ground state for a system with more strongly coordinated ligands.

It is suggested that the reductive elimination of ethane from $L_nNi(CH_3)_2$ is controlled by the possibility of a charge flow from the methyl groups to the metal atom. Such a charge flow is hindered by the presence of donating ligands L, which thus stabilize the complex. On the other hand, elimination is expected to proceed more easily when electron-attracting ligands are added to the system, which is in agreement with experiment.

We have suggested that the barrier to a concerted formation of ethane could be lowered considerably in the $^3B_2$ case, by a recoupling of the 3d electrons on the metal along the reaction path, the argument for such a mechanism being the closeness of the two states $^3B_2$ and $^1A_1$. Since such recoupling mechanisms may be of importance in other catalytic processes we intend to analyze the reaction in more detail in the future.

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Molecular Orbital Constrained Electron Diffraction Studies. Conformational Behavior of 1,2-Dimethylhydrazine

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Abstract: The results of a conformational analysis of 1,2-dimethylhydrazine are described which were obtained by applying MOCED (molecular orbital constrained electron diffraction). In this procedure primary structural parameters (differences between bond distances and bond angles), which can be reliably predicted by complete ab initio force relaxations, are used as constraints needed to interprete the gas electron diffraction data of a molecule. The diffraction data can be used to describe the conformational behavior of a molecule as a means to interpret the calculated ab initio conformational energy differences, which are usually less well established than ab initio structures because of basis set effects, correlation effects, and vibrational effects. Results for complete ab initio (4-31G) force relaxations of three gauche forms of 1,2-dimethylhydrazine are given. The investigation confirms the existence of the inner-outer conformer (CNNC torsional angle about 90°) as a major conformation. Details of analysis suggest the presence of at least one other conformer which cannot be definitely determined from the diffraction data. Both inner-inner (calculated CNNC angle 50°) and outer-outer forms (calculated CNNC angle 140°) must be considered. The study demonstrates the power of hybrid theoretical and experimental procedures in conformational analyses. It also demonstrates that ab initio conformational analyses using standard geometries can be misleading, since each conformation may deviate from the standard in an unpredictable manner.

Introduction

The ability of standard single determinant molecular orbital theory to reliably predict molecular equilibrium structures has been documented in countless studies. Primary structural parameters, such as bond distances, bond angles, and, in particular, relative differences between related parameters of this kind, can now be estimated very accurately on the basis of ab initio calculations. In some cases, such as in the recent investigations of glycine[2a] and beryllocene,[2b] the ab initio results have even affected interpretation of experimental data in a striking manner.

The power of ab initio techniques to generate molecular

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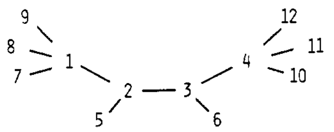


Figure 1. Atom numbers of 1,2-dimethylhydrazine.

structure is not equaled by the ability of such calculations to reliably predict small energy differences between different conformations. In fact, basis-set effects, correlation effects, and vibrational effects add an element of considerable uncertainty to calculated conformational energy differences. The vibrational effects are particularly interesting, since the factors which stabilize an equilibrium structure may generate destabilizing zero point energy contributions to its corresponding thermal average molecular conformation.[2a] The description of the conformational behavior of a system on the basis of quantum theory alone is, therefore, often difficult.

Electron diffraction data recorded from gaseous molecules contain a great deal of experimental conformational information. However, this information can often be deciphered only if differences between primary structural parameters, such as bond distances and bond angles, can be resolved. Gas electron diffraction (GED) as a tool of structural chemistry suffers from characteristic deficiencies, which are caused mainly by its inability to resolve geometrical parameters which generate overlapping signals in the radial distribution curve. For example, a particular weakness is that it is usually not possible to resolve closely spaced bond distances from GED patterns.

In traditional GED studies, arbitrary assumptions are, therefore, often made to constrain least-squares data analysis. A certain bond distance in a particular molecule, for example, may have to be assumed to be smaller than another similar bond. Or a bond angle may be assumed to be less extended than another related parameter. Such assumptions are usually made on an intuitive basis and they represent a dissatisfactory and hazardous element in studies of this kind.

In comparing the list of deficiencies of gas diffraction experiments and molecular quantum theory in conformational analysis, one will note a certain complementarity. MOCED (molecular orbital constrained electron diffraction) is an attempt to make use of this complementarity in order to remove arbitrariness from gas electron diffraction studies and in order to provide some experimental verification of somewhat uncertain ab initio conformational energy differences. In MOCED studies, the results from high-quality ab initio geometry optimizations that can be trusted (for example, calculated differences between closely spaced bond distances and bond angles) are used as constraints of GED least-squares data analysis. Once the quantum mechanical approximation has been chosen and the constraints have been determined, this results in a nearly automatic evaluation of the conformational content of GED data.

