Molecular Structure of Chlorodifluoronitrosomethane, $CClF_2NO$, As Determined in the Gas Phase by Electron Diffraction and ab Initio Calculations

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The gas-phase structure of chlorodifluoronitrosomethane, $CClF_2NO$, has been determined by electron diffraction and calculated ab initio. Theoretically, $CClF_2NO$ is predicted to consist of two conformers having C_s ($\phi = 0°$) and C_1 ($\phi = 105°$) symmetry, which are near degenerate in energy, $\Delta E = 1.1$ kJ mol^{-1} [TZ2P/MP2 + ZPE(DZP/MP2)], and separated by a barrier of around 1 kJ mol^{-1}. Equivalent C_1 conformers are predicted to be connected by a barrier of around 5−10 kJ mol^{-1}. The low predicted barriers to interconversion of the two conformers suggest that the rotation of the nitroso group can be regarded as being barely restricted over most values of the torsional angle at room temperature. This conclusion is supported by the gas-phase electron diffraction data, for which a dynamic model employing 11 conformations was needed to obtain an accurate fit to the experimental data. The final refined values of structural parameters for the two conformers (C_s/C_1) are (r_α/pm, $<_\alpha$/deg) as follows: C(1)−N(2) 156.7(5)/155.9(5), N(2)−O(3) 117.5(3)/117.9(3), C(1)−Cl(4) 173.9(2)/174.2(2), C(1)−F 132.0(2)/132.1(2) and 131.0(2), C(1)−N(2)−O(3) 110.8(12)/110.7(12), N(2)−C(1)−Cl(4) 117.5(5)/108.9(5), N(2)−C(1)−F 103.7(2)/104.2(2) and 111.6(2), Cl(4)−C(1)−N(2)−F 123.6(14)/119.2(14) and 123.7(14).

Introduction

Nitrosomethane and its derivatives represent important examples of fluxional behavior. The overall torsional potential for these compounds may be viewed as being sums of two 3-fold terms, the two terms being due to the interaction between the groups of the methyl group and either the O or the lone pair of the nitroso group. In principle this may lead to a 6-fold barrier to rotation about the C−N bond and/or barrier heights which are sufficiently small to allow rapid interconversion of conformers. Significant variations in the values of some structural parameters, particularly bond angles, may also be associated with the large amplitude internal motion since eclipsed or syn conformations appear to be preferred. At present only two molecules which belong to this class of compound, CH_3NO and CF_3NO, have been the subject of gas-phase structural studies.[1−3] Both exhibit barriers connecting equivalent conformers of less than 5 kJ mol^{-1}; however, in these cases it is expected that any other internal structural changes will be small because of the approximate 3-fold symmetry of the $-CF_3$ or $-CH_3$ unit. For molecules that do not possess such symmetry, e.g. $CClF_2NO$, structural changes may be significantly larger. The possibility of fluxional behavior and the potential for significant variation in bond angles and bond lengths as the molecule converts between two conformations make $CClF_2NO$ an intriguing target for structural studies. As part of this work we have undertaken a detailed theoretical and experimental study of $CClF_2NO$ in an attempt to understand its dynamic behavior in the gas phase.

Ab Initio Calculations

Theoretical Methods. All calculations were performed on a Dec Alpha 1000 4/200 workstation using the Gaussian 94 program.[4] Geometries and vibrational frequencies were calculated from analytic first and second derivatives, respectively. An extensive search of the potential energy surface aimed at locating all local minima and transition states to internal rotation was undertaken at the SCF and MP2 levels of theory using a DZP basis set due to Dunning.[5] To investigate the effects of both diffuse functions and higher order polarization functions on the molecular geometry, additional calculations were performed at the DZP+/MP2 and DZPf/MP2 levels. Investigation of the effect of a more complete description of electron correlation was undertaken at the DZP/MP3 and DZP/MP4SDQ levels. Final geometries were obtained using a basis set of TZ2P quality, comprising [10s,6p]/(5s,3p) basis sets for first-row[6] atoms and a [12s,9p]/(6s,5p) set for chlorine[7] and supplemented with two sets of d-type polarization functions for all atoms.

Further single-point energy calculations were undertaken at the TZ2P/MP4SDQ level employing the optimized TZ2P/MP2 geometry to obtain more reliable estimates of both the relative energies and barriers connecting the two possible conformers.

