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Molecular Structure of 1,3,5-Triazine in Gas, Solution, and Crystal Phases and by ab Initio Calculations†

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The r_α, r_0, and r_s structures of 1,3,5-triazine ($^{12}C_3{}^{14}N_3H_3$) have been determined in the gas phase by analysis of electron diffraction data and high-resolution FTIR spectra, including those for the isotopomers $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{14}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$, and $^{12}C_3{}^{14}N_3D_3$, in solution in liquid crystal solvents by NMR spectroscopy, and by ab initio calculations. Combining gas- and solution-phase data in a single analysis yields a very precise structure, with final parameter values ($r_\alpha{}^\circ$) r(C−N) 133.68(1) pm, r(C−H) 108.9(2) pm, and ∠(CNC) 113.82(9)°. The final structure obtained is also compared with the crystal structure.

Introduction

The major techniques for determining molecular structure in fluid phases are electron diffraction, rotational spectroscopy, high-resolution infrared and Raman spectroscopy, and liquid crystal NMR (LCNMR) spectroscopy. Like any experimental method, however, each has its limitations,[1] and so it is rarely that any one method alone can give a complete structural determination for any but the simplest of compounds. It is therefore common practice to combine data from these three techniques to arrive at a final solution, the best structure based on all available experimental information.[2−4] In addition, the Edinburgh group has recently developed a method (called structure analysis restrained by ab initio calculations for electron diffraction, or SARACEN[5]) for combining experimental and ab initio data to give more complete, reliable structure determinations.

When combining data obtained by different experimental methods, and particularly for molecules in different phases, it is essential that the physical meaning of geometrical parameters is consistent and that the structure in condensed phases is unaffected by neighboring molecules. A key molecule in this respect is 1,3,5-triazine, in that it is possible to determine its structure experimentally in gas, solution, and solid phases independently, and also by ab initio calculations. As it is a planar molecule with D_{3h} symmetry, it has only three structural parameters (r(C−N), r(C−H), and a ring angle), and so it is possible to refine the complete structure using only electron diffraction data or only rotation constants, and all but an overall scale factor using dipolar couplings derived from LCNMR spectra.[6] The validity of combining the data from the three techniques can thus be easily assessed. As the molecule has no dipole moment, the rotation constants are only accessible by high-resolution infrared spectroscopy.

In addition to the experimental structure determination, a series of ab initio molecular orbital calculations was carried out for 1,3,5-triazine, to provide both the molecular geometry and a scaled harmonic force field (using the ASYM40 program[7]) for comparison with experimental results. The calculated force field was used to obtain vibrational amplitudes adopted in GED structural analyses. Similarly, the vibrational corrections required to convert the rotation constants and dipolar couplings to an appropriate structural type to be included as additional structural information in the GED refinement were also obtained from the calculated force field.

The study consists of two major parts, the first based on data from single methods, the second combining data from two or more methods. Four single-method structural studies, based on ab initio calculations, LCNMR spectroscopic data, rotation constants, and GED data, are presented. In the two combined studies the GED data are progressively supplemented with information obtained from rotational and LCNMR spectroscopy. The advantages of combining data in this manner are fully discussed. Finally, there is a comparison of the gas-phase structure with some previous solid-phase structural results.[8]

Experimental and Theoretical Methods

Ab Initio Calculations. All calculations were carried out on a DEC Alpha APX 1000 workstation using the Gaussian suite of programs.[9,10]

Geometry Optimizations. A graded series of calculations was performed, from which the effects of improvement in basis set treatment and level of theory could be gauged. Geometry optimizations were performed using standard gradient techniques at the SCF level of theory using basis sets up to 6-31G*[11−13] and 6-311G**.[14,15] Basis sets up to 6-31G(2df,2pd) were used for optimizations at the MP2(FC) level of theory. We also wished to investigate the effects of higher order correlation treatments, and accordingly calculations using the 6-311G** basis set at the MP3(FC), MP4SDQ(FC), CCSD, and CCSD(T) levels of theory were also carried out.

Frequency Calculations. Vibrational frequency calculations were performed at the 3-21G*/SCF, 6-31G*/SCF, and 6-31G*/MP2 levels to verify that 1,3,5-triazine has overall D_{3h} symmetry. The force constants obtained in the highest level

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† Dedicated to Prof. Dr. Hans Bürger on the occasion of his 60th birthday with the motto: *Summa huius operis optima, si Hydrogenium licet componere Deuterio*.

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TABLE 1: Internal Coordinates and Symmetry Coordinates Used for the Theoretical Force Field of 1,3,5-Triazine

(a) Internal Coordinates

bond stretch	angle bend	out-of-plane bend
R_1 N_1-C_2	α_1 $C_2-N_1-C_1$	τ_1 $C_2-H_2-N_3-N_1$
R_2 C_2-N_3	α_2 $N_3-C_2-N_1$	τ_2 $C_3-H_3-N_2-N_3$
R_3 N_3-C_3	α_3 $C_3-N_3-C_2$	τ_3 $C_1-H_1-N_1-N_2$
R_4 C_3-N_2	α_4 $N_2-C_3-N_3$	τ_4 $C_2-N_2-C_3-C_1$
R_5 N_2-C_1	α_5 $C_1-N_2-C_2$	τ_5 $C_3-N_1-C_1-C_2$
R_6 C_1-N_1	α_6 $N_1-C_1-N_2$	τ_6 $C_1-N_3-C_2-C_3$
R_7 C_2-H_2	α_7 $H_2-C_2-N_1$	
R_8 C_3-H_3	α_8 $H_2-C_2-N_3$	
R_9 C_1-H_1	α_9 $H_3-C_3-N_3$	
	α_{10} $H_3-C_3-N_2$	
	α_{11} $H_1-C_1-N_2$	
	α_{12} $H_1-C_1-N_1$	

(b) Symmetry Coordinates

species	symmetry coordinate	description
a_1'	$S_1 = R_7+R_8+R_9$	C−H symmetric stretch
	$S_2 = R_1+R_2+R_3+R_4+R_5+R_6$	ring symmetric stretch
	$S_3 = \alpha_1-\alpha_2+\alpha_3-\alpha_4+\alpha_5-\alpha_6$	ring bend
a_2'	$S_4 = R_1-R_2+R_3-R_4+R_5-R_6$	ring asymmetric stretch
	$S_5 = \alpha_7-\alpha_8+\alpha_9-\alpha_{10}+\alpha_{11}-\alpha_{12}$	H wag
a_2''	$S_6 = \tau_1+\tau_2+\tau_3$	H symmetric out-of-plane bend
	$S_7 = \tau_4+\tau_5+\tau_6$	N symmetric out-of-plane bend
e'	$S_8 = -R_7+2R_8-R_9$	C−H asymmetric stretch
	$S_9 = 2\alpha_1-\alpha_3-\alpha_5$	ring bend
	$S_{10} = 2\alpha_1-\alpha_2-\alpha_3+2\alpha_4-\alpha_5-\alpha_6$	ring bend
	$S_{11} = \alpha_7-\alpha_8-\alpha_{11}+\alpha_{12}$	H wag
	$S_{12} = -R_1+2R_2-R_3-R_4+2R_5-R_6$	ring stretch
e''	$S_{13} = 2\tau_1-\tau_2-\tau_3$	H asymmetric out-of-plane bend
	$S_{14} = 2\tau_4-\tau_5-\tau_6$	N asymmetric out-of-plane bend

calculation were used in the construction of a harmonic force field using the ASYM40 program,[7] which was successfully scaled against the set of experimental vibrational frequencies. Scale constant values of 0.938, 0.956, and 0.919 were obtained for bond stretch, angle bend, and torsion force constants, respectively. Symmetry coordinates used to describe the various vibrational modes of the molecule in the construction of the force field are given in Table 1.

The theoretical force field was found to be in excellent agreement with one derived from experimental (infrared spectroscopy) data (see below) and with an older experimental force field.[16] The two sets of vibrational amplitudes calculated using these force fields were found to be in agreement to within 0.5%. Similarly, the vibrational corrections, required to convert rotation constants and dipolar couplings to the structural type appropriate for inclusion as additional structural information in the GED refinement, were found to agree to within 10% on average. (The larger percentage variations in some of these corrections arise from the fact that they are sums of several terms which are not all of the same sign.) Since the experimental force field is considered to be the more reliable of the two force fields, the final combined analysis refinement for 1,3,5-triazine was performed using the experimentally determined vibrational corrections.

