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Hydrogen Bonding in Pure and Aqueous Formamide

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Abstract: An extension of a recent study on the structure of liquid and aqueous formamide has been made using ab initio SCF computations and approximate calculations of proton shifts. The results, compared with the available ESCA, NMR, and dielectric constant data, seem to indicate that the dominant unit in the structure of liquid formamide is one that contains a cyclic dimer and linear chain held together by hydrogen bonds. Further evidence is presented for the structure of hydrated formamide consistent with the original model of four water molecules in the primary hydration sphere.

In a recent paper,^{2a} tentative models for the structure of liquid and aqueous formamide have been proposed on the basis of ab initio SCF computations on various polymers and polyhydrates. Further computations and reexamination of all the results in connection with the available experimental NMR, ESCA, and dielectric evidence lead to a partially modified description of these systems.

Computational Details

The supplementary SCF computations have been performed as in ref 2a using an STO-3G basis set but modified version^{2b} of the original QCPE program.³

For the computation of the variations of the chemical shifts we have used a procedure described earlier.^{4,5} In these calculations the variation of the chemical shift of a proton of a molecule A due to the interaction with a molecule B is ap-

proximated by a sum of two terms: the local magnetic anisotropy contribution and the polarization effect.⁶ For the first term we calculate the magnetic field created at the studied proton of A by the magnetic susceptibility tensors of all the atoms of molecule B through the dipolar approximation.⁷⁻⁹ (Another procedure developed by Barfield et al.¹⁰ cannot be used here since the experimental values of the principal components of the shielding tensors are not available, to our knowledge, for nitrogen and oxygen atoms of amides.)

For a proton P of molecule A the magnetic term is given by

$$\sum_Q \Delta\delta_{Q(B)}^P(A) \quad (1)$$

with the summation running over all the atoms of molecule B.

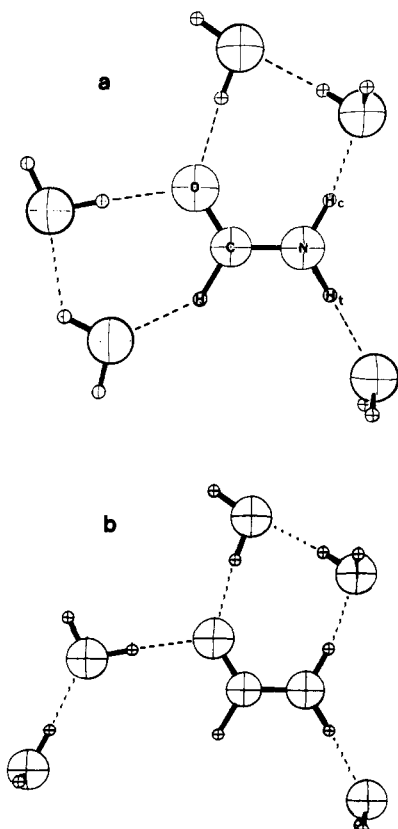


Figure 1. (a) Calcomp drawing of the pentahydrate F-5W; (b) Calcomp drawing of the pentahydrate F-4W-W. (Optimization of the fifth water molecule was achieved by keeping the geometry of the remaining four water molecules fixed.)

Each term of this sum is of the form

$$\Delta\delta_{Q(B)}^{P(A)} = -\frac{1}{3} N^{-1} \sum_{\alpha\beta} \chi_{\alpha\beta}^{Q(B)} (3R_{PQ\alpha}R_{PQ\beta} - R_{PQ}^2\delta_{\alpha\beta})/R_{PQ}^5 \quad (2)$$

R_{PQ} is the interatomic distance and $R_{PQ\alpha}$, $R_{PQ\beta}$ its α and β components, respectively. $\chi_{\alpha\beta}$ is the $\alpha\beta$ element of the magnetic susceptibility tensor of atom Q of molecule B. N is Avogadro's number. $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, zero otherwise. The calculation of the $\chi_{\alpha\beta}^Q$ is made according to the classical approximations given by Pople in 1962¹¹ and which can be written

$$\chi_{\alpha\beta}^Q = \frac{Ne^2}{4mc^2} \frac{1.5}{\zeta_Q^2} P_{\alpha Q\beta Q} + \frac{Ne^2\hbar^2}{4m^2c^2} \times \sum_R (-P_{\beta Q\gamma R} P_{\gamma Q\alpha R} + P_{\gamma Q\gamma R} P_{\alpha Q\beta R} - P_{\beta Q\alpha R} (2\delta_{QR} - P_{\gamma Q\gamma R}) - P_{\gamma Q\alpha R} P_{\alpha Q\gamma R}) \quad (3)$$

