Theoret. chim. Acta (Berl.) 22, 250—254 (1971)

A CNDO/2 Investigation on Linear Chains of Symmetrically Bonded Water Molecules

M. CIGNITTI and L. PAOLONI

Laboratories of Chemistry, Istituto Superiore di Sanità, Rome, Italy
Gruppo Chimica Teorica, Università, Palermo, Italy

Received January 18, 1971

CNDO/2 energy and electron distribution have been calculated for linear chains of 4 to 12 water molecules. The energy balance is unfavorable to their formation from free molecules. Convergence difficulties found in applying the CNDO/2 procedure to some models are discussed.

CNDO/2 Energie- und Elektronenverteilungen für lineare Ketten von 4 bis 12 Wassermolekülen wurden berechnet. Die Energiebilanz für ihre Bildung aus freien Molekülen ist ungünstig. Außerdem werden Konvergenzschwierigkeiten bei der Anwendung dieses Verfahrens diskutiert.

Calcul de l'énergie et de la distribution électronique par CNDO/2 pour des chaînes linéaires de 4 à 12 molécules d'eau. Le bilan énergétique est défavorable à leur formation à partir de molécules libres. Discussion des difficultés de convergence trouvées dans l'application du procédé CNDO/2 à certains modèles.

In a recent paper Ageno [1] has proposed a model for the so-called anomalous water [2], assuming that the molecules H_2O are associated to form closed-chain polymers made up of a continous sequence of identical units, as shown in Fig. 1. The closure of the chain without too large distortion energies requires the ring polymer to consist of about 20 molecules, or more, too many for any test of the model by a complete energy calculation.

Although recent observations [3–6] have given rise to serious doubts about the existence of anomalous water and suggested that impurities or microheterogenity in the system might explain the reported infrared and proton magnetic resonance spectra [2], water is certainly a main portion of the material condensed in the quartz capillaries, and very little is known about its structure in such a state. We therefore thought it useful to see what predictions could be made on the linear polymerization of water molecules. The scheme devised was to consider a linear chain of *n* molecules arranged as shown in Fig. 1 and to evaluate with the CNDO/2 the total energy and the charge distribution. For each value of *n* the energy was minimized as a function of the O–O distance, keeping the H–O–H angles tetrahedral and fixing the O–H bond length at the value required for symmetric hydrogen bridges.

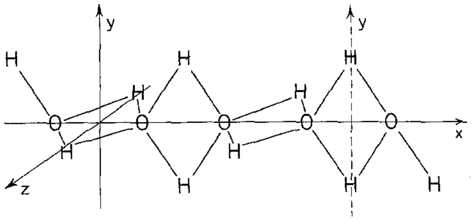

Fig. 1. Water linear chain polymer

The calculations here reported were made to investigate: (i) the dependence on n of the total energy per unit molecule in the aggregate; (ii) the energy gain for the polymer formation; and (iii) the electron distribution of the polymer unit. Our study was also intended to provide a quantitative estimate of the energy and other parameters for the model discussed by O'Konski [7] and to compare our results with those of Allen and Kollman [8] for the diborane-like tetramer, reported as the most unfavourable among several possible geometric arrangements of H_2O aggregates.

Results and Discussion

A preliminary examination was carried out for the sequence $n=4$, with the conformations shown in Fig. 2, all of which can be derived as portions of the polymer chain of Fig. 1. The O–O distance was lowered starting from 2.6 Å, but convergence was not achieved until the distance decreased below to 2 Å. The data collected in Table 1 show that the most favourable geometry apparently is that with the two terminal hydrogens on the same oxygen (Fig. 2, *c*) at an equal distance as in the O–H–O bridges. It was surprising that minor alterations of the molecular geometry, such as those in a_1 and c_1 with respect to a_2 and c_2 should produce divergence in the energy calculation.

The c_2 conformation, favoured in the linear tetramer, was assumed as the preferred one also for $n=6, 8, 10$, and 12. The data for the lowest energy c_2 conformation of each polymer are collected in Table 2, together with the energy of the monomer of the same bond length and tetrahedral H–O–H angle. The polymerization of the *deformed monomers* appears not impossible for $n \geqq 6$, and the energy gain calculated *by compounding a polymer from smaller aggregates of the same* O–O *distance*, Table 3, would indicate a formation enthalpy between 14 and 20 kcal/mole per unit H_2O.

