with half the rate of methyl radical trapping (5.0×10^7 versus 1×10^8 M^{-1} s^{-1}).

σ radical trapping is relatively unexplored in the literature. A single value of 5×10^8 M^{-1} s^{-1} hs been reported for the trapping of CF_3 by NM.[15] This value is rather similar to those for 4-carboxyphenyl and $CONH_2$ found here. The value for $^{\bullet}CO_2^-$ clearly shows this radical to be different than the other σ radicals. We note the formamide radical, $^{\bullet}CONH_2$, is a good model for a fragmented peptide bond in biological systems. In biological systems, where spin trapping has been utilized to its greatest extent, both σ and π radicals are produced, in environments of greatly varying polarity and effective pH. Reliable quantitative (and in some cases qualitative) data on biological free-radical reactions will not be available until the observed variability of free radical trapping rates can be understood and measured. We believe the TRESR pulse radiolysis method is uniquely suited to test the efficiency and selectivity of spin trapping reactions.

Acknowledgment. We gratefully acknowledge helpful conversations with Professors David Armstrong and William Bernhard. We thank Ian Duncanson of the NDRL glass shop for design assistance and construction of free flow ESR flat cells.

The r_α Structures of Pyrazine and Pyrimidine by the Combined Analysis of Electron Diffraction, Liquid-Crystal NMR, and Rotational Data

Stephen Cradock, Phillip B. Liescheski, David W. H. Rankin,* and Heather E. Robertson

Contribution from the Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, United Kingdom. *Received September 10, 1987*

Abstract: The molecular structures of pyrazine and pyrimidine have been determined by combined analyses of data obtained by gas-phase electron diffraction, rotational spectroscopy, and liquid-crystal NMR. The studies illustrate the complementary nature of information obtained by liquid-crystal NMR spectroscopy and that obtained by electron diffraction and rotational spectroscopy. Geometrical parameters (r_α) for pyrazine from the combined analysis are as follows: rCH = 108.31 (37), rCN = 133.76 (13), rCC = 139.68 (30) pm; $\angle$CNC = 115.65 (24), $\angle$CCH = 119.96 (8)°. Geometrical parameters (r_α) for pyrimidine from the combined analysis are the following: rC(5)H(9) = 108.7 (3), rC(4)H(8) = 107.9 (2), rC(2)H(7) = 108.2 (4), rCC = 139.3 (3), rC(4)N = 135.0 (7), rC(2)N = 132.8 (7) pm; $\angle$CCC = 117.8 (2), $\angle$C(5)C(4)H(8) = 120.9 (3), $\angle$CCN = 121.2 (3)°.

The chemical properties of a compound are known to be dependent upon its structure, so the knowledge of accurate structures and methods to obtain them are essential to chemistry. For many years, the structures of gas-phase molecules were determined either by electron diffraction (ED) or rotational spectroscopy. In ED, the molecules under investigation are allowed to scatter an electron beam. From the interference pattern of the scattered electrons, distances between atoms can be determined, and so information on the three-dimensional structure of the molecule can be deduced. In rotational spectroscopy, the moments of inertia of the molecule are obtained from its measured rotation constants and used to obtain structural information. Since 1962, the NMR spectra of partially oriented molecules have been used to obtain molecular structure in the liquid phase.[1] In liquid-crystal NMR (LCNMR) spectroscopy, the liquid-crystal solvent molecules in the presence of the magnetic field of the NMR spectrometer partially orientate the solute molecules under investigation. In this anisotropic fluid the intramolecular direct dipolar couplings between spin $^1/_2$ nuclei in the solute molecule no longer average to 0, and so become measurable. The direct dipolar couplings are spacially dependent internuclear interactions, so one can extract structural information from them.

Unfortunately, all of these techniques have their limitations. In rotational spectroscopy, three rotation constants at most can be measured for any single isotopic species of a particular compound. For all but the simplest compounds several isotopically substituted species must be prepared and studied in order to obtain enough structural information. To complicate the situation further, some elements, such as fluorine and phosphorus, have only one natural (stable) isotope, which can lead to a practical restriction on the number of possible isotopic species. Finally, a dipole moment is required on the molecule in order to observe its microwave spectrum. In electron diffraction, three-dimensional information (molecular structure) is reduced to one-dimensional data (radial distribution curve) since the electrons are scattered by an ensemble of randomly oriented molecules. As a result of this reduction, data on different interatomic distances that are similar in length are correlated, and thus poorly determined. Also, positions of light atoms, particularly hydrogen, are not well determined in the presence of heavy atoms, owing to their lower electron-scattering ability. In LCNMR, useful information can only be had from spin $^1/_2$ nuclei. Also, it is difficult to separate the direct dipolar couplings from their corresponding anisotropic indirect couplings, which become significant for nuclei larger than the proton. As a result, one tends to be restricted to couplings which involve protons. Finally, the orientation parameters, which are additional unknowns in the analysis of LCNMR data, are correlated to information on the absolute size of the molecule, so only bond angles and ratios of interatomic distances can be determined.

The information given by ED tends to be complementary to that given by LCNMR. It has been shown that combining the data from the two techniques can be useful.[2,3] There are three major benefits in performing a joint analysis. Firstly, ED data easily give information on the absolute size of a molecule, which is absent in LCNMR data. Secondly, the ratio of interatomic distances of similar length can be obtained from the dipolar couplings and used to reduce the correlation found using ED alone.