for the off-diagonal elements and

$$\chi_{\alpha\alpha}^Q = -\frac{Ne^2}{4mc^2} \frac{1}{\zeta_Q^2} (3P_{\alpha Q\alpha Q} + 6(P_{\beta Q\beta Q} + P_{\gamma Q\gamma Q})) + \frac{Ne^2\hbar^2}{4m^2c^2} \sum_R (P_{\gamma Q\gamma R} (2\delta_{QR} - P_{\beta Q\beta R}) + P_{\beta Q\beta R} (2\delta_{QR} - P_{\gamma Q\gamma R}) + 2P_{\beta Q\gamma R} P_{\gamma Q\beta R}) \quad (4)$$

for the diagonal ones. $P_{\alpha Q\beta R}$ is the density matrix element between orbital p_α of atom Q and p_β of atom R of molecule B.¹²

The polarization term takes into account the variation of the electronic population of the hydrogen atom of molecule A under investigation due to the electric field created by the

Table I. Binding Energy (with Respect to Four Monomers), Energy per Hydrogen Bond, and Dipole Moment of Formamide Tetramers^a

Tetramer	ΔE , kcal/mol	$\Delta E/n$, kcal/mol	μ , D
Linear	30	10.00	8.9
1-Trans	34.75	8.7	0.0
1-Cis	37.5	9.4	9.2
2-Cyclic	47.1	9.4	1.5

^a Notations as in ref 2a.

electronic and nuclear charges of molecule B¹³⁻¹⁵ through the formula

$$\Delta\delta = -2.9 \times 10^{-12} E_z - 7.4 \times 10^{-19} E^2 \quad (5)$$

where E_z is the component of the electric field E along the CH or NH bond carrying the proton studied. For the calculation of E the electronic distribution of molecule B is represented by a set of monopoles located at the nuclei.

The elements of the density matrix required for the computation of the local anisotropy term (eq 1) and the monopoles required for the polarization term (eq 5) are approximated in the practical computation by combining a Pariser-Parr-Pople wave function for the π system, with a σ distribution obtained by Del Re's procedure.¹⁶ (The parameters can be found in ref 6-18.) At first sight one might want to utilize rather the ab initio results of the SCF computations. However, the approximations developed by Pople¹¹ for the calculation of the diamagnetic susceptibility tensors, and which are utilized here, are not consistent with nonempirical computations. On the other hand, we have tested that the values obtained for the polarization effect by the semiempirical procedure, in the cases considered, are in agreement with the direct evaluation of the variation of the electronic population from the SCF computations. We are well aware that this type of computation of the variation of chemical shifts is very approximate but, at the moment, exact computations of the proton shifts by an elaborate method¹⁹⁻²¹ which satisfies the gauge invariance of the results²¹ are not yet practicable for a system of the size of a tetramer of formamide. Since calculations of the type utilized here have proven to give qualitatively reliable results for intermolecular cases^{4,13,22} we felt encouraged to use them again.

Results and Discussion

Concerning hydrated formamide, complementary arguments can be given to substantiate the proposal that the first hydration shell is composed only of four water molecules. The binding of a fifth water molecule to the CH group of formamide in the tetrahydrate to make the pentahydrate (F-5W) of Figure 1a was found to bring about an increment of binding energy of only 4.1 kcal/mol. This is appreciably less than the water-water binding energy of 6 kcal/mol in the most stable water dimer computed with the same basis set. Thus, the probability that a water molecule will detach itself from the bulk water structure to bind directly to the CH group is very small.²³ Indeed, an explicit computation of a pentahydrate of formamide (Figure 1b) where the fifth water molecule is bound to one of the water molecules of the first hydration layer (F-4W-W) yields an increment in binding energy with respect to the tetrahydrate of 8.5 kcal/mol, indicating a preference of 4.4 kcal/mol with respect to the pentahydrate (F-5W) where all five water molecules are in the first shell.

