Hydrogen Bonding in $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ Determined by Electrostatic Energy Calculations

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Electrostatic Energy Calculations, Bifurcated Hydrogen Bonds

The configuration of least electrostatic energy for the hydrogen atoms in both polytypes of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ was obtained by systematic variation of the orientations of the water molecules. The internal geometry of the H_2O group was kept constant throughout the variation. The hydrogen bonds are of the bifurcated type: $\text{O}(\text{w})-\text{H}(\text{w})-\text{Cl}$.

Recently SCHRÖDER¹ proposed to discriminate between different hydrogen bonding arrangements in the two polytypes of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ ^{2,3} by calculating the electrostatic lattice energy for three different hydrogen atom positions in the Pmn2₁ structure² and for two alternative arrangements in the Pmnb structure³. Such approach can lead to false conclusions if none of the alternatives corresponds to the extreme value of the electrostatic lattice energy.

It is possible to find the position of least electrostatic energy by varying systematically the orientation of the water molecules while keeping the dimensions of the molecules themselves constant⁴. It was found that 28 hydrogen atom positions in 6 hydrates calculated in this way agreed on the average within 0.09 Å with positions determined by neutron diffraction⁴. In several cases predicted hydrogen atom positions have been subsequently

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verified by neutron diffraction and by nuclear magnetic resonance⁵.

In both polytypes the oxygen atoms of the water molecule, O(1), are located on mirror planes. The positions of the hydrogen atoms were varied by rotation of the plane of the water molecule normal to this mirror plane. The dimensions of the water molecule were assumed to be $\text{O}(\text{w})-\text{H}(\text{w})$ 0.96 Å and $\angle \text{H}(\text{w})-\text{O}(\text{w})-\text{H}(\text{w})$ 109° corresponding to the mean of these values averaged from 81 water molecules determined by neutron diffraction^{5,6}. The extreme value of the lattice energy was found in every case when the plane $\text{H}(\text{w})-\text{O}(\text{w})-\text{H}(\text{w})$ was almost parallel to the crystallographic plane (010) (Table I). These positions are about halfway between the positions named H(2) and H(3) by SCHRÖDER¹. This corresponds to a bifurcated arrangement in which each hydrogen atom is approximately equidistant from two Cl atoms at about 2.7 Å and the angles $\text{O}(\text{w})-\text{H}(\text{w})-\text{Cl}$ are very bent (129 to 138°). The atoms Mo, O(w) and both hydrogen atoms of the water molecule are in a planar arrangement.

Table I. Coordinates of hydrogen positions of least electrostatic energy in two polytypes of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Compound	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Pmn2 ₁ $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	H(w)	0.5847	0.7565	0.3386
Pmnb $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	H(w1)	0.0847	0.5669	0.6131
Pmnb $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	H(w2)	0.0847	0.3129	0.8924

Similar geometries have been found previously. In $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ^{7,8} atom H(12) forms a bifurcated bond of similar dimensions. Also in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ two of the water molecules [O(3) and O(4)] have planar arrangements of Mn, O(w) and the hydrogen atoms. This example is also instructive because the hydrogen atom positions were predicted on the basis of electrostatic calculations in 1965⁷ and confirmed by neutron diffraction by EL SAFFAR and BROWN in 1971⁸. It is expected that the hydrogen atom positions predicted here for the two polytypes of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ are within 0.1 Å of their true positions as they can be determined by neutron diffraction.

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Table II. Environments of hydrogen atoms in two polytypes of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.

a) Pmn2 ₁			
H(w)-Cl	2.602 Å	O(1)-H(w)-Cl	137.5°
H(w)-Cl'	2.738	O(1)-H(w)-Cl'	128.9
H(w)-Mo	2.964	Mo-O(1)-H(w)	125.5
b) Pmnb			
H(w1)-ClII	2.670 Å	H(w2)-ClII	2.667 Å
H(w1)-ClI	2.725	H(w2)-ClII	2.706
H(w1)-MoI	2.918	H(w2)-MoII	2.893
O(1)I-H(w1)-ClII	137.8°	O(1)II-H(w2)-ClII	136.8°
O(1)I-H(w1)-ClI	130.0	O(1)II-H(w2)-ClII	130.1
MoI-O(1)I-H(w1)	125.4	MoII-O(1)II-H(w2)	125.4