Vibrational frequency calculations were performed at the DZP/SCF and DZP/MP2 levels to determine the nature of all located stationary points, for comparison with previously reported spectra[8] and for the calculation of root-mean-square

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(1) Davis, M. I.; Boggs, J. E.; Coffey, D. *J. Phys. Chem.* **1965**, *69*, 3727.
(2) Bauer, S. H.; Andreassen, A. L. *J. Phys. Chem.* **1972**, *76*, 3099.
(3) Coffey, D.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1968**, *49*, 591.
(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision C.2; Gaussian Inc.: Pittsburgh, PA, 1995.
(5) Dunning, T. H.; Hay, P. J. In *Modern Quantum Chemistry*; Plenum: New York, 1976; pp 1−28.
(6) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(7) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
(8) Ernsting, N. P.; Pfab, J. *Spectrochim. Acta* **1979**, *36A*, 75.

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Table 1. Theoretical Molecular Geometries (r_e) for $CClF_2NO$ Conformers[a]

		DZP/						TZ2P/	
sym	param	SCF	MP2	MP3	MP4	DZP+/MP2	DZPf/MP2	SCF	MP2
C_s	C(1)−N(2)	149.5	154.1	153.1	154.3	154.5	153.2	149.9	154.3
	N(2)−O(3)	116.6	122.7	120.2	121.2	122.4	121.7	115.3	120.7
	C(1)−Cl(4)	174.5	174.5	175.0	175.0	174.7	173.7	175.1	175.4
	C(1)−F	131.4	134.8	134.1	134.6	134.7	133.9	130.7	133.5
	C(1)−N(2)−O(3)	115.2	113.3	113.6	113.7	113.4	113.6	115.6	113.9
	N(2)−C(1)−Cl(4)	116.0	115.9	116.1	116.0	115.7	115.6	115.6	115.0
	N(2)−C(1)−F	105.6	104.9	105.1	105.0	105.0	105.0	105.6	105.1
	Cl(4)−C(1)−N(2)−F	122.5	122.9	122.8	122.9	122.7	122.8	122.4	122.5
C_1	C(1)−N(2)	149.0	153.1	152.3	153.6	153.6	152.3	149.3	153.3
	N(2)−O(3)	116.9	123.1	120.6	121.6	122.8	122.1	115.7	121.2
	C(1)−Cl(4)	175.1	175.2	175.7	175.7	175.7	174.4	175.9	176.3
	C(1)−F(5)	131.2	134.6	133.9	134.5	134.4	133.8	130.6	133.3
	C(1)−F(6)	130.6	133.9	133.2	133.8	133.8	133.0	129.9	132.6
	C(1)−N(2)−O(3)	112.7	111.1	111.3	111.5	111.1	111.3	112.9	111.3
	N(2)−C(1)−Cl(4)	107.9	107.3	107.7	107.7	107.2	106.9	107.4	106.4
	N(2)−C(1)−F(5)	106.3	105.8	107.7	107.7	105.9	105.9	107.4	106.4
	N(2)−C(1)−F(6)	112.5	112.5	112.4	112.2	112.6	112.6	112.6	112.6
	Cl(4)−C(1)−N(2)−F(5)	118.5	118.7	118.7	118.8	118.7	118.6	118.4	118.3
	Cl(4)−C(1)−N(2)−F(6)	122.4	122.7	122.7	122.6	122.4	122.6	121.9	122.1
	O(3)−N(2)−C(1)−Cl(4)	107.5	106.8	106.0	107.6	102.4	106.8	106.5	104.9

[a] Distances in pm, angles in deg.

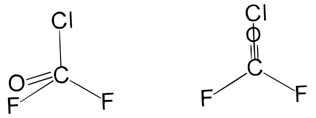

Figure 1. Molecular geometry of the gauche and syn conformers of chlorodifluoronitrosomethane viewed along the C−N bond.

amplitudes of vibration (u) and perpendicular amplitude corrections (k) to assist in the refinement of electron-diffraction data.

Results. An extensive search of the $CClF_2NO$ potential energy surface resulted in the location of two minima (see Figure 1). The two conformers can be described as having the oxygen atom of the nitroso group eclipsed with respect to either chlorine (syn-C_s symmetry) or fluorine (gauche-C_1 symmetry).

