-C-C bend for the mode where the two carbons of the ethyl group move in opposite direction. In the case of triethylamine we identified a rocking motion of the CH_2 groups adjacent to the nitrogen. The HN3 molecule is characterized by a H-C-H scissor mode in the CH_2Cl groups in addition to the C-Cl stretch modes. We again observed six N-C-C bend modes, just as in triethylamine. One difference between the spectra of the two molecules occurs in the frequencies of the CH_2 rock modes, these frequencies are around 880 cm^{-1} in triethylamine and they are around 1500 cm^{-1} in HN3. We should note that there may be some ambiguity in the latter assignments because of delocalization of the nuclear motions.

3.3 Other Amines

The remaining three molecules, diethylmethylamine, HN1 and HN2 are nonsymmetric. We analyze their spectra both by inspection of the nuclear motion and by comparison with the above four symmetric molecules. We first discuss the vibrational spectrum of diethylmethylamine, the results are presented in Table III.

The spectrum of diethylmethylamine exhibits some vibrational modes that are similar to trimethylamine and some modes that are similar to triethylamine. In fact, the vibrational spectrum of diethylmethylamine may almost be constructed by combining the spectra of of Tables I and II of the other two molecules. We can identify two of the three C-N and C-C stretch modes, four of the six N-C-C bend modes and two of the three C-N bend modes that are present in triethylamine. The other C-N stretch and bend frequencies are similar to the corresponding trimethylamine values. We also recognize one of the CH_3 rocking modes of trimethylamine and two of the CH_2 rocking modes of triethylamine. The C-H stretch modes and C-H bend modes of the three molecules are quite similar. There is not much similarity between the torsional modes.

The spectrum of bis(2-chloroethyl)methylamine (HN2) is presented in Table IV, it may be understood by comparing it with the spectrum of diethylmethylamine of Table III. The HN2 spectrum shows two C-Cl stretch frequencies, which replace two C-H stretch frequencies. Both molecules exhibit four N-C-C bend modes but their frequencies are subject to fairly large shifts. The two CH_3 rocking modes of the ethyl CH_3 groups are replaced by two H-C-H scissor modes in the CH_2Cl groups. We identified two CH_2 rocking modes in HN2 but we failed to identify similar rocking modes in diethylmethylamine. The

C-N stretch modes of the two molecules are remarkably similar. The C-N bend modes exhibit frequency shifts that are most likely caused by the mass effects of the Cl atoms. The C-H stretch and bend modes of the two molecules are quite similar.

The spectrum of bis(2-chloroethyl)ethylamine (HN1) is presented in Table VIII. It may be explained by combining the data of Table II for triethylamine with the data of Table VII for tris(2-chloroethyl)amine. Substitution of a hydrogen by a chlorine atom in the ethyl group causes a few changes in the vibrational spectrum. There are two obvious effects, first the changeover of two C-H stretch frequencies around 3300 cm^{-1} to two C-Cl stretch frequencies around 620 cm^{-1} and,second the change from two of the CH_3 rock frequencies around 880 cm^{-1} to two H-C-H scissor modes in the CH_2Cl groups around 1300 cm^{-1}. The rest of the spectrum is not greatly affected by the Cl substitution. The C-N stretch and bend modes hardly change at all, the other vibrational frequencies are shifted by varying amounts, the largest shifts of 100 to 200 cm^{-1} occur in some of the N-C-C bend modes.

3.4 Comparison with Experiment

Now that we have analyzed the vibrational spectra of all seven amines we compare the results of our computations with the available experimental information. The Raman spectrum of trimethylamine was measured by Kohlrausch[5] as early as 1936. Since that time several spectroscopic investigations of trimethylamine have been published. The most recent and most complete study of the molecule was presented in 1967 by Goldfarb and Khare[4]. The latter authors measured the IR spectrum of trimethylamine in the gas phase, the solid phase and in an argon matrix. Assignments were made by comparison with the spectrum of the deuterated molecule. We use the data of Goldfarb and Khare to compare our computed frequencies and to determine the ratios beween experimental and computed frequencies. The results are listed in Table I. It should be noted that the Raman frequencies reported by Kohlrausch[5] are quite similar to the much more recent IR frequencies of Goldfarb and Khare[4].