Gas-Phase Electron Diffraction. *Sample Preparation.* A sample of 1,3,5-triazine (97% pure) was purchased from the Aldrich Chemical Co. and used without further purification. Impurities at this level are normally undetectable in electron diffraction experiments and have no effect on any of the spectroscopic measurements. The results are therefore not measurably dependent on the sample purity.

Experiment. Electron scattering intensities were recorded on Kodak Electron Image photographic plates using the Edinburgh apparatus.[17] The sample was maintained at a temperature of 364 K and the nozzle at 387 K. The four plates (two from the long camera distance and two from the short distance) were traced digitally using a computer-controlled Joyce-Loebl MDM6 microdensitometer at the EPSRC Daresbury laboratory.[18] Standard programs were used for the data reduction[18] and least-squares refinements,[19] with the scattering factors of Ross et al.[20] The weighting points used in setting up the off-diagonal weight matrix, *s* range, scale factors, correlation parameters, and electron wavelengths are given in Table 2.

TABLE 2: GED Data Analysis Parameters

camera distance (mm)	weighting functions (nm^{-1})					correlation parameter	scale factor, k^a	electron wavelength^b (pm)
	Δs	s_{min}	s_1	s_2	s_{max}			
95.46	4	68	80	304	356	0.3965	0.843(20)	5.680
260.06	2	20	40	130	150	0.2432	0.788(6)	5.680

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

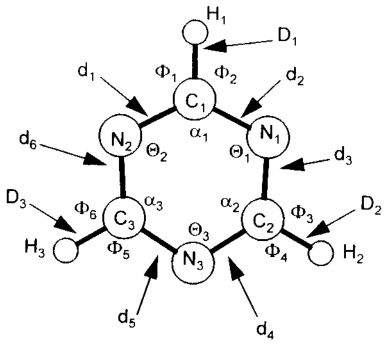

Figure 1. Internal coordinates used in the analysis of the experimental vibrational force field of 1,3,5-triazine. See Table 10. Out-of-plane wagging motions are $\eta_1 = N_2-C_1-N_1-H_1$, $\eta_2 = N_1-C_2-N_3-H_2$, and $\eta_3 = N_3-C_3-N_2-H_3$; torsions are centered on $\tau_1 = C_1-N_1$, $\tau_2 = N_1-C_2$, $\tau_3 = C_2-N_3$, $\tau_4 = N_3-C_3$, $\tau_5 = C_3-N_2$, and $\tau_6 = N_2-C_1$.

GED Model. Assuming overall D_{3h} symmetry, just three parameters are needed to define the structure of the molecule: the C−N bond distance (p_1), the CNC ring angle (p_2), and the C−H bond distance (p_3). The molecular framework is shown in Figure 1.

High-Resolution Infrared Spectroscopy. The isotopomers $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{14}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$, and $^{12}C_3{}^{14}N_3D_3$ were synthesized as described elsewhere.[21] Spectra[22] were recorded for these isotopomers and $^{12}C_3{}^{14}N_3H_3$ at room temperature, using Bruker 120 HR-FTIR spectrometers at the University of Giessen and University of Oulu, in the range 3000−600 cm^{-1} with maximum optical path difference of 330−540 cm, the effective resolution being 0.004−0.002 cm^{-1}. Stainless steel cells with KBr windows were used, with total pressure in the range 0.1−1.5 mbar. In each case about 300 scans were added, and boxcar apodization was applied. Spectra were calibrated by comparison with published CO_2 and H_2O line wavenumbers.[23] The absorption accuracy of calibration lines was between 10^{-3} and 10^{-4} cm^{-1}. The relative accuracy of the peakfinder evaluated lines is about 2×10^{-4} cm^{-1}.

Results and Discussion

Ab Initio Calculations of Molecular Geometry. Geometry optimizations for 1,3,5-triazine were performed at 14 levels in order to gauge the effects of improving the theoretical treatment upon the molecular geometry and to compare the theoretical structures with those determined experimentally. Results from all but the low-level 3-21G* and 4-21G* calculations are given in Table 3.

The C−H bond length and ring angles were largely unaffected by improvements in basis set and level of theory. However,

TABLE 3: Ab Initio Molecular Geometries and Energies of 1,3,5-Triazine (r_e/pm, ∠/deg *E*/Hartree)

basis set	level	*r*(C−N)	*r*(C−H)	∠CNC	energy
6-31G*	SCF	131.80	107.49	114.39	−278.695843
6-311G**	SCF	131.68	107.54	114.39	−278.756676
6-31G*	MP2	134.07	108.79	114.00	−279.538735
6-31G*	MP3	133.5	108.66	114.05	−279.547896
6-31G*	MP45SDQ	133.85	108.90	113.89	−279.558626
6-311G**	MP2	133.87	108.68	113.90	−279.653479
6-311G**	MP3	133.34	108.53	113.94	−279.659724
6-311G**	MP4SDQ	133.66	108.76	113.78	−279.670706
6-311G**	CCSD	133.67	108.64	113.78	−279.670951
6-311G**	CCSD(T)	134.31	108.86	113.58	−279.717181
6-311G(df,p)	MP2	133.45	108.79	113.85	−279.752373
6-311G(2df,2pd)	MP2	133.88	108.21	114.03	−279.812754

TABLE 4: Rotation Constants (*B*) and Liquid Crystal NMR Spectroscopic Dipolar Couplings (*D*) for 1,3,5-Triazine

constant	observed (B_0/MHz or D_0/Hz)	harmonic correction (MHz or Hz) experimental force field	harmonic correction (MHz or Hz) theoretical force field	corrected (B_0/MHz or D_0/Hz)	calculated[a]	uncertainty[b]
rotation constants						
B(H)	6441.338(3)	−2.96	*−3.15*	6438.428	6438.769	0.3
B(D)	5809.083(25)	−1.93	*−2.19*	5807.153	5807.153	0.2
B(^{13}C)	6241.5938(18)	−2.87	*−3.04*	6238.7238	6238.708	0.3
B(^{15}N)	6218.032(4)	−2.85	*−3.03*	6215.182	6215.209	0.3
B(^{13}C,^{15}N)	6031.7019(27)	−2.75	*−2.92*	6028.9519	6028.599	0.3
dipolar couplings[c]						
D(N$_1$,H$_1$)	80.0(6)	1.5	*1.6*	81.5	81.4	0.6
D(C$_1$,H$_1$)	−1300.0(6)	−91.2	*−79.3*	−1391.2	−1389.8	9.0
D(C$_3$,H$_1$)	−53.5(6)	−0.4	*−0.3*	−53.9	−53.3	0.6
D(N$_3$,H$_1$)	16.6(20)	0.1	*0.0*	16.7	13.6	2.0
D(H$_1$,H$_2$)	−100.3(6)	−0.8	*−0.7*	−101.1	−101.6	0.6

[a] From the final combined analysis refinement. [b] Used to weight data in structure refinement. [c] From ref 6.

the C−N bond distance varied rather more, and very large basis sets were eventually used, so that this distance could be brought as close to convergence as possible. As expected, the inclusion of electron correlation was needed for an accurate description of C−N bonds,[24] with the bond distance increasing by around 2 pm when the effects of electron correlation were introduced at the MP2 level, and further geometry optimizations were undertaken at the MP3, MP4SDQ, CCSD, and CCSD(T) levels using the 6-311G** basis set. These improvements resulted in continuing changes in the C−N and C−H bond distances; assuming that these changes would be repeated with the largest basis set, 6-311G(2df,2pd), our best estimate of *r*(C−N) is 133.82 pm, with 108.39 pm for *r*(C−H).

Excluding the results from the lowest level calculation, the range of predicted CNC bond angles was only 0.5°. Improving the basis set beyond 6-31G* at both the SCF and MP2 levels resulted in no appreciable change, and similarly, the introduction of electron correlation at the MP2 level resulted in only a slight narrowing of the CNC angle, while higher levels of theory resulted in no further significant change.

Variations in the C−H distance were similar to those observed for the C−N distance; improvements in the basis sets beyond 6-31G* led to minor changes in the value of this parameter, while calculations at the MP2 level resulted in a slight lengthening of bonds. Further improvements in the correlation treatment to MP3 and MP4 resulted in changes in bond length of just 0.1 pm.

We have demonstrated that all parameters for 1,3,5-triazine have successfully converged with respect to improvements in both the basis set and the level of electron correlation by normal standards. However, for the highly accurate work described here further improvements in the size of basis set and treatment of electron correlation are still necessary.