Predicted structural parameters for the two conformers are presented in Table 1. As might be expected for molecules containing a number of highly electronegative atoms, some geometric parameters were found to be rather sensitive to changes in the adopted theoretical treatment.[5] In particular, predicted values of the N(2)−O(3) bond length proved to vary substantially. Improvements in both basis set and the level of electron correlation beyond MP2 led to a noticeable shortening of this bond. Even at the highest level available to us (TZ2P/MP2), the N(2)−O(3) bond length (120.7 pm) is almost certainly overestimated since improvements in the correlation treatment beyond MP2 led to a substantial shortening of this bond when a smaller basis set (DZP) was employed. The choice of theoretical method was also found to be important for describing the C(1)−Cl(4) bond; in this case an accurate description of the bond is obtained only when the basis set includes f-type functions. In general, values of other geometric parameters proved less sensitive to changes in the theoretical treatment, with variations over a 1 pm or 1° range being typical for bond lengths and angles, respectively.

Notwithstanding the torsion angles, differences in structural parameters between the C_s and C_1 conformers ($\phi = 0$ or 106°) are most evident in the bond angles and can be explained readily in terms of steric repulsions. For example, the syn conformer (C_s symmetry), for which the oxygen and chlorine atoms are eclipsed, exhibits substantially wider Cl−C−N and C−N−O angles than the gauche structure (115.0° and 113.9° vs 106.4° and 111.3°; TZ2P/MP2). The full variation in values of these angles was examined at the DZP/MP2 level by performing geometry optimizations at fixed values of the torsional angle (at 15° intervals between 0 and 180°; see Figure 2). Similarly, the F−C−N angle is wider in the gauche conformer since fluorine is eclipsed with respect to the oxygen atom in this case.

Calculated harmonic vibrational frequencies (DZP/MP2) for the two conformers of $CClF_2NO$ are presented in Table 2 together with a comparison with the experimentally observed

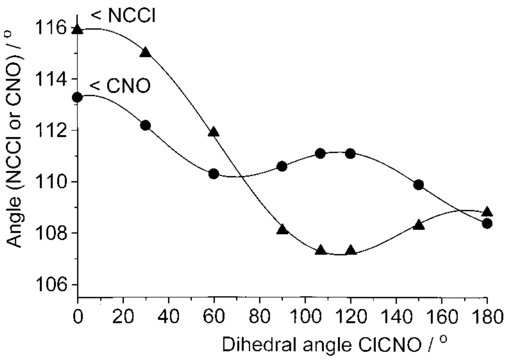

Figure 2. Variation of the N−C−Cl and C−N−O bond angles with the Cl−C−N−O dihedral angle calculated at the DZP/MP2 level.

Table 2. Calculated and Observed Vibrational Frequencies (cm^{-1}) for $CClF_2NO$ Conformers[a]

	Sym:	syn		gauche	
mode	syn/gauche	DZP/MP2	expt	DZP/MP2	expt
ν(NO)	a′/a	1530	1609	1512	1601
ν(CF)	a′/a	1192	1176	1261	1244
ν(CF)	a″/a	1192	1176	1174	1149
ν(CN)	a′/a	1047	932	979	925
ν(CCl)	a′/a	658	673	636	644
δ(NCF)	a′/a	678	679	792	774
δ($ClCF_2$)	a′/a	447	439	469	453
δ($ClCF_2$)	a″/a	443	420	451	446
δ($ClCF_2$)	a″/a	347	328	309	
δ(CNO)	a′/a	421	410	358	361
δ(NCCl)	a′/a	238	225	287	283
τ(ONCCl)	a″/a	63		75	72

[a] Experimental frequencies were taken from ref 8.