The IR absorption spectra of three additional molecules, triethylamine, diethylmethylamine and HN2 are listed in the Aldrich Atlas of IR spectra[6]. We determined the frequencies of the spectral peaks and we made assignmnts by considering both the frequencies and the intensities of the spectral lines and by comparison with trimethylamine. We are fairly confident about the accuracy of our assignments but we cannot offer absolute guarantees because of the limitations of the experimental information.

We present a comparison between the experimental and computed frequencies of the three molecules triethylamine, diethylmethylamine and bis(2-chloroethyl)amine in Tables II, III and IV, respetively. We again list the ratios between each experimental frequency and the corresponding computed frequency.

The various ratios seem to be fairly constant for each characteristic frequency and we have computed the average values. These average ratio values ate listed in Table V and we define them as our correction factors for the computed frequencies. For example, the four ratios for the symmetric (A) C-N stretch frequencies are 0.979, 0.953, 0.963 and 0.970. The average is 0.97 and we take this number as the correction factor for all computed symmetric C-N stretch frequencies.

We use the correction factors of Table V, in conjunction with 3-21G frequency computations, for predicting the frequencies of the remaining tertiary amines tris(chloromethyl)amine, HN1 and HN3. We believe that the possible errors of the original computed frequencies may be as high as 15% but that the possible errors of the corrected frequencies are only 1% to 2%. We present our predictions for tris(chloromethyl)amine in Table VI, the results for HN3 in Table VII and the results for HN1 in Table VIII. We also list the computed IR intensity values. Even though their numerical vaues are not particularly accurate they offer useful indications as to the relative strengths of the IR lines.

Finally we use the same procedure for predicting the IR frequencies and intensities of HN2, the results are presented in Table IX. We used the experimental data of HN2 in part for the derivation of the correction factors, but we felt that it might be useful to illustrate how the predicted frequencies, derived from average correction factors compare to the actual experimental values.

4. Summary and Conclusions

We believe that the procedure that we have described above constitutes a convenient and accurate method for predicting the vibrational infrared frequencies and our data semm to support that point of view. It should be noted that there are some alternative procedures for predicting vibrational frequencies from computed results. The idea of combining theoretical and experimental results for predicting vibrational frequencies is not new but a variety of different approaches have been suggested. The area of research was reviewed recently by Fogarasi and Pulay[7] and by Hess, Schaad, Carsky and Zahradnik[8].

One possible approach involves the rescaling of the force constant matrix. A simple example is the proposal by Pulay and Meyer[9,10] to multiply all diagonal stretching force constants by 0.9 and to multiply all diagonal bending force constants by 0.8. This procedure will certainly improve the agreement between computed and experimental frequencies since the computed values are usually too high by 5% to 10%. The underlying assumption here is similar to ours, namely that it is permissible to transfer scaling factors amongst similar molecules. It should be mentioned here that this approach was even applied to methylamine[11].

We feel that our introduction of scaling factors for the frequencies themselves is preferrable to the more indirect approach of scaling the force constants. Firstly, the frequencies are physical observables and the force constants are not. Secondly, the definition of the force constant matrix is not unique because the number of matrix elements is usually much larger than the number of known frequencies. The third argument in favor of our procedure is the pragmatic observation that we are primarily interested in a few major characteristic frequencies only and not in the whole spectrum.

The difference between the computed and the experimental characteristic frequencies may be due to many different factors that are usually not even considered in the theory such as anharmonicity, errors in the computed geometry, Fermi resonance, etc. Even solvent effects may lead to systematic differences between computed and observed frequencies. The introduction of a scaling factor for a single characteristic frequency is capable of accounting for all these various effects. Our procedure leads to more precise prediction for specific characteristic frequencies that are of special interest.

In summary, we believe that our method constitutes a convenient and accurate procedure for predicting characteristic frequencies for groups of similar molecules. Our results seem to confirm this.

mode	comp	exp[4]	ratio	mode	comp	exp[4]	ratio
torsion A	341.5	365	1.069	C-H bd A	1643.4	-	-
torsion E	455.6	421	0.924	C-H bd A	1672.8	-	-
C-N str A	841.0	823	0.979	C-H bd A	1689.3	1460	0.864
C-N str E	1124.9	1037	0.921	C-H bd E	1602.7	-	-
CH_3 rk A	1167.4	1098	0.940	C-H bd E	1667.8	1445	0.866
CH_3 rk E	1235.8	1187	0.960	C-H bd E	1690.9	1465	0.866
C-N bd A	1330.9	1270	0.954	C-H str A	3156.7	2779	0.880
C-N bd E	1412.9	-	-	C-H str A	3199.2	2828	0.883
-	-	-	-	C-H str A	3249.4	2946	0.907
-	-	-	-	C-H str E	3143.8	-	-
-	-	-	-	C-H str E	3196.4	2821	0.882
-	-	-	-	C-H str E	3253.9	2953	0.908

