

## Has Liquid Formamide a Linear-Chain Structure or Ring-Dimer Structure?

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The structure of liquid formamide is discussed on the basis of X-ray diffraction measurements and MO calculations. It is concluded that liquid formamide has both chain-like and ring-dimer moieties and that the former ones have a longer life time.

It is an open question if liquid formamide has a structure consisting of ring-dimers (which appear in the crystal) or if there are chain-like moieties. Conclusions so far derived may be classified into two groups: Most investigations using spectroscopic methods interpret the results in terms of chain structure [1–6]. On the other hand, from most diffraction studies [7–9], except ours [10], it was concluded that liquid formamide has a structure containing ring-dimers. In [10] we suggested that chain structure is combined with ring-dimers. However, in that work interactions among the formamide molecules beyond 400 pm were not well taken into consideration.

By assuming a crystal-like three-dimensional network in which ring-dimers are connected with each other through hydrogen-bonds, thus building puckered net-planes separated by about 310 pm [11], we could explain the reduced intensities obtained in our X-ray diffraction measurements [10] over the range  $s > 2 \times 10^{-2} \text{ pm}^{-1}$  (Figure 1). The radial distribution curve derived from the reduced intensities by Fourier transform could also be interpreted in terms of intra- and intermolecular interactions as quoted in [10] (C=O: 124 pm, N–C: 133 pm, N...O: 225 pm) and [11] (N...O: ~295 pm and other long-range interactions). The lengths of the hydrogen-bonds, 288 and 294 pm, were first attributed to the chain-structure and the ring-dimers,

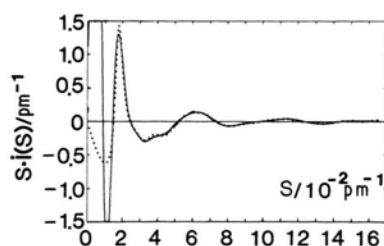


Fig. 1. The  $s \cdot i(s)$  curve of liquid formamide. The experimental and theoretical values are shown by the dotted and solid lines, respectively.

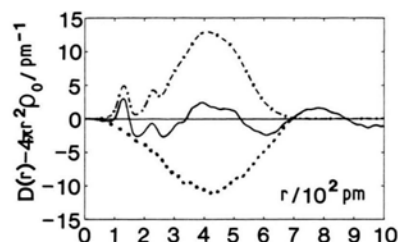


Fig. 2. Differential radial distribution curve  $D(r) - 4\pi r^2 \rho_0$ . —: Experimental; ·····: Calculated from the model shown in Fig. 3, which is based on the crystal structure; ·-·-·: Residual curve.

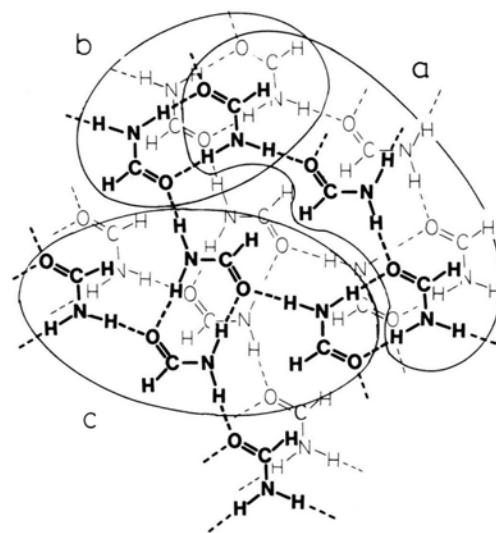


Fig. 3. The crystal-like puckered network structure of hydrogen-bonded formamide molecules. The network drawn with thin lines shows the sheet behind the thick-drawn sheet. Partial structures of formamide are indicated by lines (see text).

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respectively, which were quoted from the crystallographic data [11] in the course of the model calculations of the structure of liquid formamide, but the experimental result could be equally well analysed by taken into account only one kind of length of the hydrogen-bonds ( $\sim 295$  pm). From the results shown in Figs. 1 and 2 it is obvious that the crystal-like structure well explains the experimental data obtained by X-ray diffraction.

However, according to our *ab initio* MO calculation [10], the hydrogen-bond in the chain structure has a larger energy ( $67.8 \text{ kJ mol}^{-1}$ ; without counterpoise corrections) than in the ring-dimer structure ( $63.2 \text{ kJ mol}^{-1}$ ). This suggests that the former bond may have a longer life time than the latter. As to the

life time of the structure, we can better say that the structure of liquid formamide is chain-like. As shown in Fig. 3, formamide may have chain structure (part a) as well as ring-dimer structure (part b). The chain-and-ring structure (part c), as referred to in [10] and [12], may also be included. From the static point of view (e.g. the diffraction method), which is based on the strength of bonds between molecules, one may say that liquid formamide has a crystal-like three-dimensional structure consisting of ring-dimers. However, from the dynamic point of view (e.g. from spectroscopic methods) in which the life time of the bonds is more important in the consideration, the chain-like structure may be advocated.

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