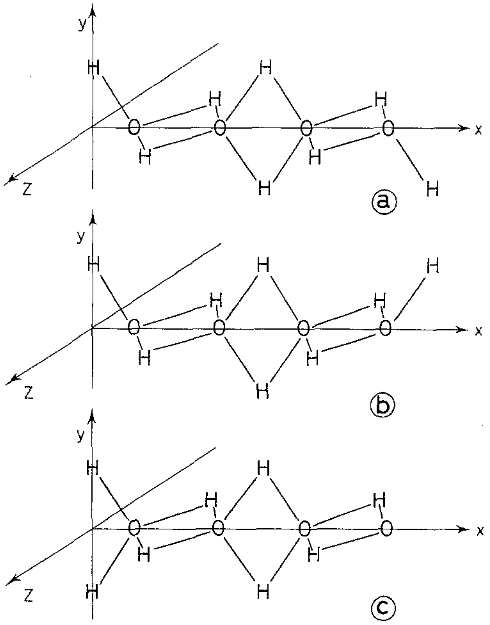

Fig. 2. Possible conformations of linear chain water polymers

Table 1. *Energy (a. u.) of linear chain tetramers*

R(O, O) Å	a_1	a_2	b_1	b_2	c_1	c_2
1.70	−78.60		−78.6005	−78.3121	−78.6871	−78.4444
1.60	−78.8229		−78.8235	−78.6237	−78.9106	−78.7668
1.50	−78.9724		−78.9736	−78.8615	−79.0642	−79.0140
1.45		−78.9323				−79.0861
1.40	−78.9820	−78.9513	−78.9816	diverg.[a]	diverg.	−79.1066
1.375		diverg.				−79.0880
1.35	−78.9079		−78.8877	−78.8877		

a_1, b_1 and c_1: bond length of terminal OH is 0.957 Å.
a_2, b_2 and c_2: bond length of terminal OH is the same as in the O–H–O bridges.
[a] The value −78.940 is obtained with 10^{-3} convergence (see discussion and Table 4).

Table 2. *Bond length, energies and charge distribution of linear polymers*[a]

n	4	6	8	10	12
R(O, O), Å	1.40	1.44	1.46	1.46	1.45
R(O, H), Å	1.213	1.246	1.264	1.264	1.256
E_{total}, a.u.	−79.1066	−118.6501	−158.1850	−197.7384	−237.3064
$(1/n)\,E_{\text{total}}$	−19.7766	− 19.7750	− 19.7731	− 19.7738	− 19.7755
E_{monomer}	−19.7936	− 19.7620	− 19.7453	− 19.7453	− 19.7537
δE	+ 0.0170	− 0.0130	− 0.0278	− 0.0285	− 0.0218
$q_o(2s)$	1.9873	1.9873	1.9896	1.9893	1.9885
$q_o(2p_x)$	0.8012	0.8299	0.8187	0.8191	0.8188
$q_o(2p_y)$	1.7096	1.6570	1.6885	1.6750	1.6855
$q_o(2p_z)$	1.6478	1.6941	1.6703	1.6850	1.6736
q_H	0.8832	0.9133	0.9089	0.9153	0.9091

[a] Orbital gross populations are those of the $(n/2)$th water molecule in the chain. The role of $2p_y$ and $2p_z$ orbitals is interchangeable due to the rotation symmetry around x.

Table 3. *Energy gain in polymerization*

Lower polymers	R(O, O), Å	n	δE, a.u.	ΔH, Kcal/mole
(4+4)	1.46	8	−0.0342	−21.4
(4+6)	1.46	10	−0.0328	−20.5
(4+4+4)	1.45	12	−0.0481	−15.0
(6+6)	1.45	12	−0.0224	−13.8

These polymerization conditions, however, are not expected to occur, neither in the gas phase condensation nor in the bulk liquid, since the monomer energy is between − 19.87 and − 19.89 a.u. (angle from 105° and 109°, and bond stretched from 0.94 to 1.03 Å), and the deformation energy required to make the supposed polymerization a favoured process is about 60 kcal/mole per unit H_2O.

The gross orbital populations of the $(n/2)$th molecule in the chain, shown in Table 2, become essentially constant when $n \geqq 8$. Molecular diagrams are given in Fig. 3. It appears from them that the 2s electrons of oxygen play the role of an inner shell lone pair, and the bond is established by the interaction of the hydrogen atoms with the p-orbital electrons. Bond order matrix elements between nearest oxygen atoms have large negative values for σ-orbitals and small positive values

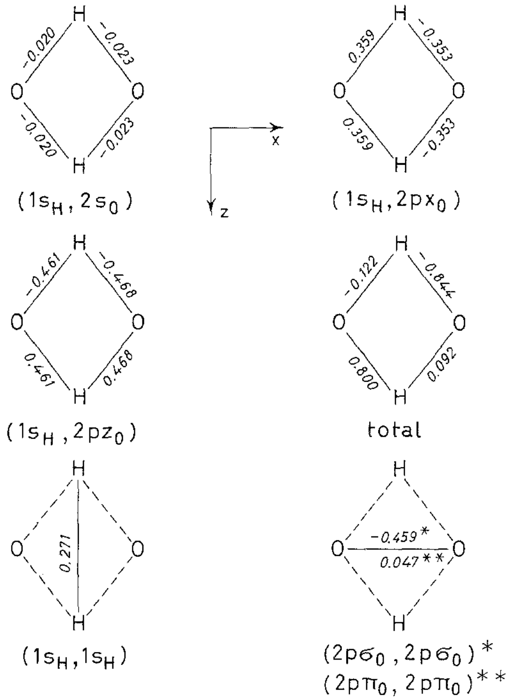

Fig. 3. Bond order matrix elements of the 5th ring in the $n=10$ water polymer chain

for π-orbitals: e.g. with $n=10$, $\langle p_{x5}; p_{x6}\rangle = -0.459$, $\langle p_{y5}; p_{y6}\rangle = +0.047$, and show the prevailing antibonding effects. The very minor role of π-bonding here found does not support the suggestion, made by O'Konski [7], of an aromatic character in the polymer chain. This chain resembles in fact a succession of deformed hydrogen molecules inserted between oxygen atoms, the whole held together by transfer of charge.