Table 3. Calculated Energy Differences and Barriers of $CClF_2NO$[a,b]

			barrier	
basis	theory	$\Delta(C_s-C_1)$	C_1/C_s	C_1/C_1
DZP	SCF	3.1 (2.8)	5.5 (4.4)	3.8 (2.6)
	MP2	1.2 (0.9)	3.6 (2.5)	8.9 (7.6)
	MP3	1.9 (1.6)	3.8 (2.7)	9.4 (8.1)
	MP4SDQ	1.5 (1.2)	3.7 (2.6)	6.8 (5.5)
DZ+P	MP2	0.9 (0.6)	3.2 (2.1)	8.1 (6.8)
DZPf	MP2	1.4 (1.1)	3.9(2.8)	9.4 (8.1)
TZ2P	SCF	3.6 (3.3)	5.8 (4.7)	12.1 (10.9)
	MP2	1.5 (1.2)	2.5 (1.4)	9.4 (8.1)
	MP3[c]	1.9 (1.6)	2.3 (1.2)	10.3 (9.0)
	MP4SDQ[c]	1.7 (1.4)	2.3 (1.2)	9.1 (7.8)

[a] Energies in kJ mol^{-1}. [b] Values in parentheses include corrections for ZPE calculated at DZP/SCF (SCF optimizations) or DZP/MP2 (optimizations including electron correlation). [c] TZ2P/MP2 geometry used for calculation of the energy difference.

gas-phase frequencies.[8] As expected for calculations at this level,[9] predicted frequencies were generally found to be overestimated by a few percent. Exceptions are the estimates of ν(N−O) and ν(C−Cl) frequencies, which are underestimated by up to 4%. Their unexpectedly low predicted values can be attributed to overestimated N−O and C−Cl bond lengths at this level.

The relative energies of the syn and gauche conformers are presented in Table 3. The two minima were predicted to be near degenerate in energy, although the gauche conformer (C_1 symmetry) was always slightly favored. The energy difference was predicted to be around 3 kJ mol^{-1} at the SCF level of theory; however, improvements in the correlation treatment reduced this value to about 1 kJ mol^{-1}, taking the effects of zero-point energy into consideration. The transition state connecting the two nonequivalent local minima was located with predictions of the barrier ranging between 5 kJ mol^{-1} at the SCF level of theory to 1.2 kJ mol^{-1} when more sophisticated treatments of electron correlation were employed. At our highest level (TZ2P/MP4SDQ//TZ2P/MP2) this barrier is just 1.2 kJ mol^{-1}. This energy barrier implies that the two conformers of $CClF_2NO$ can be regarded as freely interconverting via a low-barrier torsional motion.

A second transition state (C_s symmetry) to internal motion connecting equivalent gauche conformers was also investigated. In this case calculated barriers were found to fall in the range 5.5−9.0 kJ mol^{-1} when electron correlation was included.

Electron-Diffraction Measurements

Experimental Details. Electron scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus operating at ca. 44.5 kV (electron wavelength ca. 5.7 pm).[10] Nozzle-to-plate distances for the metal inlet nozzle were 285.86 and 128.27 mm yielding data in the s range 20−300 nm^{-1}; three plates were exposed at each camera distance The sample and nozzle temperatures were maintained at 293 K during the exposure periods.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analyzed in exactly the same way as those for $CClF_2NO$ so as to minimize systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected together in Table 4.

Table 4. Nozzle-to-Plate Distances (mm), Weighting Functions (nm^{-1}), Correlation Parameters, and Electron Wavelengths (pm) Used in the Electron Diffraction Study

nozzle-to-plate dist[a]	Δs	s_{min}	sw_1	sw_2	s_{max}	corr param	scale factor[b]	electron wavelength
285.86	2	20	40	122	144	0.437	0.986(10)	5.672
128.27	4	40	80	244	300	0.129	1.011(27)	5.672

[a] Determined by reference to the scattering of benzene. [b] Values in parentheses are estimated standard deviations.

The electron-scattering patterns were converted into digital form using a computer-controlled Joyce Loebl MDM6 microdensitometer with a scanning program described elsewhere.[11] The programs used for data reduction[11] and least-squares refinement[12] have been described previously; the complex scattering factors were those listed by Ross et al.[13]

Molecular Model. Since calculations suggest that rotation of the nitroso group is barely restricted, we wished to investigate both static and dynamic models to describe the electron-diffraction data. The former involved a description of the molecule in which both syn and gauche conformers were included. In the dynamic model, additional conformations were included to allow a more complete description of the torsional motion. In this case we also wished to allow for changes in parameter values as the nitroso group rotates about the C−N bond, since variations in some bond angles are predicted to be large. For this reason, a further series of calculations at the DZP/MP2 level were performed, in which the geometry was optimized at fixed values of the Cl−C−N−O torsional at 15° intervals between 0 and 180°. Although it is clear from earlier calculations that the absolute values of geometric parameters for these structures will be sensitive to improvements in the theoretical treatment, any errors are expected to be systematic and therefore the differences in parameter values between the 11 structures are expected to remain essentially unchanged with further improvements in the calculational method.