Structural Analysis of LCNMR Data Alone. A structural refinement based only on the five dipolar coupling constants of Marchal et al.[6] (Table 4) was performed to compare the solution-phase structure of $C_3N_3H_3$ with that found in the gas phase by GED, as documented below. The vibrational corrections required to convert the dipolar couplings from D_0 to D_α (equivalent to the $r_\alpha°$ GED structural type) were obtained from the experimental harmonic force field. Note that the vibrational corrections derived from the calculated force field are also given in Table 4 for comparison.

As 1,3,5-triazine has a 3-fold axis, only one coefficient ($S_{xx} = S_{yy} = -{}^1/_2 S_{zz}$) is necessary to characterize the orientation of the molecule in the liquid crystal solvent. In analyses of LCNMR data, orientation parameters have unknown values. It is therefore normal practice to fix one or more geometrical parameters at assumed values and to vary orientation parameters and remaining structural parameters to achieve an acceptable fit of calculated and observed coupling constants. In the present case, the orientation parameter was obtained in the combined analysis of GED and LCNMR data described below. This value was used as an additional observation in the LCNMR-only analysis, with its refined esd used as the uncertainty which defines the weight given to the extra observation.[4] The orientation parameter and all three structural parameters could then be refined simultaneously, giving esd's which take into account the uncertainty in the orientation parameter. In effect, the scaling information has been derived from the GED data.

The structure derived from LCNMR data alone is presented in column 1 of Table 5. With the C−N distance refining to a value of 133.4(7) pm and the CNC angle to 114.2(11)°, the ring parameters for 1,3,5-triazine are not as well-defined as in the GED refinement documented below. This result was expected since LCNMR spectroscopic measurements are limited to studying nuclei with spin quantum number $^1/_2$. For the 1,3,5-triazine sample studied by Marchal et al.[6] dipolar couplings were observed between the nuclei ^{1}H, ^{15}N, and ^{13}C without isotopic enrichment. Since natural abundances for the two ring atom

TABLE 5: Molecular Structure of 1,3,5-Triazine (r/pm, ∠/deg)

		results[a]					
	parameter	LCNMR data alone[b]	rotation constants[c]	rotation constants[d]	GED data alone[b]	GED + rotation constants[b]	GED + rotation constants + LCNMR[b]
	structural						
p_1	r(C−N)	133.4(7)	133.67(1)	133.41(5)	133.94(10)	133.68(1)[e]	133.68(1)[e]
p_2	r(C−H)	108.92(20)	108.62(16)	108.69(8)	110.3(6)	108.94(19)	108.91(18)
p_3	∠CNC	114.2(11)	113.95(8)	113.97(8)	113.9(2)	113.79(8)	113.82(9)
p_4	r(C−H) − r(C−D)					0.21(9)	0.20(8)
	orientational						
p_5	S_{zz}	−0.1189(4)					−0.1189(5)
	dependent						
	∠NCN	125.8(11)	126.05(8)	126.03(8)	126.1(2)	126.21(8)	126.18(9)

[a] Figures in parentheses are the estimated standard deviations in units of the last digit. [b] r_α°. [c] r_0. [d] r_s. [e] r_e = 132.88(19).

TABLE 6: Ground-State Constants [cm^{-1}] of Isotopomers of Triazine

	$C_3N_3H_3$	$^{13}C_3N_3H_3$	$C_3{}^{15}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$C_3N_3D_3$
C^{0}[b]	0.1074	0.1041	0.1037	0.1006	0.0969
B^0	0.21486156(10)	0.20819716(6)	0.20741124(12)	0.20119592(9)	0.19377014(83)
$D_J{}^0$	5.3433(58) × 10^{-8}	5.0190(29) × 10^{-8}	5.0150(57) × 10^{-8}	4.7131(39) × 10^{-8}	3.96743(40) × 10^{-8}
$D_{JK}{}^0$	−8.856(17) × 10^{-8}	−8.3267(83) × 10^{-8}	−8.283(15) × 10^{-8}	−7.8178(91) × 10^{-8}	−6.5400(12) × 10^{-8}
$D_K{}^{0}$[b]	3.970 × 10^{-8}	3.740 × 10^{-8}	3.705 × 10^{-8}	3.51 × 10^{-8}	2.921 × 10^{-8}
$H_J{}^0$	2.8(11) × 10^{-14}	1.84(42) × 10^{-14}	9.3(87) × 10^{-15}	1.41(52) × 10^{-14}	1.73(59) × 10^{-14}
$H_{JK}{}^0$	−1.46(41) × 10^{-13}	−8.9(15) × 10^{-14}	6.8(32) × 10^{-14}	−9.9(15) × 10^{-14}	−5.8(23) × 10^{-14}
$H_{KJ}{}^0$	3.08(70) × 10^{-13}	1.70(25) × 10^{-13}	−1.69(53) × 10^{-13}	2.21(23) × 10^{-13}	1.26(48) × 10^{-13}
$H_K{}^{0}$[b]	−1.73 × 10^{-13}	−9.2 × 10^{-14}	9.11 × 10^{-14}	−1.2 × 10^{-13}	−7.53 × 10^{-14}
σ	9.1 × 10^{-5}	1.194 × 10^{-4}	2.55 × 10^{-5}	1.2 × 10^{-4}	1.97 × 10^{-4}
GSCD	944	2535	4817	1562	5223

[a] Figures in parentheses are one standard deviation in units of the last significant digit. [b] From planarity conditions.

TABLE 7: Fundamentals of the Triazine Isotopomers [cm^{-1}]

	$^{12}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$	$\Gamma_{\|v\rangle}$	activity
ν_1	3052.1[a]	[3028[c,d]]	[3066[c,d]]	[3062[c,d]]	[2293[d,g]]	A_1'	Ra
ν_2	1138.1[a]	1138[c,d,f]	1100[c,d,f]	1098[c,d,f]	1083[d,f,g]	A_1'	Ra
ν_3	989.7[a]	957.1[c,d,f]	988.1[c,d,f]	957.1[c,d,f]	985[d,f,g]	A_1'	Ra
ν_4	1375[b]					A_2'	
ν_5	1000[b]					A_2'	
ν_6	3062.91[d]	3056.7[d,e]	3050.1[d,e]	3048.8[d,e]	2276.5[d]	E′	IR/Ra
ν_7	1556.34[d]	1541.67[d]	1523.95[d]	1509.6[d]	1530.8[d]	E′	IR/Ra
ν_8	1409.96[d]	1390.80[d]	1404.7[d]	1384.4[d]	1284.72[d]	E′	IR/Ra
ν_9	1172.64[d]	1165.45[d]	1152.91[d]	1145.6[d]	929.58[d]	E′	IR/Ra
ν_{10}	675.78[d]	662.56[d]	666.7[d]	653.8[d]	663.98[d]	E′	IR/Ra
ν_{11}	926.59[d]	922.04[d]	913.55[d]	909.43[d]	860.64[d]	A_2''	IR
ν_{12}	736.74[d]	728.50[d]	731.49[d]	722.56[d]	574.62[d]	A_2''	IR
ν_{13}	1032[d,g]	1033[c,d]	1023[c,d]	1021[c,d]	862[c,d]	E″	Ra
ν_{14}	339.50[d]	334.11[d]	337[c,d,f]	331[c,d,f]	309[d,g]	E″	Ra

[a] Ref 45. [b] Ref 40. [c] Solid state. [d] This work. [e] Approximately corrected for Fermi resonance $\nu_6/2\nu_7$. [f] Approximately corrected for solid or liquid-state shift. [g] Liquid state, ref 16. [ ]: not used in the force-field calculation.

isotopes are only 0.4% and 1.1%, respectively, and the magnetogyric ratios for ^{15}N and ^{13}C are small compared to ^1H (only one-tenth or one-quarter of that of ^1H, respectively), the accuracy of the ring atom positions is expected to be somewhat limited. In contrast, the natural abundance of the ^1H isotope is 100%. The structural information contained within the LCNMR dipolar couplings will therefore describe the positions of the hydrogen atoms more accurately than the ring atoms. This was indeed found to be the case; the C−H distance refined to a value of 108.9 pm, with an esd of just 0.2 pm.

The structure derived from the LCNMR data is insignificantly different from that calculated ab initio, with values for all parameters in agreement to within one standard deviation.

The LCNMR data are thus complementary to the GED data, which provide information preferentially about the heavier ring atoms. Combining the two sets of data will therefore lead to a more accurate structure. This LCNMR-only analysis demonstrates that any distortion of the structure in solution is insignificantly small and that the combination of different types of data is valid in this case.