(1) Englert, G.; Saupe, A. *Z. Naturforsch., A* **1962**, *19*, 172-177. Saupe, A.; Englert, G. *Phys. Rev. Lett.* **1963**, *11*, 462-464.

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

(3) Blair, P. D.; Cradock, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1985**, 755-759.

0002-7863/88/1510-2758$01.50/0

Table I. ED Data Analysis Parameters

camera distance (mm)	Δs[a]	s_{min}[a]	s_1[a]	s_2[a]	s_{max}[a]	correlation parameter q	scale factor k	electron wavelength (pm)
				Pyrazine				
95.13	4	80	100	304	356	0.3873	0.685 (15)	5.686
258.10	2	20	40	140	164	0.4724	0.770 (7)	5.688
				Pyrimidine				
95.60	4	80	100	304	356	0.4025	0.827 (14)	5.687
258.48	2	20	40	140	164	0.4809	0.783 (6)	5.686

[a] Units of nm^{-1}.

Thirdly, positions of protons are well determined by LCNMR data, and these parameters are usually poorly determined in ED experiments. In addition, rotation constants (if available) can also be included to supplement the structural information about the molecule. The combined analysis of electron diffraction data and rotation constants in the determination of gas-phase structures is a widely used and long-established practice.

In order to combine the information from these different techniques, one needs to know the harmonic vibrational force field of the molecule. Vibrational corrections must be included in the structural analysis since each technique averages the vibrational motion in a different manner. One generally analyzes the data to obtain an r_α structure, which differs from the equilibrium (r_e) structure only in respect of anharmonic contributions. Since the early 1960's, straightforward methods have been used to determine r_α structures from ED and rotational data.[4] More recently, a scheme has been devised to obtain r_α structures from LCNMR data.[5] With a good harmonic vibrational force field, one should be able to combine r_α structural information from the three experimental techniques and determine a more precise molecular structure.

This combination of techniques has already been applied to the structural analysis of difluorophosphine selenide[2] and difluorophosphine sulphide.[3] Unfortunately, in the case of difluorophosphine selenide the vibrational treatment of the LCNMR data was inadequate. Both molecules are rather floppy, so the effects from orientational deformation may be severe. Also, for both compounds, the direct dipolar couplings between heavy nuclei (PF, SeP, SeF, FF) were included in the data, so the neglect of their anisotropic indirect couplings (pseudo-direct couplings) may lead to errors. In this paper, pyrimidine and pyrazine were chosen as the next candidates to test this combination technique. They are fairly rigid, planar molecules with enough symmetry to illustrate clearly the utility of combining these tecniques. Their rigidity helps to reduce the effects of orientational deformation. Also, their four protons give a sufficient number of reliable direct dipolar couplings, using ^{13}C and ^{15}N isotopes in natural abundances.

Experimental Section

Samples of pyrazine (gold label, 99+% purity) and pyrimidine (99% purity) were purchased from Aldrich and used without further purification.

Electron Diffraction. Electron diffraction scattering intensities were recorded photographically on Kodak Electron Image plates using the Edinburgh apparatus[6] operating at approximately 44 kV. The samples were maintained at 340 K during the measurements, while the nozzle was maintained at 350 K. Data from three plates at the long camera distance (258 mm) and three plates at the short camera distance (95 mm) for each compound were obtained in digital form using a Joyce-Loebl MDM6 microdensitometer at the S.E.R.C. Daresbury Laboratory.[7] Calibration runs using benzene vapor were performed to measure the electron wavelength and nozzle-to-plate distances. Standard programs were used for data reduction.[7] The scattering factors of Schäfer, Yates, and Bonham[8] were used throughout. The weighting points used in setting up the off-diagonal weight matrix, s range, scale factors, correlation parameters, and electron wavelengths are presented in Table I.

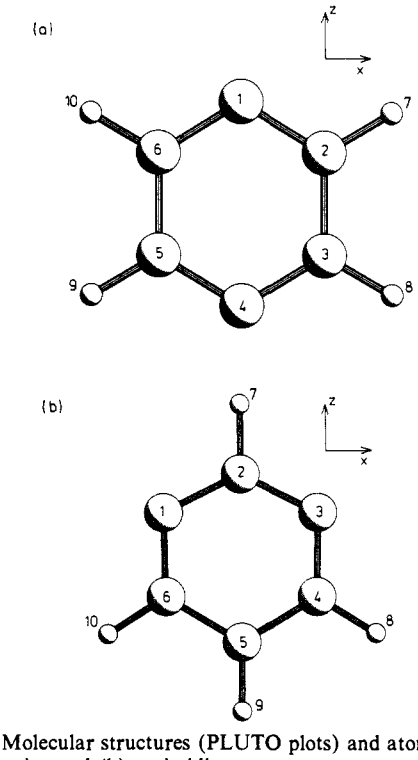

Figure 1. Molecular structures (PLUTO plots) and atom numberings for (a) pyrazine and (b) pyrimidine.