The static model, which includes descriptions of both syn (30%) and gauche (70%) conformers, is described by nine refinable geometric parameters, comprising average C−N, N−O, C−Cl and C−F bond lengths, p_1-p_4, average C−N−O, N−C−Cl, and N−C−F bond angles, p_5-p_7, the average angle between the N−C−Cl and N−C−F planes, p_8, and the O−N−C−Cl dihedral angle for the gauche conformation, p_9. Differences between average parameters values and those for each of the two conformers were fixed at values calculated ab initio.

The atomic coordinates for the dynamic model are described by the same parameters as in the static model, but with p_9 replaced by fixed dihedral angles of 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, and 150° for the 11 conformers, respectively. Structures, with $\phi = 165$ and 180° were not included, since these conformations were predicted to represent less than 1% of the total population. The relative weights of the 11 conformations were initially determined from their relative energies at the DZP/MP2 level (see Figure 3) and fitted to a

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(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(10) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954.

(11) Cradock, S.; Koprowski, J.; Rankin, D. W. H., *J. Mol. Struct.* **1981**, *77*, 113.

(12) Boyd, A. S. F.; Laurenson, G. S.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 217.

(13) Ross, A. W.; Fink, M.; Hildebrandt, R., In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Vol. C, Kluwer: Dordrecht, The Netherlands, 1992; Vol. C, p 245.

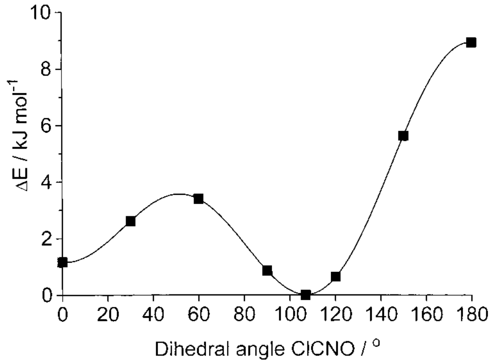

Figure 3. Variation of the relative molecular energy (ΔE) with the Cl−C−N−O dihedral angle calculated at the DZP/MP2 level.

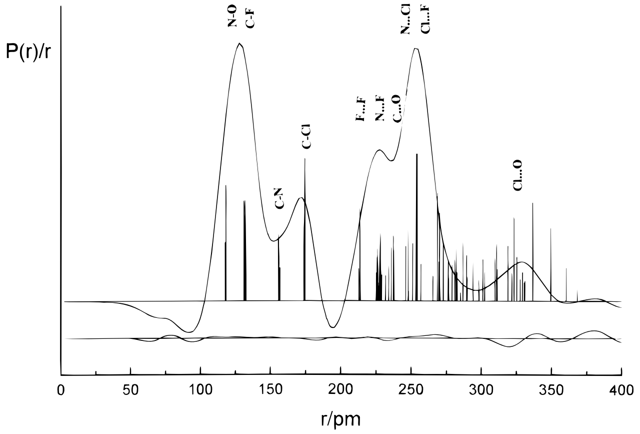

Figure 4. Observed and final difference radial distribution curves for $CClF_2NO$. Before Fourier inversion the data were multiplied by $s \exp[-0.00002s^2)/(Z_F - f_F)(Z_{Cl} - f_{Cl})]$.

torsional potential function with the general form

$$E_{rel} = A\cos\phi + B\cos 2\phi + C\cos 3\phi$$

where $A-C$ are constants and ϕ is the O−N−C−Cl torsion angle. To obtain a more accurate potential energy function for inclusion in the final refinements, values of the three constants were calculated from the relative energies of the stationary points at the TZ2P/MP4SDQ//TZ2P/MP2 level, yielding values of −1.557, 2.060, and −1.643 kJ mol^{-1} for A−C, respectively.

Changes in the values of molecular parameters due to rotation of the −NO group about the C−N bond were accounted for by fixing the differences between the parameters for the 11 conformers at the values calculated ab initio (DZP/MP2). In all refinements only the average (weighted) values of parameters were refined.