Vibration/Rotation Spectra. *Spectral Analysis.* For the planar D_{3h} molecule 1,3,5-triazine the 21 normal modes distribute according to $3a_1' + 2a_2' + 5e' + 2a_2'' + 2e''$, of which the e′ and a_2'' modes are infrared active and a_1', e′, and e″ are Raman active. The double primed species are out-of-plane vibrations, while the single primed are in-plane modes.

The fundamentals were analyzed using the ground-state combination differences (GSCD) program DIFNEU,[25] the least-squares program MILLI,[26] and the simulation program KILO.[26] For each fundamental about 3000 transitions were assigned, yielding the ground-state parameters and upper state constants up to the sixth-order terms, H. The analyses of ν_{11} and ν_{12} for all isotopomers and of ν_{14} for $^{12}C_3{}^{14}N_3H_3$ have been already published.[21,27,28] All other analyses will be the subjects of forthcoming publications.

All results necessary for the calculation of the molecular structure and force field are summarized in Table 6 (ground-state constants), Table 7 (frequencies, ν_0), Table 8 (Coriolis coupling constants, ζ), and Table 9 (amplitudes of vibration, u[29]).

TABLE 8: Experimental Coriolis Coupling Constants [Dimensionless]

	$^{12}C_3{}^{14}N_3H_3$	$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
$\zeta^z{}_6$	−0.009				
$\zeta^z{}_7$	0.4672	0.3954			
$\zeta^z{}_8$	−0.0756	−0.0207			−0.5787
$\zeta^z{}_9$	−0.7307	−0.7670	−0.74350		−0.3388
$\zeta^z{}_{10}$	−0.4300	−0.5476			−0.5352
$\zeta^z{}_{14}$	−0.00024	−0.00024			

TABLE 9: Observed rms Amplitudes of Vibration [*u*/pm] of $C_3N_3H_3$[a]

	C_1C_3	N_1C_1	C_1N_3	C_1H_1	C_1H_3	N_1N_2	N_1H_1	N_1H_3	H_1H_3
u	4.7	4.5	6.1	7.0	8.0	5.0	9.1	9.4	12.7

[a] Taken from ref 29.

The following points should be noted:

(1) Due to the lack of information on overtones and combination bands, no corrections have been made for anharmonicity effects.

(2) The frequencies of IR-active fundamentals quoted to two or more decimal places and all Coriolis coupling constants result from analyses of the high-resolution FTIR spectra with the program MILLI.

(3) The frequencies of IR-active fundamentals quoted to one decimal place are results of preliminary analyses of the high-resolution FTIR spectra.

(4) All ν_6, except that of $^{12}C_3{}^{14}N_3D_3$, are perturbed by a Fermi resonance with $2\nu_7$. The frequency of ν_6 of $^{12}C_3{}^{14}N_3H_3$ is corrected exactly for this perturbation. All other ν_6 frequencies have been adjusted approximately by using the difference between $(2\nu_7)_{obs}$ and $2\nu_7{}^0$.

(5) Frequencies of the Raman-active fundamentals, observed in the liquid or solid state, have been adjusted by applying the corresponding difference ($\nu_{gas-liq}$) or ($\nu_{gas-sol}$) measured for $^{12}C_3{}^{14}N_3H_3$.

(6) The intensities of the Raman-active fundamental, ν_1, of $^{12}C_3{}^{15}N_3H_3$, $^{13}C_3{}^{14}N_3H_3$, $^{13}C_3{}^{15}N_3H_3$, and $^{12}C_3{}^{14}N_3D_3$, observed in the solid state, seem to be heavily perturbed. These data have therefore been excluded from the force field calculation.

(7) The Coriolis coupling constants, ζ^z, cannot be observed directly. The corresponding observable is $(C\zeta_n)'$ in this case. Therefore $\zeta^z{}_n$ has to be defined as

$$\zeta^z{}_n = \frac{(C\zeta^z{}_n)'}{C_0} \tag{1}$$

This definition is not entirely satisfactory, because an upper state constant is divided by a ground-state constant, whose value is derived by the planarity rule neglecting the inertial defect, which is only an approximation.

The theoretical sum rule[30] for the e′ species is given by

$$\sum_t \zeta^z{}_t = -1 \tag{2}$$

Comparison of this value with the experimental sum of −0.778 for $^{12}C_3{}^{14}N_3H_3$ (Table 8) indicates that some of these Coriolis constants may be perturbed. In this respect, the most prominent candidates seem to be $\zeta^z{}_7$ and $\zeta^z{}_{10}$, because they have large absolute values (which are not well reproduced by the theoretical force field) and also differ substantially from the corresponding $\zeta^z{}_n$ values for $^{12}C_3{}^{15}N_3H_3$.

Structure Calculations. In the determination of the molecular structure from the rotation constants, the same model was used as in the GED refinements. To extract the three parameters on the r_0 level, rotation constants *B* of at least three different isotopomers are necessary, while the calculation of the r_s parameters requires at least four isotopomers. Rotation constants measured from pure rotational FTIR spectra in the gas phase were available for each of five different isotopomers, namely the parent species, $D_3C_3N_3$, $H_3{}^{13}C_3N_3$, $H_3C_3{}^{15}N_3$ and $H_3{}^{13}C_3{}^{15}N_3$. With the B_0 values least-squares methods can be used and applied to the evaluation of both r_0 and r_s structures.

In the r_0 method the structural parameters are adjusted in the least-squares refinement to optimize the fit to the experimental moments of inertia or rotation constants of all isotopomers. The r_s method is different. It was originally designed by Kraitchman[31] to use a minimal set of rotational constants, extended for multiple substitutions in symmetric top molecules with higher symmetry by Chutjian[32] and Nygaard[33] and developed to handle single and multiple substitutions in general and to make use of overdetermined sets of rotation constants.[34] Both methods, r_0 and r_s, have recently been reviewed.[35]

In the case of triazine, the Kraitchman equations conserving the D_{3h} symmetry can be written[32]

$$r_x{}^2 = \frac{2(P_b{}' - P_b)}{3\Delta m_x} = \frac{2(I_b{}' - I_b)}{3\Delta m_x} \qquad x = \mathrm{C, N, H} \tag{3}$$

where r_x is the distance of atom X from the center of mass. Taking into account the molecular symmetry, the structural parameters are found to be

$$r(\mathrm{C{-}H}) = r_\mathrm{H} - r_\mathrm{C} \qquad r_{N\cdots N} = r_N\sqrt{3} \tag{4,5}$$

$$r_{C-N} = \sqrt{r_C{}^2 + r_N{}^2 - r_C r_N} \qquad r_{C\cdots C} = r_C\sqrt{3} \tag{6,7}$$

$$\angle\mathrm{CNC} = \arccos[1 - 1.5(r_N/r_{C-N})^2] \tag{8}$$

$$\angle\mathrm{NCN} = \arccos[1 - 1.5(r_C/r_{C-N})^2] \tag{9}$$

Costain[36] has derived an estimate for the uncertainty of the substitution coordinates, based on the assumption that the uncertainties of the differences between planar moments of inertia, $P_b{}' - P_b$, are on the order of 0.003 Å^2. The uncertainties of the r_s coordinates in triazine are then given by

$$\sigma(r_x) = \frac{2 \times 0.003}{2 \times 3 \times \Delta m_x r_x} \approx \frac{0.001}{r_x} \tag{10}$$

In columns 2 and 3 of Table 5 the structural parameters derived by both methods are presented. It is important to note that both sets of parameters have been determined from an overdetermined set of data,[37] including experimental rotation constants for all isotopomers. The differences between the r_0 and r_s structures are very small. This may be an indication that the r_s structure is very near to the r_e structure.[38]

Refinement of the Molecular Force Field. A considerable number of attempts to settle the force field of triazine have been reported.[16,29,39−44] All of them suffered from a lack of sufficient experimental data so that the authors had to transfer constants from similar molecules or, with the improvement of quantum chemical calculation facilities, to use scaled ab initio force fields.

The new experimental data collected in this paper made it worthwhile to recalculate the force field of 1,3,5-triazine on the basis of the following data: (a) the r_s structure (Table 5); (b) the vibrational fundamentals (Table 7), including results from refs 40 and 45; (c) the Coriolis coupling constants (Table 8); (d) the centrifugal distortion constants (Table 6); (e) the rms amplitudes of vibration from the original GED study[29] (Table 9).