It should be noted that Bormans, DeWith, and Mijlhoff[9] have previously studied the gas-phase structure of pyrazine by ED. The r_a structure of pyrimidine was determined by Fernholt and Rømming.[10] The results from Bormans et al. were not used in our analyses, while the results from Fernholt and Rømming were used as initial values in the preliminary ED analysis of pyrimidine. Our r_a structure for pyrimidine agreed very well wth their results.[10]

Liquid-Crystal NMR. The experimentally observed direct dipolar couplings of Diehl, Bjorholm, and Bösiger for pyrazine and pyrimidine were used.[11] The data were collected at 300 K in Merck Phase V liquid-crystal solvent.

Rotational Data. Three rotation constants from the microwave work of Blackman, Brown, and Burden[12] for pyrimidine ($^1H_4{}^{12}C_4{}^{14}N_2$) were used. No microwave data were available for pyrazine, which has no permanent dipole moment.

Structural Analysis

For comparison, r_α structures were obtained from an ED-only analysis, an LCNMR-only analysis, and a combined data analysis for each compound. These data analyses were performed with the least-squares refinement program, ED87, which is a modified version of a program described previously.[2]

(4) Roblette, A. G. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1973; Vol. 1, p 178.
(5) Sykora, S.; Vogt, J.; Bösiger, H.; Diehl, P. *J. Magn. Reson.* **1979**, *36*, 53–60.
(6) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H., *J. Chem. Soc., Dalton Trans.* **1980**, 954–957.
(7) Cradock, S.; Koprowski, J.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *77*, 113–120.
(8) Schäfer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055–3056.
(9) Bormans, B. J. M.; DeWith, G.; Mijlhoff, F. C. *J. Mol. Struct.* **1977**, *42*, 121–128.
(10) Fernholt, L.; Rømming, C. *Acta Chem. Scand.* **1978**, *32A*, 271–273.
(11) Diehl, P.; Bjorholm, T.; Bösiger, H. *J. Magn. Reson.* **1981**, *42*, 390–395.
(12) Blackman, G. L.; Brown, R. D.; Burden, F. R. *J. Mol. Spectrosc.* **1970**, *35*, 444–454.

In using ED87, one defines a minimal set of structural parameters which completely defines the structure of the molecule. Pyrazine was assumed to be planar with D_{2h} symmetry and allowed to lie on the xz plane with its nitrogen atoms lying on the z axis of the molecular frame. Its structure was described by three bond distances (rCH, rCN, rCC) and two bond angles ($\angle$CNC, $\angle$CCH). The assigned atom numbers with the definition of the molecular frame are given in Figure 1. Pyrimidine was assumed to be planar with C_{2v} symmetry and allowed to lie on the xz plane with the z axis of the molecular frame being the C_2 symmetry axis. Its structure was described by six bond distances (rC(5)H(9), rC(4)H(8), rC(2)H(7), rCC, rC(4)N, and rC(2)N) and three bond angles ($\angle$CCC, $\angle$CCN, and $\angle$C(5)C(4)H(8)). To reduce the number of correlated parameters, the two CN bond distances were not optimized as separate parameters, but as linear combinations. One refinement parameter was chosen to describe the mean of the two CN bond distances, while another described their difference. The assigned atom numbers with the definition of the molecular frame are given in Figure 1.

Using these structural parameters, the Cartesian coordinates of each atom in the molecule can be calculated, and these coordinates are used in the generation of the theoretical electron scattering intensity curves, direct dipolar couplings, and rotation constants. The structural parameters are refined to optimize the fit of the theoretical data to the vibrationally corrected experimental data.

The theoretical electron scattering intensity curves and rotation constants were calculated by standard methods.[13] In all refinements involving ED data amplitudes of vibration must be included as parameters. To reduce the number of parameters, vibrational amplitudes were refined in groups with the ratios between values of members of groups fixed at spectroscopic values.

The direct dipolar coupling D_{ij} between nuclei i and j was calculated by the formula:

$$D_{ij} = -\gamma_i\gamma_j h(4\pi^2 r_{ij}^3)^{-1}(S_{zz}\cos^2\theta^z_{ij} + S_{yy}\cos^2\theta^y_{ij} + S_{xx}\cos^2\theta^x_{ij} + 2S_{xz}\cos\theta^x_{ij}\cos\theta^z_{ij} + 2S_{yz}\cos\theta^y_{ij}\cos\theta^z_{ij} + 2S_{xy}\cos\theta^x_{ij}\cos\theta^y_{ij})$$

where $\cos\theta^z_{ij}$ is the direction cosine for the vector joining nuclei i and j with respect to the z axis of the molecular frame. The term γ_i is the magnetogyric ratio for nucleus i, while r_{ij} is the distance between nuclei i and j. The terms S_{zz}, S_{xx}, S_{xy}, S_{xz}, and S_{yz} are the orientation parameters which must be included as additional refinement parameters in the LCNMR data analysis. Since the orientation tensor is traceless, the parameter S_{yy} depends upon S_{zz} and S_{xx} as:

$$S_{yy} = -(S_{zz} + S_{xx})$$

so at most there are only five independent orientation parameters. By choosing the z axis of the molecular frame to be along the highest symmetry axis of the molecule or along the intersection of two of its symmetry planes, the number of independent orientation parameters can be further reduced depending on the symmetry of the molecule. For the case of pyrazine and pyrimidine, only the parameters S_{zz} and S_{xx} need be refined, since S_{xy}, S_{xz}, and S_{yz} are identically 0. It should be noted that the r^{-3} spacial dependence and the orientational dependence are indicative of direct dipole–dipole interactions.