Results. The radial distribution curve for chlorodifluoronitrosomethane (Figure 4) consists of five distinct peaks at distances of ca. 130, 170, 225, 260, and 330 pm, plus weaker peaks and shoulders. The peak at 130 pm corresponds to C−F and N−O scattering, the second peak in the bonded region (170 pm) is due to C−Cl scattering, and a broad shoulder at ca. 150 pm is due to C−N scattering. The third peak, at 225 pm, corresponds to C···O, F···F, and N···F nonbonded pairs of atoms. The most intense feature in the radial distribution curve (260 pm) contains contributions from Cl···N and Cl···F atom pairs, while the broad peak centered around 330 pm arises from scattering between oxygen and the halogen atoms.

The starting parameters for the r_α structure refinements for both static and dynamic models were taken from theoretical geometries optimized at the DZP/MP2 level. Theoretical (DZP/MP2) Cartesian force fields were obtained for all conformations and converted into symmetry coordinates using the ASYM40 program.[14] Since good agreement was obtained between observed and calculated frequencies, no scaling of the force field was attempted. However, since inclusion of the low-frequency torsional mode led to overestimated predictions of the perpendicular amplitudes of vibration (k), it was excluded from force field calculations; however, the effects of this mode were included explicitly in the dynamic model.

The presence of a number of groups of similar interatomic distances made it necessary to constrain the ratios of some vibrational amplitudes to calculated values. For both models, amplitudes of each type of interatomic distance (e.g. N···F, O···Cl, etc.) were tied and refined as a group, with the value of the syn conformer ($\phi = 0°$) refining. Constraining the values of amplitudes in this way leads to 11 groups of amplitudes, 7 of which refined freely and 4 [u(N···F), u(O···F), u(C···O), and u(N···Cl)] which refined with the aid of flexible restraints according to the SARACEN method.[15]

In total 20 and 19 independent parameters were refined for the static and dynamic models, respectively. The 20 (or 19) parameters comprised 9 (or 8) geometrical parameters and 11 amplitudes of vibration. The dynamic model yielded a final R_G value of 0.093, compared to 0.112 for the two conformer model ($\phi = 0°$ (fixed), syn, $\phi = 104.0(10)°$, gauche), indicating that the motion of the nitroso group is not well described when only two conformers are included in the refinement procedure. For brevity, only the results obtained using the dynamic model are presented. Details of the structural parameters obtained in the optimum refinement are given in Table 5; the corresponding distances and amplitudes are collected in Table 6. The most significant elements of the correlation matrix are presented in Table 7. The success of the final refinement may be assessed on the basis of the difference between the experimental and calculated radial distribution curves (Figure 2), while Figure 5 offers a similar comparison between the experimental and calculated molecular scattering intensity curves.

Discussion

The ab initio molecular orbital calculations predict the presence of two nonequivalent local minima on the potential energy surface, with oxygen eclipsed by either chlorine (C_s symmetry) or fluorine (C_1 symmetry). The preferred eclipsed conformations suggest that the lone pair of electrons residing on the nitrogen atom is sterically important. The C_1 conformer ($\tau = 106°$) is predicted to be the more stable of the two conformers by around 1.5 kJ mol^{-1}, with a barrier of 1.2 kJ mol^{-1} between the two forms. This suggests that the two conformers will interconvert freely at ambient temperature. A second barrier, separating equivalent C_1 conformers, is predicted to be of higher energy, estimated at 7−8 kJ mol^{-1}.

The results obtained from ab initio calculations are supported by the gas-phase electron diffraction (GED) study. Structural refinements for chlorodifluoronitrosomethane were carried out using models comprising either 2 (syn and gauche) or 11 conformations (to allow for large amplitude motion). Results from both refinements suggest that the nitroso group can be regarded as undergoing large-amplitude internal motion in the gas phase. The simpler description, for which only syn and gauche conformers were considered, was found to lead to an

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(14) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(15) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280.