In studies of this kind, calculations of mean amplitudes are also important. Mean amplitudes are, in principle, also observables of GED experiments. They can now be calculated accurately enough so that differences between amplitudes of related distances can be used as further constraints of GED data analysis.

Conventional amplitude computations require construction of reliable molecular force fields as a prerequisite. In all but the simplest cases, force-field refinements suffer from a great deal of arbitrariness caused by the fact that the number of observables is usually smaller than the number of unknowns in vibrational calculations. Most investigators usually spend much time to refine a "best" force field in order to derive mean amplitudes of vibration.

In order to avoid these complications, we have developed a procedure[3] that allows calculating mean amplitudes without a refined force field directly from experimental vibrational frequencies. This procedure has also been applied in the present study.

To document the efficacy of MOCED we have chosen, for this paper, the case of 1,2-dimethylhydrazine (Figure 1). The molecule is ideally suited for this purpose because it possesses interesting conformational features and its structure involves geometrical parameters which generate unresolved signals in GED radial distribution. There are 30 internal degrees of freedom in one conformation of this compound. There are only five, maybe six, resolved features in its experimental radial distribution curve (Figure 2 is described below). Many workers in this field believe that the number of unknowns that can be determined from GED data should not exceed the number of resolved features in the radial distribution curve. Somehow simplifying constraints must, therefore, be imposed on the GED data analysis of 1,2-dimethylhydrazine. We believe that these constraints are best defined on the basis of well-characterized ab initio calculations.

The conformational behavior of 1,2-dimethylhydrazine has in the past found the attention of many investigators. We shall refer here only to those published results which are relevant for our investigation.[4-9] These are the photoelectron spectroscopic study,[4] an extensive report on the molecular vibrations,[5] and a study of the heat capacity[6] and of the dipole moment[7] of the compound. An early electron-diffraction study of this molecule[8] was inconclusive as to its conformational behavior. A second, more recent electron-diffraction study[9] will allow interesting comparisons of MOCED and conventional electron diffraction data analysis techniques.

Theory and Data Analysis

Single determinant MO theory with the STO-3G basis[10] was initially applied using the GAUSSIAN 70 computer program.[11] Since the STO-3G results were found to be unacceptable compared to experiment, additional calculations were performed on the 4-31G[12] level. Since geometry optimizations by ab initio force relaxations lead to significantly better geometries than energy optimizations, Pulay's FORCE program[13,14] was used to generate the ab initio equilibrium geometries of three conformations of 1,2-dimethylhydrazine, which produced the best fitting conformational mixture compared to the GED data. These optimizations were performed on the 4-31G level and made use of our normal coordinate ab initio relaxation scheme[15] when it became available, and of the variable metric minimization scheme,[16,17] in earlier calculations.

Mean amplitudes of vibration of 1,2-dimethylhydrazine were calculated using the normal coordinate program by Sellers et al.[18,19] The previously described procedure[3] was applied, which allows calculation of mean amplitudes of vibration directly from experimental frequencies without a refined force field using the method of Stølevik et al.[20] The frequency assignment of Durig et al.[5] was adopted for these calculations.

The electron-diffraction data of 1,2-dimethylhydrazine were recorded at the University of Tokyo[9,21] and specifications are given in the report of a conventional data analysis,[9] which was executed independently from our investigation and made use of constraints not obtained from ab initio calculations. The standard data analysis procedures were applied in this study.[22] Calculated molecular parameters were used as constraints of the data in the following way.

The amplitudes of those distances which appeared unresolved together in one peak of the experimental radial distribution curve (RD curve) were refined in one group. Calculated amplitude differences were retained during the least-squares

Table I. Calculated Energy Differences (kcal/mol) and Dipole Moments (D) for Various Conformations of 1,2-Dimethylhydrazine[a]

conf	set 1	set 2	μ
I	0.1	0.0	1.6
II	0.0	0.2	1.8
III	2.3	1.1	1.6
IV	1.5		(2.6)[b]
V	5.4		(1.9)[b]

[a] Set 1 represents 4-31G energy differences for STO-3G partially optimized conformations. Set 2 represents 4-31G values obtained for geometries fully optimized by force relaxation. Column μ lists the 4-31G dipole moments. The total energies (au) of I in set 1 and set 2 are −188.938 13 and −188.947 42, respectively. [b] Tentative values calculated for STO-3G partially optimized geometries.

analysis for all the members in one group, i.e., the same shift was applied to all of them in each cycle of the refinement. Six such groups were formed. The corresponding segments of the RD curve were defined from 0.8 to 1.25, 1.25 to 1.75, 1.75 to 2.2, 2.2 to 2.95, 2.95 to 3.5, and 3.5 to 4.5 Å, respectively.