The weights given to the experimental data during the least-squares refinement are important. For the ED data, an off-diagonal weight matrix is used, with elements defined as:

$$\begin{aligned}
w_{ii} &= (s_i - s_{min})/(sw_1 - s_{min}) && s_{min} \le s_i \le sw_1\\
w_{ii} &= 1 && sw_1 \le s_i \le sw_2\\
w_{ii} &= (s_{max} - s_i)/(s_{max} - sw_2) && sw_2 \le s_i \le s_{max}\\
w_{ij} &= 0 && i \ne j \pm 1\\
w_{ij} &= -0.5(w_{ii} + w_{jj})q_k && i = j \pm 1
\end{aligned}$$

where sw_1 and sw_2 are weighting points for the distance k and are chosen by inspection, and q is the correlation parameter.[14] For the LCNMR and rotational data, the weight matrix is extended with diagonal terms only. These diagonal weighting terms are inversely proportional to the squared uncertainties of the observations and are scaled to the standard deviation of the fit of the ED data points.[2]

Harmonic Vibrational Force Field Treatment. Normal-mode analyses using GAMP[15] were performed to determine the amplitudes of vibration and vibrational corrections for pyrimidine and pyrazine, so that for each compound the data from the three experimemtal techniques could be combined to obtain a single r_α structure. For pyrimidine[16] and pyrazine[17] harmonic vibrational force fields which fit the observed vibrational frequencies of several isotopic species were obtained. Vibrational data concerning the out-of-plane modes were also included in the force field analyses. Details of the force fields used in this work are given in Tables S1–S4 (supplementary material).

The uncertainties in the vibration correction terms were also estimated in the harmonic analyses. A series of refinements of the force field parameters was performed with a range of initial parameter values. The elements of the force field refined to slightly different values, depending on the starting value, because the force field is underdetermined. The scatter in the final values of the correction terms from the different refinements was used as a measure of their uncertainties. These uncertainties are, of course, only estimates, but they are based on observations of how widely the terms vary when different force fields are used. All the force fields fit the experimental frequencies, and all are based on reasonable assumptions about the starting values. We believe that this approach is safer than simply saying that we do not know how large the uncertainties are and then proceeding as if they were zero. The latter approach has been widely used in dealing with LCNMR data, and we believe that the errors in the refined geometrical parameters have consequently been seriously underestimated.[11,18,19]

In ED, r_a distances are measured directly, while r_0 distances are determined from ground-state rotation constants. With the harmonic force field, the r_a structure was converted to the r_α^0 structure according to the expression:

$$r_\alpha^0 = r_a + u_T^2/r_a - 3a(u_T^2 - u_0^2)/2 - K_T$$

where T and 0 signify the temperature during the experiment and absolute zero, respectively. The terms u and a are the amplitude of vibration and the Morse anharmonicity parameter, while K is the perpendicular amplitude correction coefficient. The r_α^0 structure is the limit of the r_α structure as the temperature approaches absolute zero. Also with the harmonic force field, the rotation constants B_0 were converted to B_z. The corrected rotation constants B_z were used as the experimental data in the refinement of the molecular structure, since they can be used to determine r_α^0 ($=r_z$) structures.

The harmonic vibrational corrections d^h, for the direct dipolar couplings, were calculated by the method of Sykora, Vogt, Bösiger, and Diehl with the program VIBR.[5] The experimentally observed direct dipolar couplings D^{exptl} were converted to the vibrationally corrected direct dipolar couplings D^α according to the expression:

$$D^\alpha = D^{exptl} - d^h$$

The D^α couplings were used as the experimental data in the structural refinement. The corrected couplings D^α give information about the r^α structure but not the r_α^0 structure, as no allowance has been made for the temperature dependence of the anharmonic

(13) Robiette, A. G. In ref 4, pp 160–197.

(14) Murata, Y.; Morino, Y. *Acta Crystallogr.* **1966**, *20*, 605–609.
(15) Cradock, S.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1981**, 187–190.
(16) Chappell, P. J.; Ross, I. G.; *J. Mol. Spectrosc.* **1977**, *66*, 192–205. Fereydeon Milani-nejad; Stidham, H. D. *Spectrochim. Acta, Part A* **1975**, *31*, 1433–1453.
(17) Scrocco, M.; diLauro, C.; Califano, S. *Spectrochim. Acta* **1965**, *21*, 571–577. Arenas, J. F.; Lopez-Navarrette, J. T.; Marcos, J. I.; Otero, J. C. *J. Mol. Struct.* **1986**, *142*, 295–298.
(18) Jokisaari, J.; Hiltunen, T.; Väänänen, T. *Mol. Phys.* **1984**, *51*, 779–791.
(19) Diehl, P.; Bösiger, H. *J. Mol. Struct.* **1977**, *42*, 103–108. Diehl, P.; Bösiger, H. *Org. Magn. Reson.* **1977**, *9*, 98–100.