TABLE 1. Comparison of computed and experimental vibrational frequencies of trimethylamine

mode	comp	exp[6]	ratio	mode	comp	exp[6]	ratio
torsion A	448.9	-	-	C-H bd A	1453.5	-	-
torsion E	493.7	-	-	C-H bd A	1573.1	-	-
C-N str A	769.9	734	0.953	C-H bd A	1662.6	-	-
C-N str E	1150.0	1060	0.921	C-H bd A	1668.1	-	-
C-C str A	1053.8	1000	0.949	C-H bd A	1689.9	1468	0.869
C-C str E	983.3	917	0.933	C-H bd E	1462.9	-	-
N-C-C bd A	1197.6	-	-	C-H bd E	1568.9	1381	0.880
N-C-C bd E	1211.4	1136	0.938	C-H bd E	1661.4	-	-
N-C-C bd A	1552.8	-	-	C-H bd E	1675.8	-	-
N-C-C bd E	1533.9	-	-	C-H str A	3175.6	2800	0.882
CH_3 rk A	885.0	800	0.904	C-H str A	3203.0	-	-
CH_3 rk E	880.8	800	0.908	C-H str A	3215.3	-	-
C-N bd A	1280.4	1208	0.943	C-H str A	3263.2	-	-
C-N bd E	1355.0	1295	0.956	C-H str A	3271.3	-	-
-	-	-	-	C-H str E	3166.6	-	-
-	-	-	-	C-H str E	3204.4	-	-
-	-	-	-	C-H str E	3213.9	2865	0.891
-	-	-	-	C-H str E	3264.7	2958	0.906
-	-	-	-	C-H str E	3274.1	2976	0.909

TABLE 2. Comparison of computed and experimental vibrational frequencies of triethylamine.

mode	comp	exp[6]	ratio	mode	comp	exp[6]	ratio
torsion	418.5	-	-	C-H bd	1459.6	-	-
torsion	475.6	-	-	C-H bd	1473.6	-	-
torsion	506.7	-	-	C-H bd	1567.0	-	-
C-N str	787.4	758	0.963	C-H bd	1570.0	-	-
C-N str	1129.4	-	-	C-H bd	1620.2	-	-
C-N str	1155.6	1063	0.920	C-H bd	1663.4	-	-
CH_3 rk,e	889.1	806	0.907	C-H bd	1664.9	1449	0.870
CH_3 rk,e	893.0	806	0.903	C-H bd	1667.0	-	-
CH_3 rk,m	1232.1	1205	0.978	C-H bd	1676.1	-	-
C-C str	974.5	909	0.933	C-H bd	1680.4	-	-
C-C str	1038.3	-	-	C-H bd	1683.3	-	-
N-C-C bd	1194.2	1149	0.962	C-H bd	1690.4	-	-
N-C-C bd	1216.6	-	-	C-H bd	1692.6	-	-
N-C-C bd	1536.9	1351	0.879	C-H str	3157.3	-	-
N-C-C bd	1545.9	1379	0.892	C-H str	3159.4	-	-
C-N bd	1294.0	1235	0.954	C-H str	3168.9	2793	0.881
C-N bd	1351.8	1290	0.954	C-H str	3200.7	-	-
C-N bd	1380.8	1312	0.950	C-H str	3203.9	-	-
-	-	-	-	C-H str	3205.9	-	-
-	-	-	-	C-H str	3212.1	-	-
-	-	-	-	C-H str	3216.8	-	-
-	-	-	-	C-H str	3256.3	-	-
-	-	-	-	C-H str	3266.1	-	-
-	-	-	-	C-H str	3266.5	-	-
-	-	-	-	C-H str	3275.9	-	-
-	-	-	-	C-H str	3278.3	2967	0.905

TABLE 3. Comparison of computed and experimental vibrational frequencies of diethylmethylamine.