Table 5. GED Structural Parameters for $CClF_2NO^a$

		GED (r_α)		TZ2P/MP2 (r_e)		
param	no.	av	syn	gauche	syn	gauche
		Independent Parameters				
C(1)−N(2)	p_1	156.1(5)	156.7(5)	155.9(5)	154.3	153.3
N(2)−O(3)	p_2	117.9(3)	117.5(3)	117.9(3)	120.7	121.2
C(1)−Cl(4)	p_3	174.1(2)	173.9(2)	174.2(2)	175.4	176.3
C(1)−F	p_4	131.7(2)	132.0(2)	132.1(2)/131.0(2)	133.5	133.3/132.6
C(1)−N(2)−O(3)	p_5	110.8(12)	110.8(12)	110.7(12)	113.9	111.3
N(2)−C(1)−Cl(4)	p_6	112.6(5)	117.5(5)	108.9(5)	115.0	106.4
N(2)−C(1)−F	p_7	106.2(2)	103.7(2)	104.2(2)/111.6(2)	105.1	106.4/112.6
Cl(4)−C(1)−N(2)−F	p_8	122.4(2)	123.6(14)	119.2(14)/123.7(14)	122.5	118.3/122.1
		Dependent Parameters				
F−C−F			108.0(4)	108.6(4)	109.0	109.4
Cl−C−F			111.5(2)	111.6(2)/111.7(2)	111.0	111.0/111.2

[a] See text for parameter definitions. Distances in pm, and angles in deg. [b] Calculated parameter values are for C_s and C_1 structures, respectively. [c] Average of the two nonequivalent parameter values.

Table 6. Interatomic Distances (r_a) and Amplitudes of Vibration (u) for the C_s (Syn) and C_1 (Gauche) Conformations of $CClF_2NO^a$

	i	atoms	dist (r_i)	amplitude (u_i)^b
C_s	1	C(1)−N(2)	156.7(5)	6.4(8)
	2	N(2)−O(3)	117.6(3)	4.8(7)
	3	C(1)−Cl(4)	173.8(2)	6.0(4)
	4	C(1)−F	132.0(2)	5.8(4)
	5	C(1)−O(3)	226.9(14)	5.9(6)
	6	N(2)−F	227.5(6)	7.1(7)
	7	N(2)−Cl(4)	282.6(8)	7.8(9)
	8	F(5)−F(6)	213.5(4)	7.5(5)
	9	Cl(4)−F	253.9(2)	6.9(2)
	10	O(3)−Cl(4)	282.1(30)	9.5(9)
	11	O(3)−F	311.3(5)	5.9(6)
C_1	12	C(1)−N(2)	155.7−156.4	6.2−6.3
	13	N(2)−O(3)	117.7−118.2	4.8−4.9
	14	C(1)−Cl(4)	173.6−174.4	5.9−6.0
	15	C(1)−F	131.0−132.3	5.7−5.8
	16	C(1)−O(3)	225.1−229.1	5.9−6.1
	17	N(2)−F	227.4−237.2	6.3−7.4
	18	N(2)−Cl(4)	268.5−282.1	7.9−9.9
	19	F(5)−F(6)	212.7−213.5	7.4−7.5
	20	Cl(4)−F	253.5−254.4	6.9−7.0
	21	O(3)−Cl(4)	286.9−368.3	5.8−9.4
	22	O(3)−F	247.9−331.0	6.0−9.2

[a] Distances and ampitudes in pm, with estimated standard deviations in parentheses. [b] See text for amplitude tying scheme.

Table 7. Correlation Matrix (×100) for Structure Refinement for $CClF_2NO^a$

	p_1	p_2	p_4	p_5	p_6	u_1	u_2	u_4	u_4
p_5	−55				54			51	
p_7				−56	−52				
p_8					63				
u_1			−56				71		
u_3						53	−55	88	
u_4		58	−57				56		
u_7				−52	−66				54
u_{11}				−55					
k_1								53	

[a] Only elements with absolute values greater than 50 are shown.

unusually large O···Cl amplitude of vibration (33 pm), while the introduction of additional conformations used to model the torsional motion of the nitroso group lead to a substantially better fit to the experimental data.

Final refined parameter values represent weighted averages for all values of the torsional angle. Parameter values calculated at the highest level adopted (TZ2P/MP2) are, for the most part, in good agreement with refined ones. Exceptions are the N(2)−O(3) and C(1)−Cl(4) bond lengths, for which it is shown that improved levels of electron correlation and higher order polarization functions are needed for an accurate description.