Table II. r_α Structure of Pyrazine

parameters	results		
	ED alone	LCNMR alone	ED + LCNMR
structural			
p_1 rCH (pm)	109.6 (6)	107.9 (6)	108.31 (37)
p_2 rCN	133.68 (17)	131.6 (23)	133.76 (13)
p_3 rCC	140.0 (5)	139.68 (fixed)	139.68 (30)
p_4 ∠CNC (deg)	115.72 (24)	118.7 (33)	115.65 (24)
p_5 ∠CCH	117 (7)	119.94 (9)	119.96 (8)
orientational			
p_6 S_{zz}		0.0933 (10)	0.0938 (5)
p_7 S_{xx}		0.01322 (15)	0.01329 (7)
R_G	0.0676		0.0706

Table III. Interatomic Distances (r_a) and Amplitudes of Vibration for Pyrazine

i	atoms	distance (pm)	amplitude u_i (pm)
1	C(3)–H(8)	109.9 (4)	7.9 (7)
2	C(2)–C(3)	139.7 (3)	4.8 (2)
3	C(3)–N(4)	133.8 (1)	4.8 (tied to u_2)
4	H(7)···H(8)	248.6 (5)	16.3 (fixed)
5	H(8)···H(9)	414.8 (7)	13.3 (fixed)
6	H(8)···H(10)	483.0 (8)	11.8 (fixed)
7	C(3)···C(5)	226.3 (2)	7.0 (6)
8	C(3)···C(6)	265.9 (3)	6.5 (5)
9	N(1)···N(4)	282.0 (4)	6.9 (8)
10	N(1)···C(3)	239.3 (2)	6.9 (3)
11	N(1)···H(8)	336.5 (4)	13.4 (10)
12	N(4)···H(8)	208.2 (3)	11.8 (9)
13	C(2)···H(8)	215.7 (4)	11.9 (tied to u_{12})
14	C(6)···H(8)	374.6 (5)	9.8 (14)
15	C(5)···H(8)	325.0 (5)	13.6 (tied to u_{11})

potential terms on the couplings. Fortunately, at 300 K the differences between the r_α and r_α^0 distances (ca. 0.01 pm) are an order of magnitude smaller than the final structural uncertainties.[20]

Results and Discussion

Pyrazine. Pyrazine is a highly symmetrical molecule and so provides a simple illustration of the complementary nature of the ED and LCNMR techniques. The r_α structural parameters determined from the ED data alone are listed in Table II. In this case, the positions of the H atoms are not well determined, and this is particularly obvious from the large standard deviation for the CCH angle. The positions of the heavy atoms (C, N) are better determined; however, one expects correlation between the parameters rCN and rCC, since these distances are similar in magnitude. This correlation contributes to their uncertainties.

Since LCNMR data give no information on the absolute size of the molecule, one distance parameter must be fixed. In the case of pyrazine, the CC bonded distance was fixed at 139.84 pm. The remaining r_α structural parameters refined to the values listed in Table II. Using only LCNMR data, the positions of the H atoms are well determined which is obvious from the high precision of the ∠CCH and rCH parameters. The positions of the heavy atoms are less well defined. The positions of the N atoms are poorly determined since there is only one LCNMR datum which contains information on the position of the ^{15}N nuclei; furthermore, this datum is the sum of two direct dipolar couplings: $D_{1,7}$ and $D_{1,8}$. From these results it is apparent that structural parameters which are best determined in this refinement are those which are poorly determined in the ED-only refinement, and vice versa.

The refined r_α structural parameters as determined in a joint analysis of both ED and LCNMR data are also given in Table II. Now the positions of all atoms are well determined, and the use of LCNMR data has reduced the correlation between the rCN and rCC parameters, which now have lower uncertainties. All the interatomic distances and amplitudes of vibration determined in this final refinement are given in Table III. The molecular

(20) Diehl, P.; Niederberger, W. *J. Magn. Reson.* **1973**, *9*, 495–502.

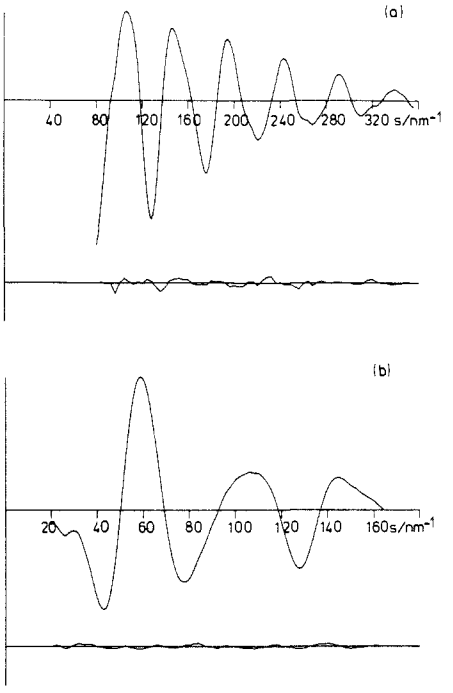

Figure 2. Observed and final weighted difference molecular scattering intensities for pyrazine at nozzle-to-plate distances of (a) 95.13 mm and (b) 258.10 mm.

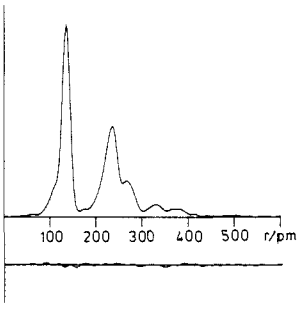

Figure 3. Observed and final difference radial distribution curves, $P(r)/r$, for pyrazine. Before Fourier inversion the data were multiplied by $s \exp(-0.00002s^2)/(Z_C - f_C)(Z_N - f_N)$.