TABLE 10: Symmetry Coordinates[a] Used to Fit the Experimental Force Field

S_1: $D_1 + D_2 + D_3$
S_2: $\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 + 2(\Theta_1 + \Theta_3 + \Theta_2) - 2(\alpha_1 + \alpha_2 + \alpha_3)$
S_3: $d_1 + d_2 + d_3 + d_4 + d_5 + d_6$
S_4: $\Phi_1 - \Phi_2 + \Phi_3 - \Phi_4 + \Phi_5 - \Phi_6$
S_5: $d_1 - d_2 + d_3 - d_4 + d_5 - d_6$
S_{6a}: $2D_1 - D_2 - D_3$
S_{7a}: $0.454418(d_1 + d_2) - (d_3 + d_6) + 0.545582(d_4 + d_5)$
S_{8a}: $\Phi_3 - \Phi_4 - \Phi_5 + \Phi_6$
S_{9a}: $-(d_1 + d_2) + 0.058983(d_3 + d_6) + 0.941017(d_4 + d_5) + 0.161235[-2(\Phi_1 + \Phi_2) + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 + 2(2\alpha_1 - \alpha_2 - \alpha_3)] - 0.514025(2\Theta_3 - \Theta_1 - \Theta_2)$
S_{10a}: $0.531340[-2(\Phi_1 + \Phi_2) + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 + 2(2\alpha_1 - \alpha_2 - \alpha_3)] + (2\Theta_3 - \Theta_1 - \Theta_2)$
S_{6b}: $-D_2 + D_3$
S_{7b}: $-(d_1 - d_2) + 0.058983(d_3 - d_6) - 0.941017(d_4 - d_5)$
S_{8b}: $2(\Phi_1 - \Phi_2) - (\Phi_3 - \Phi_4 - \Phi_5 + \Phi_6)$
S_{9b}: $-0.454418(d_1 - d_2) + (d_3 - d_6) + 0.545582(d_4 - d_5) + 0.249203[\Phi_3 + \Phi_4 - \Phi_5 - \Phi_6 - 2(\alpha_2 - \alpha_3)] - 0.794468(\Theta_1 - \Theta_2)$
S_{10b}: $0.531340[\Phi_3 + \Phi_4 - \Phi_5 - \Phi_6 - 2(\alpha_2 - \alpha_3)] + (\Theta_1 - \Theta_2)$
S_{11}: $-\eta_1 - \eta_2 - \eta_3 + \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$
S_{12}: $2(\eta_1 + \eta_2 + \eta_3) + \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$
S_{13a}: $2\eta_1 - \eta_2 - \eta_3$
S_{14a}: $(\tau_1 - \tau_6) + 0.058983(\tau_2 - \tau_5) - 0.941017(\tau_3 - \tau_4)$
S_{13b}: $\eta_2 - \eta_3$
S_{14b}: $0.454418(\tau_1 + \tau_6) - (\tau_2 + \tau_5) + 0.545582(\tau_3 + \tau_4)$

Redundancies

R_1: $\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 + 2(\Theta_1 + \Theta_2 + \Theta_3) + 3(\alpha_1 + \alpha_2 + \alpha_3)$
R_2: $\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 - \Theta_1 - \Theta_2 - \Theta_3$
R_3: $\tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6$
R_4: $2(\Phi_1 + \Phi_2) - \Phi_3 - \Phi_4 - \Phi_5 - \Phi_6 + 2\alpha_1 - \alpha_2 - \alpha_3$
R_5: $\Phi_3 + \Phi_4 - \Phi_5 - \Phi_6 + \alpha_2 - \alpha_3$
R_6: $(d_1 + d_2) - 0.058983(d_3 + d_6) - 0.941017(d_4 + d_5) + 0.241607[-2(\Phi_1 + \Phi_2) + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6 + 2(2\alpha_1 - \alpha_2 - \alpha_3)] - 0.770254(2\Theta_3 - \Theta_1 - \Theta_2)$
R_7: $0.454418(d_1 - d_2) - (d_3 - d_6) - 0.545582(d_4 - d_5) + 0.373424[\Phi_3 + \Phi_4 - \Phi_5 - \Phi_6 - 2(\alpha_2 - \alpha_3)] - 1.190491(\Theta_1 - \Theta_2)$
R_8: $-0.454418(\tau_1 - \tau_6) - (\tau_2 - \tau_5) - 0.545582(\tau_3 - \tau_4)$
R_9: $(\tau_1 + \tau_6) - 0.058983(\tau_2 + \tau_5) - 0.941017(\tau_3 + \tau_4)$

[a] Not normalized. Coefficients are related to the r_S structure.

These last values were used because information on amplitudes of vibration derived from this force field was used in the current refinements of electron diffraction data, and it was essential to avoid the possibility of circular argument.

In previous calculations different sets of internal coordinates have been utilized. Following the treatments of refs 29, 39, and 40, we used the set of 30 internal coordinates shown in Figure 1: 9 bond stretches, 12 bond angle bendings, 3 out-of-plane waggings, and 6 torsions. Since there are only 21 normal modes, 9 redundancies have to be eliminated. Symmetrizing the internal coordinates according to D_{3h}, 5 redundancies are identified simply by inspection. However, the remaining 4 redundancies, belonging to the symmetry blocks E′ and E″, have no simple coefficients and were determined using the program GTAUZ.[46] Orthogonalizing the symmetry coordinates with respect to the latter redundancies, the final symmetry coordinates given in Table 10 in unnormalized form were derived. This choice was also guided by avoidance, where possible, of high correlations during the fitting process and by the potential energy distributions.

On this basis the force field was fitted by weighted least-squares using the program ASYM40.[7] Starting values for the force constants were taken from a scaled ab initio force field obtained at the 6-31G*/MP2 level. During the fitting procedure prohibitively high correlations (i.e. $|r| > 0.99$) were encountered, because not all force constants are sensitive to the frequencies, to the vibration−rotation interactions, and to the vibrational mean-square amplitudes. The interaction constants $F_{1,2}$, $F_{1,3}$, $F_{2,3}$, $F_{4,5}$, $F_{7,10}$, and $F_{13,14}$ were therefore fixed at the initial values. The final force field is presented in Table 11. Following a suggestion of Watson[47] for the reproduction of the calculated values of the data, more digits of the F_{ij} are retained than seem justified by the uncertainties. The molecular constants calculated with this force field are summarized in Tables 12, 13, and 14.

TABLE 11: Force Constants [mdyn, normalized with $r = 1$ Å][a]

Symmetry Species a$_1'$
$F_{1,1}$: 5.1014 (150)
$F_{3,3}$: 9.6949 (1030)
$F_{2,2}$: 0.9925 (118)
$F_{1,3}$: 0.2417 fix
$F_{1,2}$: 0.1039 fix
$F_{2,3}$: 0.4140 fix
Symmetry Species a$_2'$
$F_{5,5}$: 2.7039 (4545)
$F_{4,4}$: 0.5899 (757)
$F_{4,5}$: 0.3117 fix
Symmetry Species a$_2''$
$F_{11,11}$: 0.1467 (1)
$F_{12,12}$: 0.5993 (7)
$F_{11,12}$: −0.0253 (3)

Symmetry Species e′
$F_{6,6}$: 5.2191 (251)
$F_{7,7}$: 7.1216 (459)
$F_{8,8}$: 0.6382 (33)
$F_{10,10}$: 1.1282 (79)
$F_{9,9}$: 4.9518 (499)
$F_{6,7}$: 0.2555 (3303)
$F_{6,8}$: 0.0958 (936)
$F_{7,8}$: −0.3058 (237)
$F_{6,10}$: −0.1644 (721)
$F_{7,10}$: 0.5124 fix
$F_{8,10}$: −0.0359 (126)
$F_{6,9}$: −0.6173 (1262)
$F_{7,9}$: −0.5590 (1064)
$F_{8,9}$: −0.2272 (145)
$F_{10,9}$: 0.1032 (276)
Symmetry Species e″
$F_{14,14}$: 0.1534 (14)
$F_{13,13}$: 0.5134 (583)
$F_{13,14}$: 0.1233 fix

sum of weighted squares of differences, total DWD = 5637.1

[a] $F_{1,2}$, $F_{1,3}$, $F_{2,3}$, $F_{4,5}$, $F_{7,10}$, and $F_{13,14}$ are fixed values from the scaled ab initio calculation. Errors in parentheses are given in units of the last significant digit.