In refining geometrical parameters similar constraints were introduced. The C–H and N–H bonds and the N–N and C–N bonds formed two unresolved maxima in the RD curve. The ab initio differences between the C–H and N–H bonds and between the N–N and C–N bonds were, therefore, retained and kept constant during the least-squares data analysis.

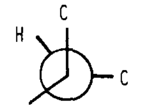
All CNN, NNH, and NCH angles were also grouped together, if the corresponding nonbonded distances appeared unresolved in one peak of the RD curve, by retaining the calculated differences between them.

Differences between calculated geometrical parameters rather than their magnitudes were used as constraints of the data analysis, since the calculated distances are r_e whereas the experimental values are r_a or r_g. The magnitudes of these distance types are different by definition. Our procedure therefore is approximate by implying that $\Delta r_e \simeq \Delta r_a$ for C–N and N–N bonds and for C–H and N–H bonds, respectively. This approximation is reasonable in view of the experimental error limits of these parameters (see below).

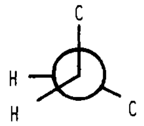
The CNNC torsional angle was refined without constraint in all unmixed models. In some conformational mixtures, the CNNC torsions of the minor components were not refined, but were kept constant at their calculated values. No attempts were made to refine the NNCH and the HNNC torsions. The ab initio values were used for these parameters in all refinements.

Results and Discussion

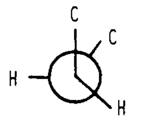
At the beginning of this investigation, the conformational space of 1,2-dimethylhydrazine was analyzed by considering all possible combinations of the HNNH, CNNC, and CNNH torsional angles in increments of 30°. This generated 19 different conformations all of which belong to one of the following conformational types: gauche (forms I, II, and III), trans (forms such as IV), and eclipsed (forms such as V). I, II, and III have been called[9] inner-outer, outer-outer, and inner-inner, respectively.



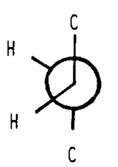
I



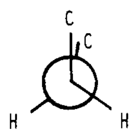
II



III



IV



V

The geometries of all 19 conformations were then partially optimized by lowering their energies using the STO-3G basis set. After this optimization, the STO-3G and the 4-31G energies of all those geometries in which the two C–N bonds are eclipsed with respect to each other or to the adjacent N–H bonds were found to be more than 5 kcal/mol less stable than the trans or gauche forms, the energies of which are closer to one another (Table I). In spite of the uncertainties of ab initio energies outlined in the Introduction, 5 kcal/mol was considered a safe margin and no eclipsed forms were considered in the subsequent investigations.

Selection of conformations for the subsequent quantum mechanical geometry optimizations, which required several hundred hours of CPU time on our IBM 370/155, was guided by diffraction data analysis.

When we attempted to reproduce the electron diffraction data by individual (unmixed) trans models, such as IV, the refinements led to physically meaningless solutions. In the same way as documented in greater detail for II below, best fit to the data was obtained for individual trans models only by distorting the values of important groups of amplitudes to unacceptable values. Since conformational mixtures involving trans forms did not lead to the clear improvements observed for other mixtures (for example, for the mixture of I and II described below), it was concluded that trans forms are not major conformers in vapors of 1,2-dimethylhydrazine. Hence, data analysis was allowed to overrule the relatively small ab initio energy differences between trans and gauche forms (Table I) and no trans form was considered in the subsequent investigations.

Of the remaining gauche forms, a mixture of I and III was found by the conventional GED investigation[9] to reproduce the data best. Forms I and III were therefore fully optimized on the 4-31G level.

In further analyses of the data we found that mixtures of I and II also reproduced the experimental intensities satisfactorily. The geometry of II was therefore also fully optimized on the 4-31G level.

In all these calculations, each conformation was optimized in about 15 cycles without any constraint by relaxing the forces on the atoms. Each cycle required about 7 h of CPU time on our IBM 370/155. The resulting energies are listed in Table I; the resulting geometries are listed in Table II; they are in excellent agreement with those experimental parameters (Table III) the values of which can be estimated from the diffraction data. All theoretical bond distances (r_e), notably, are smaller than the experimental values (r_a), as they should be.