mode	comp	exp[6]	ratio	mode	comp	exp[6]	ratio
torsion	472.5	-	-	C-H bd	1420.9	-	-
torsion	478.6	-	-	C-H bd	1535.0	1299	0.846
torsion	507.3	-	-	C-H bd	1555.2	-	-
C-Cl str	620.8	-	-	C-H bd	1617.7	-	-
C-Cl str	625.1	664	1.062	C-H bd	1624.7	-	-
C-N str	760.1	737	0.970	C-H bd	1626.5	1408	0.866
C-N str	1165.6	-	-	C-H bd	1636.9	-	-
C-N str	1226.8	1117	0.910	C-H bd	1656.1	-	-
CH_3 rk,m	1264.5	-	-	C-H bd	1683.0	1471	0.874
C-C str	1098.7	1053	0.958	C-H bd	1687.5	-	-
C-C str	1114.3	1071	0.961	C-H str	3176.8	2857	0.899
N-C-C bd	934.7	907	0.970	C-H str	3184.1	-	-
N-C-C bd	992.9	-	-	C-H str	3193.1	-	-
N-C-C bd	1003.0	-	-	C-H str	3224.5	-	-
N-C-C bd	1020.9	974	0.954	C-H str	3231.3	2941	0.910
C-N bd	992.9	943	0.950	C-H str	3235.5	-	-
C-N bd	1433.7	1316	0.918	C-H str	3261.2	-	-
C-N bd	1497.3	1370	0.915	C-H str	3315.1	-	-
CH_2 rk	1291.9	1227	0.950	C-H str	3317.3	-	-
CH_2 rk	1502.2	1370	0.912	C-H str	3394.0	-	-
H-C-H sc	1336.2	-	-	C-H str	3401.1	-	-
H-C-H sc	1355.2	1266	0.934	-	-	-	-

TABLE 4. Comparison of computed and experimental frequencies of bis(2-chloroethyl)methylamine.

mode	corr.	mode	corr.
C-N str (symm)	0.97	torsion	1.00
C-N str (nonsym)	0.92	C-N bend	0.94
C-C stretch	0.95	N-C-C bend	0.93
C-H stretch	0.90	$CH_{2,3}$ rock	0.93
C-Cl stretch	1.06	H-C-H sciss	0.93
-	-	C-H bend	0.87

TABLE 5. Correction factors for 3-21G computed frequencies of tertiary amines.

mode	comp	int	corr	mode	comp	int	corr
torsion A	-	-	-	CH_2 rock A	1357.8	0	1263
torsion E	493.7	5	494	CH_2 rock E	1419.7	90	1320
C-Cl stretch A	485.1	14	514	C-H bend A	1450.7	138	1262
C-Cl stretch E	624.0	151	661	C-H bend A	1671.3	16	1454
C-N stretch A	770.4	290	747	C-H bend E	1635.9	7	1423
C-N stretch E	1239.6	351	1140	C-H stretch A	3324.7	38	2992
C-N bend A	945.2	4	884	C-H stretch A	3398.5	0	3059
C-N bend E	1536.7	164	1444	C-H stretch E	3317.2	2	2985
H-C-H sc A	982.6	0	850	C-H stretch E	3405.9	3	3065
H-C-H sc E	1035.2	142	963	-	-	-	-

TABLE 6. Computed and corrected vibrational frequencies of tris(chloromethyl)amine. The relative intensities of the lines are also listed.

mode	comp	int	corr	mode	comp	int	corr
torsion A	482.7	24	483	C-H bd A	1462.4	7	1272
torsion E	518.8	2	519	C-H bd A	1572.2	3	1368
C-Cl str A	604.2	37	640	C-H bd A	1628.4	23	1417
C-Cl str E	615.8	168	653	C-H bd A	1655.3	29	1440
C-N str A	731.3	0	709	C-H bd E	1540.6	19	1340
C-N str E	1244.4	52	1145	C-H bd E	1621.3	10	1411
C-C str A	1028.7	5	972	C-H bd E	1636.3	4	1424
C-C str E	1029.7	84	978	C-H str A	3209.3	54	2888
C-N bd A	924.0	27	869	C-H str A	3244.7	4	2920
C-N bd E	1517.9	134	1427	C-H str A	3329.7	1	2997
N-C-C bd A	999.6	1	930	C-H str A	3413.8	0	3072
N-C-C bd A	1110.3	57	1033	C-H str E	3202.3	25	2882
N-C-C bd E	1111.7	1	1034	C-H str E	3253.2	19	2928
N-C-C bd E	1244.4	52	1157	C-H str E	3330.0	18	2997
CH_2 sc A	1301.2	4	1210	C-H str E	3413.5	4	3072
CH_2 sc E	1326.8	45	1234	-	-	-	-
CH_2 rk A	1383.8	1	1287	-	-	-	-
CH_2 rk E	1416.9	45	1318	-	-	-	-