The frequencies of the IR-active fundamentals, the centrifugal distortion constants, and the root-mean-square amplitudes are nicely reproduced. The generally poorer fit to the $^{12}C_3{}^{14}N_3D_3$ data reflects the difference of the anharmonicities and the imbalance of the numbers of the H and D molecules. As expected, the Raman frequencies, observed in the liquid and solid state, and ν_6, a C−H stretching mode, show larger deviations. Finally, the Coriolis constants are less well reproduced. The quoted value of $\zeta^z{}_{10}$ for $^{12}C_3{}^{14}N_3H_3$ is merely an effective value, as we have no information about the nature of the perturbation involved.

TABLE 12: Frequencies of Fundamentals [cm^{-1}] Calculated from the Experimental Force Field[a]

	$^{12}C_3{}^{14}N_3H_3$		$^{12}C_3{}^{15}N_3H_3$		$^{13}C_3{}^{14}N_3H_3$		$^{13}C_3{}^{15}N_3H_3$		$^{12}C_3{}^{14}N_3D_3$	
	calc	obs − calc	calc	obs − calc	calc	obs − calc	calc	obs − calc	calc	obs − calc
ν_1	3052.10	−0.00	3052.10		3041.63		3041.63		2266.90	
ν_2	1130.13	7.97	1126.30	11.70	1095.86	4.14	1089.74	8.26	1084.69	−1.69
ν_3	991.50	−1.80	961.23	−4.13	985.65	2.45	957.67	−0.57	983.86	1.14
ν_4	1375.02	−0.02	1372.94		1371.75		1369.46		1032.18	
ν_5	1001.02	−1.02	985.96		979.28		964.17		993.49	
ν_6	3063.14	−0.23	3063.08	−6.38	3055.25	−5.15	3055.17	−6.37	2245.80	30.70
ν_7	1556.41	−0.07	1541.94	−0.27	1525.01	−1.06	1511.01	−1.41	1525.44	5.36
ν_8	1410.06	−0.10	1390.68	0.12	1403.10	1.60	1383.26	1.14	1284.66	0.06
ν_9	1172.79	−0.15	1164.30	1.15	1151.99	0.92	1142.20	3.40	929.26	0.32
ν_{10}	675.74	0.04	662.23	0.33	664.83	1.87	652.15	1.65	663.87	0.11
ν_{11}	927.38	−0.79	922.97	−0.93	914.07	−0.52	909.10	0.33	859.81	0.83
ν_{12}	737.76	−1.02	729.32	−0.82	732.27	−0.78	723.14	−0.58	573.27	1.35
ν_{13}	1037.58	−5.58	1037.05	−4.05	1024.32	−1.32	1023.80	−2.80	855.59	6.41
ν_{14}	339.50	0.00	334.05	0.06	335.62	1.38	330.06	0.94	306.73	2.27

[a] $C_3N_3H_3$, $C_3N_3D_3$: master. $C_3{}^{15}N_3H_3$, $^{13}C_3N_3H_3$, $^{13}C_3{}^{15}N_3H$: nonmaster.

TABLE 13: Coriolis Coupling Constants (Dimensionless) and Centrifugal Distortion Constants [10^{-8} cm^{-1}] Calculated from the Experimental Force Field

	$C_3N_3H_3$		$C_3{}^{15}N_3H_3$		$^{13}C_3N_3H_3$		$^{13}C_3{}^{15}N_3H_3$		$C_3N_3D_3$	
	calc	obs − calc	calc	obs − calc	calc	obs − calc	calc	obs − calc	calc	obs − calc
$\zeta^z{}_6$	−0.0536	0.0446	−0.0536		−0.0540		−0.0540		−0.0484	
$\zeta^z{}_7$	0.5563	−0.0891	0.4960	−0.1006	0.5476		0.4755		0.6606	
$\zeta^z{}_8$	−0.0855	0.0099	0.0212	−0.0005	−0.0563		0.0602		−0.7516	0.1729
$\zeta^z{}_9$	−0.7321	0.0014	−0.7751	0.0081	−0.7489	0.0054	−0.7919		−0.2582	−0.0806
$\zeta^z{}_{10}$	−0.6851	0.2551	−0.6884	0.1408	−0.6884		−0.6898		−0.6023	0.0671
$\zeta^z{}_{14}$	0.0000	0.0002	0.0000	0.0002	0.0000		0.0000		0.0000	
D_J	5.3173	0.0026	5.0151	0.0001	5.0045	0.0145	4.6952	0.0179	3.9774	−0.0100
D_{JK}	−9.0006	0.1446	−8.4348	0.1518	−8.4782	0.1515	−7.9515	0.1337	−6.7046	0.1646

TABLE 14: rms Amplitudes of Vibration [pm] Calculated from the Experimental Force Field

	$^{12}C_3{}^{14}N_3H_3$		$^{12}C_3{}^{15}N_3H_3$	$^{13}C_3{}^{14}N_3H_3$	$^{13}C_3{}^{15}N_3H_3$	$^{12}C_3{}^{14}N_3D_3$
atoms	calc	diff	calc	calc	calc	calc
C_1C_3	5.2	−0.5	5.2	5.2	5.2	5.2
N_1C_1	4.6	−0.1	4.6	4.6	4.5	4.6
C_1N_3	5.8	0.3	5.7	5.7	5.7	5.8
C_1H_1	7.7	−0.7	7.7	7.7	7.7	6.6
C_1H_3	9.2	−1.2	9.2	9.2	9.2	8.1
N_1N_2	5.2	−0.2	5.2	5.2	5.2	5.2
N_1H_1	9.2	0.1	9.1	9.2	9.1	8.2
N_1H_3	9.6	−0.2	9.5	9.6	9.5	8.3
H_1H_3	12.5	0.2	12.5	12.5	12.5	10.7

Analysis of GED Data Alone. In our study of the molecular structure of 1,3,5-triazine in the gas phase we wished to demonstrate the benefits of including non-GED information in the structural analysis. For this reason we have undertaken three refinements using GED data. The first, using GED data alone, is described here. The results of the second and third refinements, incorporating first rotation constants and then dipolar couplings, are given below.

The results from the GED data-only refinement are shown in column 4 of Table 5. The R_G factor of 6.0% indicates that the data are of good quality. The C−N distance refined to a value of 133.94(10) pm and the CNC angle to 113.9(2)°. The standard deviations recorded are extremely small, which is expected, since the ring can be fully described in terms of any two of the four independent ring distances. It is clear from the radial distribution curve obtained in the final refinement (see Figure 2) that correlation effects between the individual distances are low. Thus, with all four ring distances well defined, the two parameters defining the ring should also be very well defined. In contrast the C−H distance is less well defined, because hydrogen atoms contribute relatively little to the total scattering.

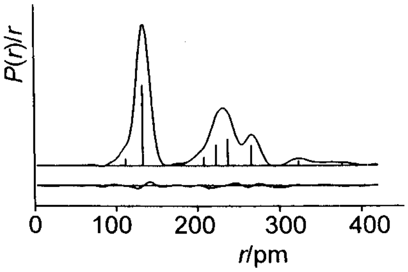

Figure 2. Observed and final difference radial-distribution curves for 1,3,5-triazine. Before Fourier inversion the data were multiplied by s $\exp(-0.00002s^2)/(Z_C - f_C)(Z_N - f_N)$.

In addition to the three geometric parameters refining, four of the nine amplitudes of vibration were also refined successfully at this stage. These correspond to the four most prominent features on the radial distribution curve, namely u_1(N−C), u_3(N···N), u_5(C···C), and u_6(N···C). The five remaining amplitudes of vibration which could not be refined all involved hydrogen atoms. These vibrational amplitudes were therefore fixed at values obtained from the scaled 6-31G*/MP2 harmonic force field.

Combined Analysis of GED Data and Rotation Constants. Rotation constants measured from high-resolution FTIR spectra in the gas phase were available for each of five different isotopomers of 1,3,5-triazine. The vibrational corrections necessary to convert the rotation constants from B_0 to B_Z structural type (which is equivalent to the $r_\alpha{}^\circ$ structural type derived in the GED refinement) were obtained from the experimental harmonic force field. These agreed to within about 10% with those obtained from the scaled ab initio 6-31G*/MP2 force field. The experimental rotation constants, both sets of vibrational corrections, and calculated rotation constants (based on the final structure reported in the next section) are given in Table 4. Note that the uncertainties used to weight the data combine the experimental standard deviations with a conserva-

TABLE 15: Comparison of Structural Parameters for 1,3,5-Triazine (*r*/pm, ∠ /deg) in the Three Phases and Calculated ab Initio

		combined analysis[a] (gas phase)	LCNMR[a] (solution phase)	neutron diffraction[b] (solid phase) 25 °C	ab initio[c] [6-311G(2df,p)/MP2)]
p_1	*r*(C−N)	133.68(1)[d]	133.4(7)	133.6	133.38
p_2	*r*(C−H)	108.94(19)[e]	108.9(2)	105.9	108.21
p_3	∠CNC	113.79(8)	114.2(11)	114.7	114.03

[a] $r_\alpha°$. [b] Corrected for librational effects. [c] r_e. [d] r_e = 132.88(19) pm. [e] r_e = 107.65(32) pm.

tive estimate of 10% error in the vibrational corrections to allow for anharmonic effects.