For pure formamide, we found that the interaction energies of the two tetramers involving a cyclic dimer have been erroneously given with respect to an inappropriate reference, so that the values are not comparable to that of the corresponding linear tetramer presented in the same table of ref 2a. In addi-

Table II. Computed Proton Chemical Shift Variations (ppm) for the Various Models^a

Model	$\Delta\delta_{\text{CH}}$	$\Delta\delta_{\text{NH}_c}$	$\Delta\delta_{\text{NH}_t}$
Linear trimer ^b /F-5W	+0.01 -1.51 -1.52	+0.05 -1.46 -1.51	-2.05 -1.78 +0.27
/F-4W-W	+0.01 -0.07 -0.08	+0.05 -1.55 -1.60	-2.05 -1.83 +0.22
/F-4W	+0.01 -0.06 -0.07	+0.05 -1.55 -1.60	-2.05 -1.82 +0.23
/F-3W	+0.01 -0.14 -0.15	+0.05 -0.10 -0.05	-2.05 -2.00 +0.05
1-Cis tetramer/F-4W	-0.08 -0.06 +0.02	-2.22 -1.55 +0.67	-1.98 -1.82 +0.16
1-Trans tetramer/F-4W	-0.08 -0.06 +0.02	-3.39 -1.55 +1.84	-2.38 -1.82 +0.16
2-Cyclic tetramer/F-4W	+0.01 -0.06 -0.07	-2.89 -1.55 +1.34	-1.98 -1.82 +0.16

^a Positive value: upfield shift. The values are in the order polymerization/hydration/dilution. ^b The trimer was chosen for simplification. The addition of the fourth or fifth formamide to the linear trimer produces only minor numerical differences in the calculated variations.

Table III. Level Splittings (au) with Respect to Isolated Formamide (STO-3G)

Level	Cyclic dimer	(F _t) ₄	1-Trans	1-Cis	2-Cyclic
8 σ	0.067	0.104	0.102	0.070	0.100
9 σ	0.031	0.115	0.084	0.081	0.073

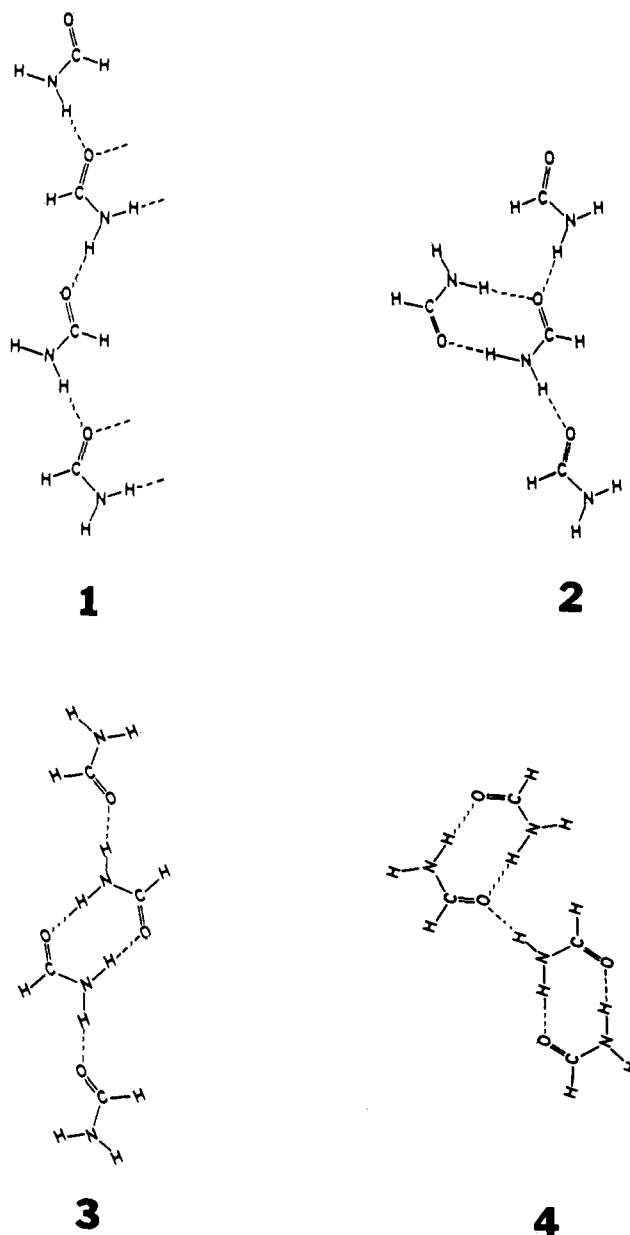
tion, the tetramer made of two hydrogen-bonded cyclic dimers was not considered. The appropriate values of the four tetramers, linear, 1-cis, 1-trans, and 2-cyclic (Figure 2), are given in Table I. They indicate that the tetramers containing the cyclic dimer(s) represent the intrinsically most stable structures if the total binding energy is considered. Interestingly, the energy per H bond is the largest in the linear structure.