The optimized parameters of Table II show an unusual and interesting feature which deserves special comment. The two C–N bonds in conformation I did not approach the same equilibrium value. $r_e(C_1–N_2)$ = 1.4516 Å and $r_e(C_4–N_3)$ = 1.4502 Å were calculated for this conformation. In contrast to this, the same value, r_e = 1.449 Å, was found for these parameters in conformation II (Table II).

It is possible that this effect in I is the consequence of incomplete geometry optimization. The largest residual forces (in I) were of the order of magnitude of 0.004 mdyn. On the other hand, the difference in the C–N bonds may very well be a true feature of the structure of I, since the interactions of the methyl groups with the adjacent nitrogen lone pair, for example, are not symmetrical. Indeed, in II, where the two C–N bonds adopted the same minimum, this interaction appears to be nearly the same for both methyl groups, as a qualitative inspection of its structure seems to indicate. We have en-

Table II. Bond Distances (Å) and Angles (deg) for the 4-31G Optimized Conformations I, II, and III of 1,2-Dimethylhydrazine[a]

	conformations		
	I	II	III
	Bond Lengths		
C_1-N_2	1.4516	1.4489	1.4520
C_4-N_3	1.4502	1.4493	1.4520
N_2-N_3	1.4068	1.4068	1.4022
N_2-H_5	0.9950	0.9994	0.9939
N_3-H_6	1.0005	0.9991	0.9939
C_1-H_7	1.0909	1.0888	1.0814
C_1-H_8	1.0811	1.0819	1.0808
C_1-H_9	1.0804	1.0785	1.0875
C_4-H_{10}	1.0785	1.0887	1.0814
C_4-H_{11}	1.0823	1.0818	1.0808
C_4-H_{12}	1.0882	1.0784	1.0875
	Bond Angles		
$C_1N_2N_3$	116.31	113.75	118.72
$C_4N_3N_2$	114.03	113.72	118.72
$H_5N_2N_3$	110.73	113.49	111.20
$H_6N_3N_2$	113.48	113.54	111.20
$H_5N_2C_1$	114.98	114.45	115.61
$H_6N_3C_4$	114.78	114.43	115.61
$H_7C_1N_2$	113.39	113.30	109.31
$H_8C_1N_2$	109.44	108.87	108.49
$H_8C_1H_7$	108.36	108.60	107.88
$H_9C_1N_2$	109.53	108.86	114.52
$H_9C_1H_7$	108.09	108.20	108.22
$H_9C_1H_8$	107.88	108.94	108.22
$H_{10}C_4N_3$	108.85	113.25	109.31
$H_{11}C_4N_3$	108.88	108.83	108.49
$H_{11}C_4H_{10}$	108.51	108.61	107.88
$H_{12}C_4N_3$	113.77	108.87	114.52
$H_{12}C_4H_{10}$	108.08	108.24	108.22
$H_{12}C_4H_{11}$	108.63	108.97	108.22
	Torsional Angles		
$C_1N_2N_3C_4$	93.93	140.39	50.16
$C_1N_2N_3H_6$	−40.03	−86.43	−87.68
$C_4N_3N_2H_5$	−132.37	−86.42	−87.67
$H_6N_3N_2H_5$	93.68	46.76	134.49
$H_7C_1N_2N_3$	60.01	59.88	56.32
$H_8C_1N_2N_3$	−178.88	−179.18	173.72
$H_9C_1N_2N_3$	−60.81	−60.55	−65.29
$H_{10}C_4N_3N_2$	62.66	59.94	56.32
$H_{11}C_4N_3N_2$	−179.22	−179.17	173.72
$H_{12}C_4N_3N_2$	−57.92	−60.51	−65.29

[a] All optimizations were executed without any geometrical constraints by using Pulay's force method. The largest residual forces in the relaxed geometries are of the order of magnitude of 0.007 mdyn in II and 0.004 mdyn in I and III.

countered similar differences in N-H and C-H bonds in our ab initio studies of formamide[15] and acetamide.[23] In some of these cases the calculated differences can be correlated to hydrogen bonding. They must be considered as real, even though they cannot be observed by any experiment.

The results of our STO-3G calculations will not be reported in greater detail, because they were found to be unacceptable compared to experiment. The superiority of the split-valence basis has been demonstrated in countless studies by Pople and his group.[24] Our confidence in the 4-31G basis is supported by many successful 4-21G geometry predictions by Boggs, Pulay, and co-workers[25] and by our own group.[2a,15,23]

The STO-3G results were found to be unacceptable compared to experiment because optimized bond distances turned out to be larger than experimental values. From the conventional electron diffraction data analysis,[9] r_g(C-N) = 1.463 (5) Å, r_g(N-N) = 1.419 (11) Å, r_g(C-H) = 1.119 (12) Å, and r_g(N-H) = 1.034 (16) Å were obtained. Quotation of these values seems to indicate that the corresponding parameters are easily and reliably determined by conventional gas electron diffraction. It must be emphasized, however, that the C-N and N-N bonds and the C-H and N-H bond distances are essentially unresolved in the GED data. Many different pairs of values can usually satisfy the data in cases of this kind and very little is known about the true error limits of such highly correlated parameters. They are, therefore, less well established than parameters which are resolved in GED experiments. Additional confirmation, for example by ab initio calculations, is desirable and useful.