It is important to allow for the change in the C−H distance on deuteriation, so with the introduction of the rotation constants for the two deuterated isotopic species a fourth parameter, the difference between *r*(C−H) and *r*(C−D), was incorporated into the model defining the structure. This parameter was assigned a restraint of 0.20(10) pm to aid refinement in accordance with the SARACEN method,[5] with the value and uncertainty adopted from spectroscopic measurements.[48] With the restraint this parameter refined to 0.21(9) pm, indicating that the information contained within the rotation constants is concordant with values observed by spectroscopy. Calculated rotation constants were found to be in excellent agreement with the vibrationally corrected experimental values.

The results from this combined refinement are given in column 5 of Table 5. The addition of the five rotation constants was found to have no significant effect on the overall geometry, but the precision of all three geometric parameters was greatly improved, with the C−N distance determined to within 0.01 pm, *r*(C−H) to within 0.2 pm, and ∠CNC to within 0.08°. Both *r*(C−N) and *r*(C−H) were found to shorten slightly with the inclusion of the extra data. In addition, four extra amplitudes of vibration could now be refined, namely u_2(C−H), u_4(N_1···H_1), u_7(C_1···H_2), and u_9(N_1···H_3). The one vibrational parameter which remained unable to refine, amplitude u_8(H_1···H_2), corresponds to a feature whose intensity is just 0.4% of that of the most intense peak in the radial distribution curve and is therefore of very small weighting in the overall structural determination. The R_G factor rose slightly in the combined refinement to 6.6%.

Combined Analysis of GED Data, Rotation Constants, and Dipolar Couplings. To obtain the best possible structure in light of all available experimental information, the five dipolar couplings of Marchal et al.[6] were also included in the refinement.

The five new pieces of structure-related information resulted in only minor improvements in the quality of the final structure, the main effect being a slight improvement in the precision of four refining amplitudes of vibration, namely u_2(C−H), u_4(N_1···H_1), u_7(C_1···H_2), and u_9(N_1···H_3). This result was expected since the dipolar coupling constants mostly contain information relating to the hydrogen atom positions. The orientation parameter S_{zz} (p_5) was also now able to refine freely without the aid of a restraint. The experimental dipolar coupling values, vibrational corrections (both experimental and theoretical), and the calculated values based on the final structure obtained are reported in Table 4. The quoted uncertainties are a combination of experimental standard deviations with estimated 10% errors in the vibrational corrections to allow for anharmonic effects. From Table 4 it can be seen that all calculated dipolar couplings are in good agreement with the vibrationally corrected values; the poorest agreement is for *D*(N_3,H_1), which differs by just over 1.5 estimated standard deviations.

The results from this final combined analysis refinement are given in column 6 of Table 5; the final R_G factor was 6.7%. With all geometric parameters and all significant amplitudes of vibration refining the final standard deviations returned in the combined analysis refinement were found to be extremely small. The C−N distance refined to a final value of 133.68 pm, with a standard deviation of just 0.01 pm, the ring angle to 113.82(8)°, and the C−H distance to 108.9(2) pm. This exceptionally high precision reflects the high symmetry of the molecule, the consequent very high ratio of observations to refinable parameters, and the complementary nature of GED, high-resolution FTIR, and LCNMR spectrocopic data.

The experimental structures of free, and therefore undistorted, molecules in gas/solution phases should be directly comparable to those calculated ab initio, but there are small differences between the static equilibrium structure (r_e) for one discrete molecule, given by ab initio calculations, and the vibrationally averaged experimental $r_\alpha°$ structure of the undistorted molecule. For 1,3,5-triazine ab initio calculations with the largest basis set, 6-311G(2df,2pd) yield a distance of 133.38 pm for C−N and a CNC ring angle of 114.03°, compared to the experimental values of 133.68(1) pm and 113.82(9)°, while the C−H bond distances were found to be 108.21 pm ab initio, 108.9(2) pm by experiment (Table 15).

The discrepancy between the theoretical (r_e) and experimental ($r_\alpha°$) *r*(C−N) is significant enough to warrant further analysis. Treating the symmetric C−N stretching mode as a Morse oscillator, the difference between these distances is given by

$$r_\alpha° - r_e = (3/2)au(0)^2 \qquad (6)$$

where *a* is the anharmonic constant and *u*(0) is the amplitude of vibration for a C−N atom pair at 0 K. These constants were determined by ab initio calculations at the 6-31G*/MP2 level and from the resulting force field as *u*(0) = 4.4(3) pm and *a* = 0.027(5) pm^{-1}, with conservative estimates of their uncertainties. The correction to the distance is thus 0.80(19) pm, giving r_e(C−N) = 132.88(19) pm. The agreement with our best calculated estimate of 133.82 pm for this distance is well outside the experimental error limits. For *r*(C−H) a similar calculation using *u*(0) = 6.6(4) pm and *a* = 0.019(4) pm^{-1} gives r_e(C−H) = 107.65(32) pm, compared with the best calculated value of 108.39 pm. These discrepancies remain unexplained, although we note that even at the highest levels of theory and with the largest basis sets, changes on the order of 0.5 pm in both distances were still occurring.

The full list of bond distances, along with the final vibrational amplitude values, is given in Table 16 and the covariance matrix in Table 17. The two molecular scattering and difference curves, for the long and short camera distance plates, are shown in Figure 3 and the final radial distribution and difference curves in Figure 2.

Comparison of Molecular Structures Obtained in the Gas and Solid Phases. Three independent crystal structure determinations of 1,3,5-triazine at 297−299 K have previously been reported by Coppins[8] using X-ray (both copper and molybdenum radiation sources) and neutron diffraction studies. The crystal parameters, reported in Table 18, were not found to deviate from D_{3h} molecular symmetry. Individual C−N bond distances

TABLE 16: Interatomic Distances [r_α/pm] and Amplitudes of Vibration [*u*/pm] for the Combined GED/Rotation Constants/LCNMR Study of 1,3,5-Triazine

i	atoms	distance	amplitude
1	N_1-C_1	133.7(1)	5.1(2)
2	C_1-H_1	110.2(2)	5.3(11)
3	$N_1\cdots N_2$	238.4(1)	6.2(4)
4	$N_1\cdots H_1$	207.3(1)	12.4(12)
5	$C_1\cdots C_2$	224.0(1)	6.1(5)
6	$N_1\cdots C_2$	266.9(1)	6.5(4)
7	$C_1\cdots H_2$	323.0(2)	13.1(16)
8	$H_1\cdots H_2$	413.0(3)	12.6(f)[a]
9	$N_1\cdots H_3$	375.9(2)	12.0(29)

[a] f = fixed at the value derived from the experimental force field.

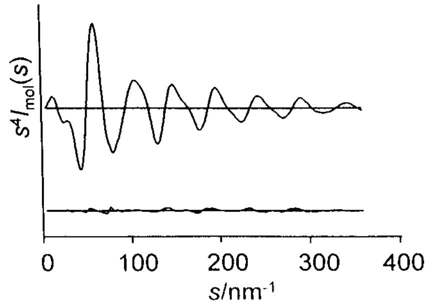

Figure 3. Observed and final difference combined molecular scattering curves for 1,3,5-triazine. Theoretical data are shown for the regions *s* = 0−20 and 356−360 nm^{-1}, for which no experimental data are available.

varied from 131.5 to 131.7 pm, about 2 pm shorter than that found in the gas phase, and the CNC ring angle from 113.4(1)° by X-ray diffraction to 114.8° by neutron diffraction, compared to the gas-phase angle of 113.82(9)°. The apparent ring contraction in the solid phase can be readily attributed to two factors. First, there exists a difference in bond length definition between gas-phase methods and X-ray diffraction, with the former measuring internuclear distances and the latter the differences between centers of electron density. Second, vibrational averaging effects are different, both because of the different techniques and because the experiments were performed at different temperatures. Since neutron diffraction, like GED, measures internuclear distances, correcting this structure for librational effects should result in a structure that is directly comparable to that observed in the gas phase, provided there are no strong intermolecular interactions in the solid phase giving rise to molecular distortion.