Table IV. Least-Squares Correlation Matrix[a] for Pyrazine

	structure				amplitudes		
	p_1	p_2	p_3	p_6	u_2	u_7	u_8
p_3		−77					
p_4		−58	68		−50		
p_5		69	−73				
p_6	85						
p_7	90			81			
u_2		54	−61				
u_9							65
u_{10}						69	
k_2					66		

[a] All elements are scaled by a factor of 100, and only off-diagonal elements with absolute values >50% are included.

Table V. Direct Dipolar Coupling Data for Pyrazine

	obsd[11] D^{expt}	vibrationally corrected D^α	calcd from joint structure D^α
$D_{7,8}$ (Hz)	−712.99 (5)	−740.0 (10)	−739.7
$D_{8,10}$	−36.73 (5)	−36.84 (5)	−36.88
$D_{8,9}$	−21.83 (5)	−22.46 (5)	−22.46
$D_{2,8}$	−231.26 (12)	−237.6 (4)	−237.5
$D_{2,7}$	−731.65 (12)	−800.0 (50)	−792.9
$D_{1,8} + D_{1,7}$	37.81 (19)	39.20 (20)	39.02
$D_{2,10} + D_{2,9}$	−33.47 (15)	−33.82 (20)	−33.74

Table VI. r_α Structure of Pyrimidine

parameters	results: ED alone	LCNMR alone	ED + LCNMR + MW
structural			
p_1 rC(5)H(9) (pm)	108.8 (4)	107.7 (9)	108.7 (3)
p_2 rC(4)H(8)	108.8 (=p_1)	107.6 (7)	107.9 (2)
p_3 rC(2)H(7)	108.8 (=p_1)	106.9 (9)	108.2 (4)
p_4 rCC	138.9 (9)	139.33 (fixed)	139.3 (4)
p_5 mean rCN	134.0 (4)	133 (6)	133.9 (2)
p_6 rC(4)N(3) − rC(2)N(3)	−3.0 (16)	−2.8 (51)	2.2 (7)
p_7 ∠CCC (deg)	117.5 (3)	118.3 (4)	117.8 (2)
p_8 ∠C(5)C(4)H(8)	116 (10)	121.1 (5)	120.9 (3)
p_9 ∠CCN	122.4 (4)	121 (5)	121.2 (3)
rC(4)N(3)	132 (2)	132 (8)	135.0 (7)
rC(2)N(3)	135 (2)	135 (8)	132.8 (7)
orientational			
p_{10} S_{zz}		0.0256 (6)	0.0263 (2)
p_{11} S_{xx}		0.0529 (8)	0.0530 (3)
R_G	0.0445		0.0525

Table VII. Interatomic Distances (r_a) and Amplitudes of Vibration for Pyrimidine

i	atoms	distances (pm)	amplitudes u_i (pm)
1	C(5)–H(9)	109.8 (3)	7.8 (5)
2	C(4)–C(5)	139.4 (4)	4.8 (2)
3	C(4)–H(8)	109.6 (2)	7.8 (tied to u_1)
4	N(3)–C(4)	135.1 (3)	5.0 (tied to u_2)
5	C(2)–N(3)	132.9 (4)	5.0 (tied to u_2)
6	C(2)–H(7)	109.7 (4)	7.8 (tied to u_1)
7	C(4)···H(9)	216.8 (4)	11.6 (7)
8	H(8)···H(9)	251.7 (3)	15.7 (fixed)
9	N(3)···H(9)	337.5 (3)	12.8 (tied to u_{19})
10	C(2)···H(9)	374.2 (4)	8.6 (tied to u_{27})
11	H(7)···H(9)	482.7 (7)	11.4 (fixed)
12	C(6)···H(8)	337.9 (6)	12.8 (tied to u_{19})
13	H(8)···H(10)	429.8 (8)	13.0 (fixed)
14	N(3)···H(8)	209.2 (5)	12.1 (tied to u_7)
15	C(2)···H(8)	325.0 (3)	13.4 (tied to u_{19})
16	H(7)···H(8)	412.8 (4)	13.4 (fixed)
17	C(5)···H(8)	216.2 (4)	11.8 (tied to u_7)
18	N(3)···H(7)	205.2 (7)	12.1 (tied to u_7)
19	C(4)···H(7)	324.3 (4)	13.1 (9)
20	C(5)···H(7)	373.9 (5)	8.6 (tied to u_{27})
21	N(3)···C(5)	238.8 (2)	7.4 (tied to u_{26})
22	C(2)···C(5)	265.2 (3)	5.5 (3)
23	C(4)···C(6)	238.5 (6)	7.0 (tied to u_{26})
24	N(1)···C(4)	274.1 (2)	6.3 (tied to u_{22})
25	C(2)···C(4)	226.9 (3)	7.7 (tied to u_{26})
26	N(1)···N(3)	238.7 (5)	6.6 (2)
27	N(3)···H(10)	382.5 (2)	8.9 (11)

scattering intensity curves are shown in Figure 2 and the radial distribution curves in Figure 3. The final least-squares correlation matrix is given in Table IV. In Table V, the observed direct dipolar couplings,[11] our vibrationally corrected couplings with estimated errors and the calculated couplings from the joint structural analysis are presented.