The N-N and C-N bond average and the N-H and C-H bond average are true observables, however, and their values can be used to rule out the STO-3G optimized values which were found for conformation I, for example, as r_e(C-N) = 1.4854 Å, r_e(N-N) = 1.4492 Å, r_e(N-H) = 1.0366 Å, and r_e(C-H) = 1.0902 Å. These r_e values should be smaller than the experimental r_g values, whereas all of them, except C-H, are larger. The same deficiencies were observed for the STO-3G parameters of all the other conformations. The geometrical parameters of Table II are also interesting because they demonstrate that conformational analyses based on standard geometries can be misleading. When individual conformations of a molecule are relaxed, they obtain geometries which can differ in unpredictable ways from geometry standards. (See, for example, the results obtained for I, II, and III in Table II, or the results obtained for several glycine conformations.[2a]) True SCF energy differences can, therefore, only be obtained from completely relaxed geometries.

Calculated dipole moments of 1,2-dimethylhydrazine are given in Table I. The experimental moment[7] has been reported as 1.35 D. Since it was measured in solution, it is of little help for conformational studies in the gaseous state. As the moment calculated for conformation IV indicates (Table I) the experimental value cannot be taken as a basis to rule out all trans forms for this compound. (Calculated dipoles for IV and V are for nonoptimized geometries and are therefore very uncertain at best.)

To judge the theoretical models described above by their relations to the experimental GED data, the material of Table IV should be consulted.

When attempts were made to reproduce the experimental data by the individual (unmixed) models I, II or III, no acceptable least-squares minimum was obtained except for conformation I.

The radial distribution of conformation II, for example, is so different from experimental radial distribution that best fit can be achieved only at the cost of distorting some of the amplitudes of this model to such an extent (Table IV) that they become physically meaningless compared to calculated amplitude values. For II this effect was demonstrated, for example, for the distances between atom pairs 1-4, 1-10, 1-11, 1-12, 2-11, 3-8, 4-7, 4-8, and 4-9 (Table IV).

No stable least-squares minimum was found corresponding to model III. Instead, data refinement forced its CNNC torsional angle to a value of about 90°, the value of the CNNC torsional angle of conformation I. For the inner-inner form, III, this torsional angle is only 30° (or a few kcal/mol) away from an energy maximum (eclipsed form) which is about 11 kcal/mol less stable than I (4-31G value for STO-3G partially optimized geometries), and it is too far away from the calculated optimum geometry to be acceptable. Again, as discussed above, the energy difference quoted is uncertain, but its magnitude allows for a safe margin.

In contrast to these results for II and III, conformation I did find a stable least-squares minimum which was, at the same time, close to the calculated geometry and produced a best fit without assuming unreasonable amplitudes of vibration for any of its distances (Tables III and IV). We want to use these results as a basis to identify I, but not II and III, as a major

Table III. Selected Internal Coordinates (Distances, r_a, in Å, Angles in deg) of Conformations I and II of 1,2-Dimethylhydrazine Obtained by Least-Squares Refinement of the Gas Electron Diffraction Data[a]

	conformation I (unmixed)	conformation II (unmixed)	conformation I (in mixture)	conformation II (in mixture)
		Bond Distances		
C_1-N_2	1.466 ± 0.013	1.465 ± 0.011	1.467 ± 0.044	1.465 ± 0.044
N_2-N_3	1.421 ± 0.013	1.423 ± 0.011	1.423 ± 0.044	1.423 ± 0.044
N_2-H_5	1.011 ± 0.115	1.014 ± 0.100	1.008 ± 0.080	1.012 ± 0.080
C_1-H_7	1.107 ± 0.115	1.104 ± 0.100	1.104 ± 0.080	1.102 ± 0.080
		Valence Angles		
$C_1N_2N_3$	113.1 ± 1.7	112.3 ± 1.9	113.0 ± 2.3	110.4 ± 2.3
$H_6N_3N_2$	109.7 ± 13.0	110.3 ± 17.2	110.2 ± 17.0	110.3 ± 17.0
$N_2C_1H_7$	109.9 ± 12.6	112.0 ± 16.0	111.1 ± 17.3	111.0 ± 17.3
		Torsional Angle		
$C_1N_2N_3C_4$	88.0 ± 7.0	149.1 ± 8.8	88.2 ± 9.4	150.9 ± 32.8