- ¹ F. A. SCHRÖDER, *Z. Naturforsch.* **32b**, 361 [1977]; in this paper the positional parameters of H2II should read 0.1, 0.65, 0.6 and not 0.1, 0.65, 0.82 (private communication from F. A. SCHRÖDER).
- ² F. A. SCHRÖDER and A. NØRLUND CHRISTENSEN, *Z. Anorg. Allg. Chem.* **392**, 107 [1972].
- ³ H. SCHULZ and F. A. SCHRÖDER, *Acta Crystallogr.* **A29**, 322 [1973].
- ⁴ W. H. BAUR, *Acta Crystallogr.* **19**, 909 [1965]; program for calculating electrostatic energies, MANIOC.
- ⁵ W. H. BAUR, *Acta Crystallogr.* **B28**, 1456 [1972].
- ⁶ The O(w)-H(w) distances assumed by Schröder range from 1.3 to 1.9 Å, the angles (Hw)-O(w)-H(w) vary from 57 to 93°. None of these values are realistic.
- ⁷ W. H. BAUR, *Inorg. Chem.* **4**, 1840 [1965].
- ⁸ Z. M. EL SAFFAR and G. M. BROWN, *Acta Crystallogr.* **B27**, 66 [1971].

Effect of Ortho Substitution on the Aminolysis of Active Esters in Aprotic Solvents

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Kinetics, Aminolysis, Active Ester,
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Kinetics of the piperidinolysis of active esters of acetic acid in acetonitrile and chlorobenzene was investigated. The rate data show intramolecular catalysis for the aminolysis of 2-nitro- and 2-cyanophenyl esters, while reactions of 2,6-disubstituted compounds are hindered by steric inhibition.

The active ester procedure of amide bond formation plays an important role in peptide syntheses. From the time of the introduction of this technique a number of leaving phenoxy groups have been examined many of them containing ortho substituent(s)¹. Though the activation observed when introducing electron-withdrawing substituents into the meta and para position of the leaving group was supported by kinetic studies², the effect of ortho substitution on the kinetics of amide bond formation has not been investigated so far.

This paper presents kinetic data on the aminolysis

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of several active esters in two aprotic solvents. For this study active esters of acetic acid were used³ because a) aminolysis of carboxylic acid esters (including aminoacyl derivatives) proceeds through a common mechanism⁴, and b) intramolecular interactions between the leaving group and the acyl portion (as it may occur when using esters of aminoacids⁵) are absent.

Under the pseudo first order conditions of excess amine all the reactions followed the general rate equation for ester aminolyses in aprotic solvents⁶:

$$-\frac{d[\text{ester}]}{dt} = (k_2[\text{amine}] + k_3[\text{amine}]^2)[\text{ester}].$$

Our second and third order rate constants together with literature pK_a values for the leaving phenoxy groups are summarized in the Table.

In accord with the early observation that aminolytic reactivity of active esters strongly depends on the basicity of their leaving group⁸, with the exception of 2,6-disubstituted compounds which exhibit negative deviations, logarithms of k_2^{AN} and k_3^{CB} values in the Table can be correlated linearly with the pK_a 's of the leaving groups (not shown). Since the extent of the lag behind the expected rates for the aminolyses of 2,6-disubstituted reactants is related to the steric requirements for the *o,o'*-substituents ($H < F < Cl < CH_3 \approx Br$), steric inhibition is that hinders the aminolysis in these cases.

The facts that k_2^{AN} and k_3^{CB} for the reaction of 2-nitro- and 2-cyanophenyl acetate fit the above correlation, while k_2^{CB} constants are considerably higher than expected (leading to slight solvent dependences for k_2 and low k_3^{CB}/k_2^{CB} ratios), clearly indicate⁷ anchimeric assistance by the *o*-nitro- and *o*-cyano functions. These results provide the first example of intramolecular participation by an *o*-cyano group in ester aminolyses, and suggest that aminolytic reactivities of 2-nitrophenyl esters of aminoacids exceeding those of the 4-nitro analogues are, at least in part, due to the intramolecular catalysis by the *o*-nitro group.