Further indications concerning the structure of both the liquid and aqueous formamide may be obtained from the directions of the ¹H NMR chemical shifts observed²⁴ upon dilution of liquid formamide with water, where an *upfield* shift is characteristic of all protons, in the order NH_c > CH > NH_t (t is here trans to the carbonyl).

We have performed an explicit computation of these shifts using the procedure described above. The variation, upon dilution, of the proton chemical shift ($\Delta\delta$) is obtained as the difference between the variation (with respect to isolated formamide) of the proton shifts of the central formamide molecule in the model chosen for the liquid and the variation of the shift of the same protons in the model of the hydrate. The values obtained using the different models are given in Table II.

Examination of these values indicates that (a) the upfield shift of the CH proton can be obtained only if the CH group is not involved in direct binding to water; (b) an upfield shift of the NH trans proton is obtained in all cases; but (c) an upfield shift of the cis NH proton can be obtained only when NH_c is involved in a hydrogen bond with another formamide molecule in the model of the liquid. This situation is realized in the models of liquid formamide containing the cyclic dimer but only the 1-cis and 1-trans structures indicate that an upfield shift will be observed for the CH proton upon dilution by water.

Another indication of the structure of the liquid may be obtained by comparing theoretical results with ESCA data: the splittings of the valence levels of formamide in going from the vapor to the liquid have been assigned by comparison of the ESCA spectra of the two species.²⁵ The most striking perturbation was observed for the 8 σ and 9 σ levels of formamide with a definitely larger splitting for the 9 σ level. On the basis that the corresponding values obtained in theoretical computations^{25,26} on the linear and cyclic dimers of formamide yield the order 9 σ > 8 σ and 8 σ > 9 σ , respectively, the authors concluded that linear rather than cyclic dimers are more likely to represent the dominant unit in the structure of the liquid. We have calculated the values of these splittings in our four tetramers. They are reported in Table III with the corresponding

**Figure 2.** The four tetramers considered. (1) Linear, (2) 1-cis, (3) 1-trans, (4) 2-cyclic.

ones for the cyclic dimer. The values calculated for the cyclic dimer with the STO-3G basis set show indeed an ordering opposite to that observed experimentally.²⁵ This is also true for the 2-cyclic and 1-trans tetramers, but the experimental order appears both in the purely linear and in the 1-cis models indicating that either one is compatible with the trends in the observed splittings.

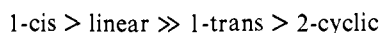
Table IV. Compatibility of the Various Model Tetramers with the Observed Properties

	Linear	1-Cis	1-Trans	2-Cyclic
NMR	-	+ ^a	+	-
ESCA	+	+	-	-
ε	+	+	-	-

^a The numerical values of the computed shifts are more favorable for the 1-cis than for the 1-trans tetramer (see Table II).

Finally, some indication on the dominant units in the liquid may perhaps be given by considering the dielectric properties: the high dielectric constant of formamide²⁷ has been considered^{2a,25} as being in favor of the dominance of linear chains because they are endowed with large dipole moments. Although such a relationship between the static dielectric constant of a liquid and the dipole moment of the dominant unit may be inferred from the Kirkwood-Onsager-Froehlich equations,²⁸ it should certainly be taken with caution particularly if different species with different dipole moments are present. In the present context, it is nevertheless interesting to compare the dipole moments of the various tetramers considered in this paper (Table I). It is seen that the 1-cis tetramer has a moment of the same order of magnitude (9 D) as the linear tetramer, whereas the value for the 2-cyclic tetramer is only 1.5 D and that for the 1-trans tetramer is zero, like that of the cyclic dimer. Thus insofar as one may invoke a dielectric constant/dipole moment relationship, the 1-cis tetramer and the linear tetramer would appear equally compatible with the dielectric data.

In order to sort out what inferences may be made on the dominance of various units in liquid formamide based on the results presented, we have summarized in Table IV, for the four tetramers considered here, their compatibilities with the NMR, ESCA, and dielectric experimental evidence. Examination of this table shows that the 1-cis tetramer is compatible with all the data whereas the 2-cyclic structure is compatible with none. One may conclude that if there were only one species present, it would have to be the cis tetramer rather than the linear chain. If (a perhaps more likely situation) different species are present, the order of their dominance as far as the tetramers are concerned would appear to be



We do not feel that a more quantitative determination of the contribution of each structural unit discussed above to the liquid can be made at present. However, our study, within the limits of its accuracy, seems to indicate that a structure based upon the 1-cis model is the dominant species.

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