[a] The numbers of this table are not true observables, because the corresponding parameters are not resolved in the experimental data. The error limits shown are, therefore, not physical error limits but merely three times the standard deviations from the least-squares refinement. These numbers are presented as effective parameters only to document the nature of our conformational models. Uncertainties are relatively large compared to conventional electron-diffraction studies due to the many constraints imposed on our least-squares data analysis. Three sets of parameters are given obtained by refining unmixed models representing 100% of I, 100% of II, and a model representing a conformational equilibrium of I and II, respectively. In similar refinements of conformational equilibria involving conformation III, its refined CNNC torsional angle always attained values of about 37°.

Table IV. Some Selected Mean Amplitudes of Vibration for Conformations I, II, and III[a]

No. I dist	type	calcd	100%	(I,II)	(I,III)	(I,II,III)
3.26	1-4	0.117	0.161 (0.064)	0.118 (0.069)	0.130 (0.063)	0.109 (0.077)
3.75	1-10	0.200	0.157 (0.141)	0.186 (0.290)	0.138 (0.125)	0.154 (0.191)
4.15	1-11	0.151	0.108 (0.141)	0.137 (0.290)	0.090 (0.125)	0.106 (0.191)
3.31	2-11	0.105	0.149 (0.064)	0.106 (0.069)	0.118 (0.063)	0.098 (0.077)
3.34	3-8	0.105	0.149 (0.064)	0.106 (0.069)	0.118 (0.063)	0.098 (0.077)
3.13	4-5	0.119	0.162 (0.064)	0.120 (0.069)	0.131 (0.063)	0.111 (0.077)
3.81	4-7	0.200	0.157 (0.141)	0.186 (0.290)	0.139 (0.125)	0.155 (0.191)
4.13	4-8	0.151	0.108 (0.141)	0.138 (0.290)	0.090 (0.125)	0.106 (0.191)
R			0.105	0.102	0.105	0.102
concn				78% (± 22) of I	83% (±15) of I	72% (±31) of I 15% (±23) of II

No. II dist	type	calcd	100%
3.66	1-4	0.084	0.496 (0.411)
4.15	1-10	0.155	0.567 (0.411)
4.45	1-11	0.130	0.543 (0.411)
3.81	1-12	0.182	0.594 (0.411)
3.33	2-11	0.105	0.153 (0.200)
3.33	3-8	0.105	0.153 (0.200)
4.15	4-7	0.155	0.567 (0.411)
4.45	4-8	0.130	0.543 (0.411)
3.81	4-9	0.182	0.594 (0.411)
R			0.122

[a] Column "dist" gives the internuclear distances (Å) for atom pairs listed in column "type"; "calcd" gives the calculated mean amplitudes of vibration (Å); the column headed 100% gives the mean amplitudes of vibration refined from the electron diffraction data for the individual (unmixed) conformations I and II; columns (I,II), (I,III), and (I,II,III) give the results of the least-squares electron-diffraction data refinements for conformation I in mixtures with II,III and both II and III, respectively. In the refinements of the conformational mixtures, the amplitudes of the minor components were kept constant at their calculated values. Numbers in parentheses represent three times the standard deviations from the least-squares refinement. Note that the amplitudes listed were not refined individually but in groups as described in the text. Rows *R* give the *R* factors of the best fit; "concn" gives the concentrations of the best fitting mixtures. The refined values of all the other amplitudes of I, II, and III, which are not listed in this table, did not deviate significantly more than about 10% from the calculated values.

conformation of 1,2-dimethylhydrazine in its vapor state at room temperature.

The data adjusted mean amplitudes of Table IV are the results of attempts to generate the best agreement between a given model and the experiment. Only those amplitudes are presented in this table whose refined values differ by significantly more than 10% from the calculated ones. In general, all refined amplitudes of the models tested were found to be in good agreement with calculated ones for all those distances, which do not depend on internal rotation.