Similar conclusions hold for the diborane-like diprotonated tetramer $H_{10}O_4^{+2}$, mentioned by O'Konski [7] as the linear tetramer examined by Allen and Kollman [8][1]. The energy starts converging at 1.8 Å and the minimum (steps of 0.1 Å) was found at 1.4 Å, with $E = -79.7511$ a.u. Using the CNDO/2 values given by Allen and Kollman [8] for the isolated molecule and the process $H_2O + H^+ \rightarrow H_3O^+$, one obtains an energy loss of 380 kcal/mole.

Conclusions

Whatever the outcome of the current investigations on anomalous water [3–6], the aim of our work was to stimulate the search for structures derived from non-conventional arrangements of atoms [9] and to determine the limitations of a procedure which gives fairly reliable results for known molecules of comparable complexity.

In discussing the data collected in Table 1 we pointed out that some minor changes in the molecular geometry made it impossible to minimize the energy.

---

[1] We thank Professor Allen for pointing us out that this was an incorrect quotation of their work.

Table 4. *Energy (a.u.) of linear chain polymers*

$R(O, O)$, Å	6	8	10	12
1.43	-118.33^a			
1.44	-118.6501			-236.46^c
1.45	-118.6420	-157.85^a	-197.43^b	-237.3064
1.46	-118.6302	-158.1850	-197.7384	-237.2922
1.47	-118.6153	-158.1679	-197.7189	-237.2708

[a] Best convergence 2×10^{-2}. [b] Best convergence 6×10^{-2}. [c] Best convergence 9×10^{-2}.

(The computations were carried out on an IBM 7040 and on a Univac 1108, with the original program written by Segal, Q.C.P.E. n. 91). Divergence appears outside of a certain range of interatomic distances in a way which seems unpredictable: e.g. aggregates with $n = 10$ (geometry *a* of Fig. 2) have a 10^{-4} a.u. convergence only in the range 1.50 – 1.60 Å of the O–O distance. If the convergence condition is less restrictive, e.g. 10^{-2} a.u., then a distance O–O is found which gives the energy minimum, but the convergence is not always maintained when the 10^{-4} condition is restored. After a few convergent iterations the energy value diverges or oscillates between two slowly divergent limits. Examples are shown in Table 1 and in Table 4 (where the significant portion of the minimization process is reported for $n = 6, 8, 10$, and 12).

Difficulties of this type with the CNDO procedure seem not to have been reported before[2]. We suggest that the convergence dependence on interatomic distance should be checked when dealing with arbitrary structures, because the convergence obtained at one single geometry might be purely accidental.

Acknowledgements. This work was carried out with the support of the Consiglio Nazionale delle Ricerche, C. N. R., Rome. The cooperation of Mr. A. Verdecchia, Mr. B. Giuli and Mr. P. Corradini, of the Computing Center, Laboratories of Physics, Istituto Superiore di Sanità, is gratefully aknowledged.

References

1. Ageno, M.: Theoret. chim. Acta (Berl.) **17**, 334 (1970).
2. Lippincott, E. R., Stromberg, R. R., Grant, W. H., Cessac, G. L.: Science **164**, 1482 (1969).
3. Rousseau, D. L., Porto, S. P. S.: Science **167**, 1715 (1970).
4. Kurtin, S. L., Mead, C. A., Mueller, W. A., Kurtin, B. C., Wolf, E. D.: Science **168**, 1720 (1970).
5. Rabideau, S. W., Florin, A. E.: Science **169**, 48 (1970).
6. Everett, D. H., Haynes, E. M., McElroy, P. J.: Nature **226**, 1033 (1970).
7. O'Konski, C. T.: Science **168**, 1091 (1970).
8. Allen, L. C., Kollman, P. A.: Science **167**, 1443 (1970).
9. — Science **169**, 718 (1970).
10. Azman, A., Koller, J., Hadzi, D.: Chem. Physics Letters **5**, 157 (1970).

Prof. L. Paoloni
Gruppo Chimica Teorica
Istituto di Chimica dell' Università
Via Archirafi, 20
I-90123 Palermo, Italy

---

[2] In a recent paper on ring models of anomalous water [10] it is stated "...the O–O distance was fixed at 2.3 Å because the energy converged to minimum for this distance ...". This seems to imply that divergence is found at other distances, as reported here.