Pyrimidine. The pyrimidine molecule has lower symmetry than pyrazine and is thus more complex and interesting to analyze. The model for pyrimidine involves six bond distances and three bond angles. There are now two different CN bond distances of similar length. To reduce the number of correlated parameters in the model, the mean and difference of the two CN distances were used as the refinement parameters, even though the individual lengths and uncertainties of the two CN bonds are reported and used in the discussion. Also, because of lower symmetry, there are now three different CH bond distances, which cannot be distinguished in the ED analysis.

The r_α structural parameters as obtained by analysis of the ED data alone are listed in Table VI. Not only is it impossible to refine the three CH bond distances separately, but the angle

Table VIII. Least-Squares Correlation Matrix[a] for Pyrimidine

	structure: p_3	p_5	p_8	p_9	p_{10}	p_{11}	amplitudes: u_2	u_{22}
p_1	69				−55	90		
p_2			58		84			
p_3						77		
p_4		−99	−63	−66			−81	
p_5			62	65			79	
p_6				−76			−63	−55
p_7			52	−52				
p_9							67	
p_{10}						−62		

[a] All elements are scaled by a factor of 100, and only off-diagonal elements with absolute values >50% are included.

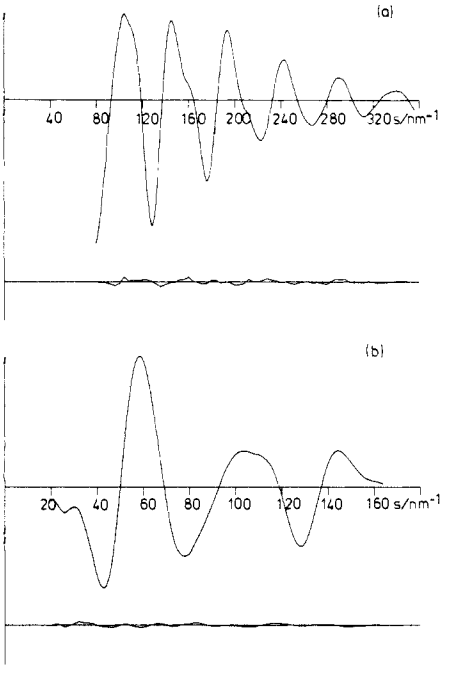

Figure 4. Observed and final weighted difference molecular scattering intensities for pyrimidine at nozzle-to-plate distances of (a) 95.60 mm and (b) 258.48 mm.

∠C(5)C(4)H(8) is also poorly determined. The CC and CN bond distances also have large uncertainties, owing to correlation between them. The mean value of the CN bond distances is 134.0 (4) pm, while their difference is −3.0 (16) pm. Fortunately, the heavy atom bond angles are well determined.

In the LCNMR-alone analysis of pyrimidine, the CC bond distance was fixed at 139.33 pm, and the parameters listed in Table VI were obtained. Now the three CH bond distances can be optimized separately; however, their uncertainties are larger than expected. These uncertainties can be traced to the large absolute errors in the vibrational corrections to the CH bonded direct dipolar couplings. This situation shows the importance of a good vibrational force field in a structural analysis and the need to estimate errors in the vibrational corrections to the couplings. The two CN bond distances and the CCN angle are poorly determined. The positions of the N atoms are not well known from the LCNMR data since the direct dipolar couplings $D_{1,7}$, $D_{1,8}$, $D_{1,9}$, and $D_{1,10}$, which involve ^{15}N nuclei, have much larger relative errors than the other couplings. The CCC and C(5)C(4)H(8) angles are fairly well determined.

In the case of pyrimidine, microwave rotational data[12] were available to us. In our last analysis of pyridimine, we combined the data from ED and LCNMR with three vibrationally corrected rotation constants. The r_α structural parameters as determined from the joint analysis are also given in Table VI. The interatomic distances and amplitudes of vibration are listed in Table VII, and the least-squares correlation matrix is given in Table VIII. The molecular scattering intensity curves are shown in Figure 4 and

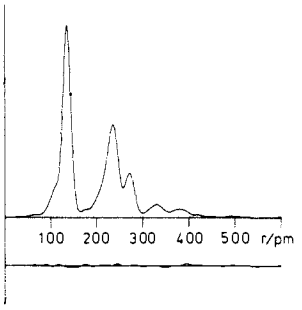

Figure 5. Observed and final radial distribution curves, $P(r)/r$, for pyrimidine. Before Fourier inversion the data were multiplied by $s \exp(-0.00002s^2)/(Z_C - f_C)(Z_N - f_N)$.

Table IX. Direct Dipolar Coupling Data for Pyrimidine

	obsd[11] D^{expt}	vibrationally corrected D^α	calcd from joint structure D^α
$D_{7,8}$ (Hz)	−56.74 (7)	−57.46 (8)	−57.46
$D_{7,9}$	−27.88 (11)	−28.02 (11)	−28.18
$D_{2,7}$	−573.09 (110)	−632.00 (410)	−626.59
$D_{3,7}$	47.58 (78)	48.64 (78)	50.08
$D_{4,7}$	−27.32 (78)	−27.59 (78)	−26.51
$D_{5,7}$	−15.07 (70)	−15.17 (70)	−15.24
$D_{8,9}$	−339.71 (5)	−350.00 (100)	−348.33
$D_{8,10}$	−79.50 (13)	−80.26 (13)	−80.54
$D_{2,8}$	−34.97 (65)	−35.33 (65)	−33.45
$D_{3,8}$	42.83 (104)	44.17 (110)	42.74
$D_{4,8}$	−1031.42 (43)	−1136.00 (300)	−1133.30
$D_{5,8}$	−155.00 (45)	−159.50 (46)	−158.82
$D_{2,9}$	−15.00 (54)	−15.11 (54)	−15.19
$D_{3,9}$	9.42 (59)	9.50 (59)	9.38
$D_{4,9}$	−100.43 (59)	−103.00 (66)	−102.37
$D_{5,9}$	−561.86 (73)	−618.00 (210)	−618.69
$D_{3,10}$	10.07 (105)	10.13 (105)	10.19
$D_{4,10}$	−39.84 (54)	−40.22 (54)	−41.10

the radial distribution curves in Figure 5.