The relatively small differences between calculated and refined mean amplitudes which do exist in conformation I (Table IV) may be indicative of the presence of a second less populated conformer in vapors of 1,2-dimethylhydrazine. In-

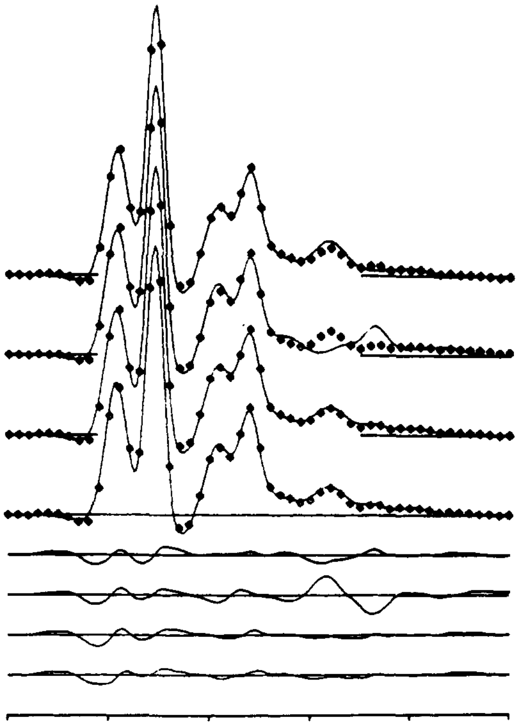


Figure 2. Experimental (dotted lines) and theoretical (solid lines) radical distribution curves of various models for 1,2-dimethylhydrazine. From top to bottom: conformation I with calculated mean amplitudes; conformation II with calculated mean amplitudes; mixture of I and II with calculated amplitudes; mixture of I and II with refined mean amplitudes (Table IV). The following curves are the corresponding differences (experiment minus theory) in the same sequence. All damping factors were 0.0025 Å^2. All curves extend from 0.0 to 5.0 Å.

deed, when a mixture of conformations I and II was refined, a stable least-squares minimum was attained for a conformational equilibrium with a composition of 78% (±22) of I and 22% of II, with all refined mean amplitudes being very close to calculated ones (Table IV).

It must be emphasized that the GED data do not allow identification of the second most important conformer with certainty. Energy considerations aside, refinements of various mixtures of I with other conformations also yielded potentially satisfactory results. In fact, a mixture of inner–outer (conformation I) and inner–inner (conformation III) was presented as the best solution of the conventional GED study.[9] When our constraints are used in refining a mixture of I and III, the result is not significantly worse than that obtained for the mixture of I and II, even though it does not represent our best fitting model (Table IV). On the basis of our constraints, it is therefore not possible to exclude the presence of either II or III in vapors of 1,2-dimethylhydrazine.

The theoretical RD curve of the mixture of I and II still shows some minor deviations from experiment in the conformationally sensitive range (Figure 2). These deviations might be interpreted as an indication for the presence of other conformers in small concentrations. Some ternary mixtures were therefore tested and indeed produced acceptable results (those for a mixture of I, II, and III are given in Table IV). But the details of these refinements are so uncertain that they do not allow any meaningful conclusion. The differences between theory and experiment are now so insignificant that the essential features of the GED data can be considered explained. Examples documenting the close agreement between theoretical and experimental radial distribution are presented in Figure 2.

The differences between theory and experiment which are apparent in the conformationally independent part of the radial distribution curve ($0 < r < 1.8$ Å; Figure 2) may at first sight suggest reasons to question the reliability of the data analysis. These disagreements indicate that the theoretical constraints (differences between calculated bond distances and between their mean amplitudes of vibration) do not correspond exactly to the experimental parameters. In fact, the effects of our constraints may be visible in slight shifts of our refined bond distances (Table III) as compared to the conventional study,[9] even though both sets of data are within error limits. In view of the approximations applied, this inaccuracy in our analysis is not amazing. At the same time, its effect does not question our conclusions, since the deviations observed can be caused by differences of a few thousandths of an ångstrom in the corresponding parameters. Experimental uncertainty is much larger, namely, 0.013 Å for the C–N and N–N bonds and 0.115 Å for the N–H and C–H bonds. Imperfections of this kind can be found in many GED studies (see, for example, ref 26 and 27) and are usually not considered to be important.

The heat capacity and entropy study[6] of 1,2-dimethylhydrazine allowed two alternatives for the conformational behavior of this molecule. The entropy calculated was in agreement with the entropy measured for a pure form consisting of 100% of an inner–outer conformation and for a mixture consisting of about 70% of an outer–outer form and 30% of an inner–outer conformation.[6] The vibrational analysis of 1,2-dimethylhydrazine yielded a 69:31% mixture of gauche conformers.[5] If the photoelectron spectra of the compound are interpreted in terms of CNDO/2 calculations,[4] there is a contrast to our best solution (the mixture of I and II), since the experimental nonbonding splitting is not in agreement with the nonbonding splitting calculated for II.[4] It is now impossible to determine whether this definitely rules out the presence of II or whether it indicates the need for a different interpretation of the photoelectron spectra.