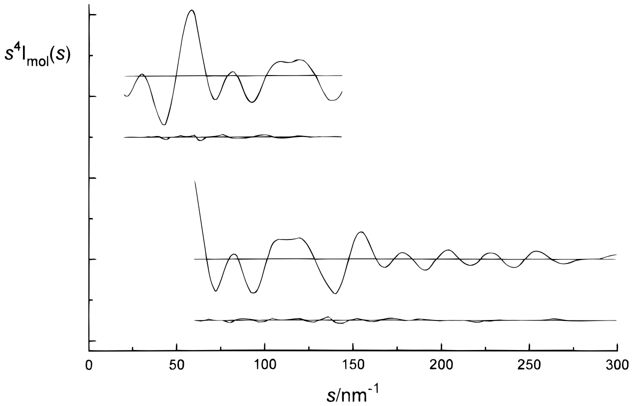

Figure 5. Electron diffraction molecular scattering intensity and final difference curves for $CClF_2NO$.

The shape of the predicted potential energy surface proved to be sensitive to changes in the theoretical treatment. In particular, values of the barrier connecting equivalent gauche conformers did not converge satisfactorily leading to a predicted potential which may not be completely accurate. During the analysis of the GED data, refinement of the constants describing the torsional potential (*A*−*C*) was unsuccessful, and for this reason the theoretical potential was adopted for the final refinements. The relatively poor fit to the experimental data in the range of 300−360 pm is probably due, at least in part, to inaccuracies in the theoretical description of the potential.

The observed behavior of $CClF_2NO$ compares well with that of the closely related CF_3NO compound. CF_3NO has been the subject of two previous electron diffraction studies and like $CClF_2NO$ is reported to undergo significant internal rotation about the C−N bond in the gas phase.[1,2] Equivalent syn conformers for CF_3NO are estimated to be separated by a barrier of approximately 4.5 kJ mol^{-1}. Structurally, the two compounds are also similar. For example, both exhibit unusually long C−N bonds, i.e. 156.7(5) or 155.9(5) pm for the syn or gauche conformers of $CClF_2NO$ vs 155.5(15)[1] or 154.6(9) pm[2] (CF_3NO), compared to more typical single carbon-to-nitrogen (sp^2 hybridized) bond lengths of around 146 pm found in previous gas-phase studies of $CF_3{-}N{=}N{-}CF_3$ [146.0(6) pm],[16] CH_3-

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(16) Bürger, H.; Pawelke, G.; Oberhammer, H. *J. Mol. Struct.* **1982**, *84*, 49.

N═N−CH_3 [146.0(6) pm],[17] and C_6H_5−HC═N−C_6H_5 [143.2(15) pm].[18] The elongation of this bond in CF_3NO has previously been attributed to a substantial contribution to the structure from the ionic form $CF_3^-NO^+$.[2] The C−F bond lengths (pm), 132.0(2) (syn) and 132.1(2) or 131.0(2) (gauche), for $CClF_2NO$ are also close to those reported by Davis[1] [132.1(4)] and Bauer[2] [132.6(3)] for CF_3NO. Similarly the observed N−O bonds for $CClF_2NO$, 117.5(3) pm (syn) and 117.9(3) pm (gauche), are similar to those found for CF_3NO [117.1(8)[1] and 119.7(5)[2]]. Although the difference in the observed average of the N−C−F bond angles in $CClF_2NO$ compared to CF_3NO is small, observed values of the C−N−O angle vary considerably. The two electron-diffraction studies of trifluoronitrosomethane yield surprisingly different angle values of 121.0(16) and 113.2(13)°. In this present study the value of the C−N−O angle for chlorodifluoronitrosomethane was found to be poorly defined by the experimental data and refined in the range 110−115° at various stages of the refinement procedure. Presumably the difference in the value of this parameter in trifluoronitrosomethane in the studies of Bauer and Davis is due to the data containing only a limited amount of information about this parameter due to the C···O and N···F peaks being correlated. Our final refined values of the C−N−O bond angles are 110.8(12) and 110.7(12)° for the syn and gauche conformers, respectively. This value is consistent with an observed angle of 113.2(13)° from the study of CF_3NO due to Bauer[2] and a value of 112.6° from a microwave spectroscopic study of nitrosomethane.[3] The number of observed solid-phase values of C−N−O bond angles is surprisingly few, with values anywhere in the range of 103−120°.

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(17) Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *24*, 1230.

(18) Traetteberg, M.; Hilmo, I.; Abraham, R. J.; Ljunggren, S. J. *J. Mol. Struct.* **1978**, *48*, 395.