Now all of the structural parameters are well determined. The esd's of the two CN bond distances, which are large in both the ED-alone and LCNMR-alone analyses, are much smaller in the joint analysis. We attribute this improvement to the inclusion of the three rotation constants. The precisions of the CH bond distances have increased as compared to the results of the LCNMR-alone analysis. It is apparent that the ED and rotational data have contributed some additional information on the positions of the H atoms, and have helped in extracting more information from the LCNMR data by aiding in the determination of the orientation parameters. In Table IX, the observed direct dipolar couplings,[11] our vibrationally corrected couplings with estimated errors and the calculated couplings from the joint structural analysis are presented. The observed rotation constants,[12] our vibrationally corrected data with estimated errors and the calculated rotation constants from the joint analysis are presented in Table X.

Finally, it should be noted that the discrepancies between our LCNMR-alone results and the results of Diehl, and Bjorholm, and Bösiger,[11] which are based on the same data, stem from the use of different force fields, and the allowance for errors in the vibrational corrections. At the time of the earlier work, there was little information on the out-of-plane modes of pyrazine and pyrimidine, so data for the out-of-plane modes for benzene were substituted into the vibrational analyses for the nitrogen-containing compounds. Our force fields include data from recent work on the out-of-plane modes of both,[16,17] and we were also able to estimate the errors in the vibrational corrections to the direct dipolar couplings for both molecules.

Table X. Rotation Constants for Pyrimidine

	obsd[12] B_0	vibrationally corrected B_z	calcd from joint structure B_z
A	6276.86	6275.60 (20)	6275.44
B	6067.18	6065.26 (50)	6064.17
C	3084.49	3083.83 (10)	3084.00

Conclusion

In this paper, we have demonstrated the complementary nature of information from LCNMR and information from ED. It has been clearly shown that the data from ED determine heavy atom positions, while the LCNMR data help to pinpoint the hydrogen atom positions. We have also learned from this work the importance of a good harmonic force field for a molecule under structural investigation.

The fundamental assumption behind this technique is that molecular structures in the liquid-crystal phase are comparable to structures in the gas phase. The present results suggest that this is a good assumption for rigid, small-ringed molecules, such as pyrazine and pyrimidine. The ultimate goal of this long-range project is to demonstrate the soundness of this assumption, or to pinpoint conditions under which this assumption is good.

There is much experimental evidence that molecular structure, as determined from LCNMR, tends to vary among different liquid-crystal solvents. This apparent variation has been attributed to orientational deformation. Lounila and Diehl[21] have developed a theoretical model to treat this orientational deformation and determine a solvent-independent structure. Unfortunately their model is difficult to apply to a general case and involves the refinement of many additional parameters which account for solvent–solute interactions.[22,23] Empirically, it has been discovered that the apparent structure of a solute molecule is not significantly distorted in a liquid-crystal solvent in which the direct coupling $D_{CH}(CH_4)$ of dissolved [^{13}C]methane vanishes.[18,22-24] Structures that have been measured in these mixtures tend to agree well with gas-phase structures. Lounila, Diehl, Hiltunen, and Jokisaari have argued that this observation is in agreement with their orientational deformation theory for the case of rigid molecules that contain CH bonds.[22] Fortunately, this case covers a good number of small-ringed organic compounds. It is also known that liquid crystals that orient the solute molecules to a high degree give better structural information than those which orient the solute molecules[25] poorly. Using the above information we plan to combine LCNMR couplings with ED and rotational data in order to determine better r_α structures for a range of small-ringed organic compounds.

Acknowledgment. One of us (P.B.L.) is being supported by the North Atlantic Treaty Organization under a grant awarded in 1987.

Supplementary Material Available: Tables of symmetry coordinates and force fields for pyrazine and pyrimidine (Tables S1–S4) (5 pages). Ordering information is given on any current masthead page.

(21) Lounila, J.; Diehl, P. *J. Magn. Reson.* **1984**, *56*, 254–261. Lounila, J.; Diehl, P. *Mol. Phys.* **1984**, *52*, 827–845.
(22) Lounila, J.; Diehl, P.; Hiltunen, Y.; Jokisaari, J. *J. Magn. Reson.* **1985**, *61*, 272–283.
(23) Kellerhals, M.; Diehl, P.; Lounila, J.; Wasser, R. *J. Mol. Struct.* **1987**, *156*, 255–260.
(24) Jokisaari, J.; Hiltunen, Y. *Mol. Phys.* **1983**, *50*, 1013–1023.
(25) Dombi, G.; Diehl, P.; Lounila, J.; Wasser, R. *Org. Magn. Reson.* **1984**, *22*, 573–575.