The structure obtained by neutron diffraction after correcting for librational effects is also given in Table 18 for comparison. From this it can be seen that the C−N distance lengthens by about 2 pm to 133.6 pm, compared to the gas-phase distance ($r_\alpha°$) of 133.68(1) pm, while the ∠CNC ring angle remains largely unaffected by the process. In effect, the ring contraction effect observed in the solid phase has been removed by the librational correction, with both the carbon and nitrogen atoms moving out from the center of the ring by about 2 pm. The difference in internal ring angle of about 1° may be due to molecular packing effects.

Conclusions

The molecular structure of 1,3,5-triazine has been determined independently by ab initio calculations, gas-phase electron diffraction, vibration/rotation spectroscopy, and liquid crystal NMR spectroscopy data. All four methods yield structures that agree with one another to within one standard deviation. Thus the inclusion of solution-phase data derived from LCNMR spectroscopy into the combined structural analysis is validated.

A reliable force field derived from experimental data has been obtained for the first time, and this is in excellent agreement with the force field obtained by ab initio calculations. The force field gave vibrational corrections, used in a combined analysis, in which the GED data were progressively supplemented with five rotation constants and five LCNMR dipolar couplings. The complementary nature of information provided by the different techniques enables the combined analysis to give a structure of greatly improved precision. Agreement between experiment and theory is less good than expected, and calculations well beyond present resources may be needed.

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TABLE 17: Least-Squares Correlation Matrix (×100) for the Combined GED/Rotation Constants/LCNMR Study of 1,3,5-Triazine[a]

p_2	p_3	p_4	p_5	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_9	k_1	k_2	
−93	−15	**-93**	**62**	4	−4	−4	−3	−12	0	−1	3	17	5	p_1
	−17	**93**	**−62**	−4	3	−3	5	2	0	2	−2	−16	−3	p_2
		6	−1	−2	0	26	−6	29	−2	−1	0	−2	−3	p_3
			-60	−4	3	2	3	9	0	1	−2	−17	−4	p_4
				2	−2	0	−2	−5	0	−1	1	11	2	p_5
					3	17	9	17	16	−1	4	49	**69**	u_1
						−1	−2	0	−2	1	0	−10	−9	u_2
							52	**64**	14	2	−2	23	23	u_3
								42	−4	5	0	10	13	u_4
									5	1	−2	22	21	u_5
										−16	3	10	24	u_6
											−12	1	−2	u_7
												3	6	u_9
													40	k_1

[a] The most significant values are shown in **bold**. *k* is a scale factor.

TABLE 18: Structural Parameters Obtained for 1,3,5-Triazine in the Solid Phase[a]

	X-ray crystallography		neutron diffraction		
	Cu	Mo	uncorrected	librational correction[b]	corrected
r(C−N)	131.5	131.7	131.7	1.9	133.6
r(C−H)			104.5	1.4	105.9
∠CNC	113.4	113.4	114.8	−0.1	114.7

[a] Ref 8. [b] This work.

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References and Notes

(1) Liescheski, P. B.; Rankin, D. W. H. *J. Mol. Struct.* **1988**, *178*, 227−241.

(2) Abdo, B. T.; Alberts, I. L.; Attfield, C. J.; Banks, R. E.; Blake, A. J.; Brain, P. T.; Cox, P. T.; Pulham, C. R.; Rankin, D. W. H.; Robertson, H. E.; Murtagh, V.; Heppeler, A.; Morrison, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 209−216.

(3) Hedberg, L.; Hedberg, K. *J. Phys. Chem.* **1993**, *97*, 10349−10351.

(4) Cradock, S.; Liescheski, P. B.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1988**, *110*, 2758−2763.

(5) 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*, 12280−12287; Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589−4596.

(6) Marchal, J. P.; Canet, D. *J. Chem. Phys.* **1977**, *66*, 2566−2568.

(7) ASYM40 version 3.0, update of program ASYM20. Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117−142.

(8) Coppens, P. *Science* **1967**, *158*, 1577−1579.

(9) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision F.4; Gaussian, Inc.: Pittsburgh, PA, 1992.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; 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.

(11) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.

(12) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(13) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−168.

(14) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.*,**1980**, *72*, 5639−5648.

(15) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(16) Lancaster, J. E.; Stamm, R. F.; Colthup, N. B. *Spectrochim. Acta* **1961**, *17*, 155−165.

(17) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954−957.

(18) Cradock, S.; Koprowski, J.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *77*, 113−126.

(19) Boyd, A. S. F.; Laurenson, G. S.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 217−226.

(20) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, Boston, MA, and London, 1992; Vol. C, p 245.

(21) High-Resolution FTIR Spectroscopy of 1,3,5-Triazine. The Parallel Bands ν_{11} and ν_{12} of $C_3N_3H_3$, $^{13}C_3N_3H_3$, $^{13}C_315N_3H_3$ and $C_3N_3D_3$. Bodenmüller, W.; Pfeffer, M.; Ruber, R.; Ruoff, A. *Z. Naturforsch.*, to be published.

(22) Lists of observed and calculated wavenumbers have been deposited in the "Sektion Spektren- und Strukturdokumentation", University of Ulm, D-89069 Ulm, Germany (Dr. J. Vogt).

(23) Guelachvili, G. *Handbook on Infrared Standards*; Academic Press: London, 1986.

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

(25) DIFNEU, program for analysis of ground-state combination differences. Essig, H.; Zeisberger, E. Sektion Schwingungspektroskopie, Universität Ulm, Germany.

(26) MILLI and KILO, least-squares analysis and simulation programs. Graner, G. Université de Paris-Sud, Orsay, France.

(27) Bodenmüller, W.; Ruoff, A.; Manceron, L. *Z. Naturforsch.* **1992**, *47a*, 1197−1203.

(28) Bodenmüller, W.; Ruoff, A. *J. Mol. Spectrosc.* **1995**, *173*, 205−222.

(29) Pyckhout, W.; Callaerts, I.; van Alsenoy, C.; Geise, H. J.; Almenningen, A.; Seip, R. *J. Mol. Struct.* **1986**, *147*, 321−329.

(30) Lord, R. C.; Merrifield, R. E. *J. Chem. Phys.* **1952**, *20*, 1348−1350.

(31) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17−24.

(32) Chutjian, A. *J. Mol. Spectrosc.* **1964**, *19*, 361−370.

(33) Nygaard, L. *J. Mol. Spectrosc.* **1976**, *62*, 292−293.

(34) Typke, V. *J. Mol. Spectrosc.* **1978**, *69*, 173−178.

(35) Rudolph, H. D. *Adv. Mol. Struct. Res.* **1995**, *1*, 63−114.

(36) Costain, C. C. *Trans. Am. Cryst. Assoc.* **1996**, *2*, 157−164.

(37) Typke, V. *J. Mol. Struct.* **1996**, *384*, 35−40.

(38) Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864−874.

(39) Navarro, A.; López González, J. J.; Fernández Gómez, M.; Marquez, F.; Otero, J. C. *J. Mol. Struct.* **1996**, *376*, 353−362.

(40) Navarro, A.; López González, J. J.; Kearly, G. J.; Tomkinson, J.; Parker, S. F.; Sivia, D. S. *Chem. Phys.* **1995**, *200*, 395−403.

(41) Califano, S.; Crawford, B., Jr. *Spectrochim. Acta* **1960**, *16*, 900−909.

(42) Nagarajan, G. *Ind. J. Pure Appl. Phys.* **1963**, *1*, 327−331.

(43) Cardenete, A.; López González, J. J.; Arenas, J. F. *Opt. Pura. Apl.* **1986**, *19*, 137−143.

(44) Navarro, A.; López González, J. J.; Fernández Gómez, M.; Escribano, R. M. *Vib. Spectrosc.* **1997**, *13*, 187−194.

(45) Zeindl, S. Diplomarbeit, Universät of München, 1992.

(46) GTAUZ, program for determining redundancies. Typke, V. Universitätsrechenzentrum, Universität Ulm, Germany.

(47) Watson, J. K. G. *J. Mol. Spectrosc.* **1977**, *66*, 500−502.

(48) Robiette, A. G. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports; The Chemical Society, 1972; Vol. 1, p 191.

(49) The United Kingdom Chemical Database Service. Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

(50) 3D Search and Research using the Cambridge Structural Database. Allen, F. H.; Kennard, O. *Chemical Automation News* **1993**, *8* (1), 1 and 30−37.