TABLE 7. Computed and corrected vibrational frequencies of tris(2-chloroethyl)amine. The relative intensities of the lines are also listed.

mode	comp	int	corr	mode	comp	int	corr
torsion	472.8	19	473	C-H bd	1458.7	18	1269
torsion	502.4	2	502	C-H bd	1531.3	23	1332
torsion	512.1	4	512	C-H bd	1565.2	11	1362
C-Cl str	614.5	49	651	C-H bd	1570.0	3	1366
C-Cl str	621.8	73	659	C-H bd	1616.9	9	1407
C-N str	738.9	1	717	C-H bd	1627.5	11	1416
C-N str	1214.1	31	1117	C-H bd	1635.1	1	1423
C-N str	1255.6	35	1450	C-H bd	1647.3	9	1433
C-C str	1009.5	18	959	C-H bd	1666.5	5	1450
C-C str	1025.4	34	974	C-H bd	1668.2	10	1451
C-C str	1040.3	7	988	C-H bd	1678.2	2	1460
C-N bd	1180.6	15	1110	C-H str	3187.6	28	2869
C-N bd	1519.4	37	1428	C-H str	3189.5	14	2871
C-N bd	1541.8	12	1449	C-H str	3195.7	69	2876
CH_2 rk	872.0	6	811	C-H str	3200.7	24	2881
N-C-C bd	934.4	5	869	C-H str	3228.1	5	2905
N-C-C bd	943.7	13	878	C-H str	3235.6	21	2912
N-C-C bd	1105.9	29	1028	C-H str	3241.4	3	2917
N-C-C bd	1108.2	8	1031	C-H str	3262.2	48	2936
N-C-C bd	1349.4	27	1255	C-H str	3279.4	31	2951
N-C-C bd	1406.5	4	1308	C-H str	3319.7	11	2988
H-C-H sc	1296.2	4	1205	C-H str	3323.0	10	2991
H-C-H sc	1324.7	14	1232	C-H str	3402.0	3	3062
CH_2 rk	1418.0	22	1319	C-H str	3405.9	2	3065
CH_2 rk	1497.8	65	1393	-	-	-	-

TABLE 8. Computed and corrected vibrational frequencies of bis(2-chloroethyl)ethylamine. The relative intensities of the infrared absorption lines are also listed.

mode	comp	int	corr	mode	comp	int	corr
torsion	472.5	2	472	C-H bd	1421.0	22	1236
torsion	478.6	25	479	C-H bd	1535.0	26	1335
torsion	507.3	1	507	C-H bd	1555.2	7	1353
C-Cl str	620.8	61	658	C-H bd	1617.7	3	1407
C-Cl str	625.1	51	663	C-H bd	1624.7	9	1413
C-N str	760.1	0	737	C-H bd	1626.5	10	1415
C-N str	1165.6	64	1072	C-H bd	1636.9	1	1424
C-N str	1226.8	27	1129	C-H bd	1656.1	12	1441
CH_3 rk,m	1264.5	5	1176	C-H bd	1683.0	6	1464
C-C str	1098.7	12	1044	C-H bd	1687.5	8	1468
C-C str	1114.3	15	1059	C-H str	3176.8	47	2859
N-C-C bd	934.7	4	869	C-H str	3184.1	28	2866
N-C-C bd	992.9	22	923	C-H str	3193.1	56	2874
N-C-C bd	1003.0	20	933	C-H str	3224.5	5	2902
N-C-C bd	1020.9	21	949	C-H str	3231.3	45	2908
C-N bd	992.9	22	933	C-H str	3235.5	21	2912
C-N bd	1433.7	17	1348	C-H str	3261.2	14	2935
C-N bd	1497.3	32	1407	C-H str	3315.1	14	2984
CH_2 rk	1291.9	3	1201	C-H str	3317.3	13	2986
CH_2 rk	1502.2	60	1397	C-H str	3394.0	4	3055
H-C-H sc	1336.2	8	1243	C-H str	3401.1	2	3061
H-C-H sc	1355.2	19	1260	-	-	-	-

TABLE 9. Computed and corrected vibrational frequencies of bis(2-chloroethyl)methylamine. The relative intensities of the infrared absorption lines are also listed.

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