Comparison of MOCED with the Conventional GED Analysis

The recent conventional GED investigation[9] of 1,2-dimethylhydrazine provides an opportunity to compare MOCED with traditional data analysis techniques.

Both studies agree in identifying the inner–outer form (conformation I) as a major conformer in the gas phase. Both studies agree in concluding that the presence of a second conformer can be inferred from the diffraction data. But, whereas only the inner–inner form is identified as the second component in the conventional analysis,[9] our constraints also force us to consider a mixture of inner–outer and outer–outer as a possible solution to the diffraction data.

As mentioned above, the electron-diffraction data do not allow identification of the second conformer with certainty. When our constraints are used, a mixture of inner–outer and inner–inner also represents an acceptable solution (Table IV), even though it is not our best solution. Some of the amplitudes refined for the best fitting mixture of I and III are undoubtedly too small (Table IV) when our constraints are used. However, if these amplitudes were set constant at their calculated values during the least-squares refinement, the resulting model would not be in significant disagreement with experiment.

In contrast to this it was possible to refine all amplitude groups for the mixture of I and II and the refined values turned out to be closer to the calculated ones than those of any other model (Table IV). To compare this result to the ab initio energies of the optimized structures (Table I), it is important to realize that I is favored over both II and III by a degeneracy factor of 2. There are four different combinations of HNNH, CNNC, and CNNH torsional angles which will yield conformation I (deg): 90, 90, 330; 90, 90, 210; 270, 270, 150; 270, 270, 30, respectively. There are only two combinations of the

HNNH, CNNC, and CNNH torsional angles which will yield forms such as II (30, 150, 270; 330, 210, 90, respectively) or III (150, 30, 270; 210, 330, 90).

All the factors mentioned above represent a suggestive trend, but they are not sufficient to definitely establish the presence of II, or to rule out the models representing 100% of I or the mixture of I and III. This result means, rather, that it is not possible to rule out the presence of II on the basis of the diffraction data, as the conventional analysis seems to imply.[9]

The conventional GED investigation[9] also confirms that a number of constraints must be used to analyze the GED data. The authors[9] used the following constraints (the list given here is not complete):

(1) All the structural parameters for the two conformers are equal to each other except for the dihedral angles.

(2) All the C–H bond lengths are equal. Two methyl groups have local C_{3v} symmetry and have no tilt.

(3) The N–N–H angles are equal to those in hydrazine.

(4) The C–N–H angles are equal to that in methylhydrazine.

(5) The methyl torsional angles are estimated by calculation of nonbonded interactions among the hydrogen atoms in such a way that the total energy takes a minimum.

Compared to the optimized ab initio geometries, these constraints are subject to the following uncertainties:

(1) The structural parameters in different conformations are not the same (Table II). Bond distances between framework atoms can vary by more than 0.004 Å; bond angles determining the framework of the molecule can vary by 5°; similar variations are observed for angles involving hydrogen atoms.

(2) The C–H bonds are not equal, but can vary by 0.01 Å within one conformer; the methyl groups do not have local C_{3v} symmetry and are tilted by several degrees (N–C–H angles can vary by nearly 5°).

(3) The N–N–H angles can differ by more than 4° from the corresponding values in hydrazine.

(4) The C–N–H angles can vary by more than 12° from the methylhydrazine value.

(5) The nonbonded hydrogen interactions are certainly an important factor, but not the only important factor in determining the methyl torsional angles. The empirical constraints can, therefore, differ from our calculated values by more than 12°. Similar uncertainties must probably be expected for the CNNH torsions, for which the empirical constraints were not specified.

This list of ab initio estimates of uncertainties in the empirical constraints does probably not represent an absolutely accurate image of reality. But, certainly, inaccuracies of this kind undoubtedly must exist. Some of the individual discrepancies also may seem to be insignificant. But, quite apart from the present case, nobody can make a general a priori prediction as to what effect the sum total of such inaccuracies in individual parameters can have on the outcome of such conformational analyses. It is our claim that geometrical constraints in diffraction data analyses obtained from high-quality molecular orbital calculations are more consistently accurate than empirical guesses.

The fact that, except for indicating the existence of an additional plausible solution to the diffraction data, the results of the conventional study and of our own investigation in this case turned out to be the same is not destructive to the purpose of this paper. Our concern is general and, whenever the number of observables is smaller in any experiment than the number of unknowns, any additional relevant evidence is worthwhile to be considered.

Certainly, the intimate connection of theory and experiment which we were able to use is absolutely enjoyable. The characteristic imperfections of gas electron diffraction seem to make it particularly well suited for conjoining observation and deduction in this novel manner.

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