on the $^nJ_{H-H}$'s is negligible as expected.[4] The magnitudes (and signs) of $^nJ_{H-P}$ in (I) are of interest in connection with studies of effects of ring substituents on these parameters. *Ortho* substituents have been found to have a large influence on both J_{H-P} and J_{C-P} in aromatic phosphines through a twisting of the ring planes with respect to the orientation of the phosphorus lone pair of electrons.[8] CNDO/2 calculations of $^nJ_{H-P}$ in phenylphosphine for different conformations of the $-PH_2$ substituent with respect to the ring plane [9] support these experimental results. Calculations for a dihedral angle (between the ring plane and the C – P – X plane, X = lone pair) of 70°, *i.e.* in the region of the most stable conformation expected for triphenylphosphine,[10] gives values ($^3J_{H_2-P} = 6.69$ Hz, $^4J_{H_3-P} = 1.71$ Hz and $^5J_{H_4-P} = 0.97$ Hz) in good agreement with the experimental results reported here for triphenylphosphine.

Experimental. ^1H NMR spectra were recorded at 100.1 MHz in the continuous wave mode on a Varian XL-100-15 spectrometer and at a temperature of 31°. Spectra were recorded using internal ^1H lock (TMS), a sweep width of 0.5 Hz/cm and a sweep rate of 0.01 Hz/sec. Relative line positions are the average of values for the two sweep directions and are believed to be correct to within ±0.03 Hz. Solutions were prepared in 5 mm o.d. tubes using benzene-d_6 as solvent and TMS as internal standard and lock signal source. The solutions were carefully degassed by the freeze-pump-thaw technique and sealed under vacuum.

Calculations were performed on the CDC 6400 computer system at R.E.C.A.U., University of Aarhus.

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On the Structure of Deuterated Iminodiacetic Acid Hydrochloride, $C_4H_4D_3NO_4.DCl$

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The crystal structure of iminodiacetic acid hydrochloride, $C_4H_7NO_4.HCl$ (denoted IDAC), has been reported previously.[1] These crystals decompose within two months at room temperature after being removed from the mother liquor. However, a more stable compound is obtained when the acid hydrogen atoms are replaced by deuterium. This compound (denoted DIDAC) is prepared by repeated recrystallizations of IDAC from $D_2O + DCl$ (containing more than 99.5 % D). The crystal structure of DIDAC has been determined in order to study if the observed difference in the stabilities of the two compounds can be correlated with any structural differences.

Powder photographs of DIDAC were taken as described in Ref. 1. The spectra could be indexed using the lattice parameters of IDAC. The unit cell dimensions were then improved by least-squares refinement. The orthorhombic unit cell dimensions are $a = 12.380$ (1),* $b = 5.718$ (1), and $c = 5.111$ (1) Å.

A single crystal with the dimensions $0.25 \times 0.20 \times 0.17$ mm was mounted in a thin-walled glass capillary and used for the collection of X-ray intensity data on a four-circle diffractometer of type CAD-4. Experimental conditions and data reduction are described in Ref. 1. The systematically absent reflexions indicated the same space groups as for IDAC, *Pmmn* or $Pm2_1n$.

The atomic parameters of the non-hydrogen atoms from IDAC were used as starting parameters in a least-squares refinement assuming the space group to be *Pmmn*. After including an isotropic extinction parameter in the refinement,[2] a difference map, calculated from data with $\sin\theta/\lambda < 0.5$ Å^{-1}, revealed the remaining atoms. In the further calculations, the H and D atoms were given a fixed isotropic temperature factor (3.0 Å^2). The refined value of the extinction parameter, 2.5×10^4, corresponds to a mosaic spread of 2.4″ or a domain size of 3.8×10^{-4} cm. Weights used in the last cycle of refinement, $w = 1/(\sigma_c^2 + 0.0001|F_o|^2 + 4.0)$, gave $R = 0.074$, $R_w = 0.096$ and a smooth weighting scheme. The resulting positional and thermal parameters are given in Table 1. Tables with $|F_o|$, $|F_c|$, $\sin^2\theta_o$, and $\sin^2\theta_c$ can be obtained from the author.

* Figures within parentheses represent e.s.d.'s in the least significant digits.

Table 1. Positional and thermal parameters $\beta_{ij} \times 10^4$ with e.s.d.'s. The expression used is $\exp[-(\beta_{11}h^2+\cdots+2\beta_{12}hk+\cdots)]$. The atoms are denoted in accordance with Ref. 1.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	1/4	3/4	0.5304(7)	34(2)	253(12)	563(27)	0	0	0
N	1/4	1/4	0.274(2)	42(6)	306(39)	242(38)	0	0	0
O(1)	0.4356(5)	1/4	0.532(1)	53(4)	383(26)	291(31)	0	4(7)	0
O(2)	0.5369(4)	1/4	0.170(1)	39(4)	386(26)	380(31)	0	16(8)	0
C(1)	0.4442(6)	1/4	0.300(2)	45(5)	222(29)	349(36)	0	9(9)	0
C(2)	0.3501(6)	1/4	0.117(2)	44(5)	384(38)	324(38)	0	13(10)	0
D(1)	1/4	0.15(1)	0.39(2)						
H(2)	0.349(4)	0.10(1)	0.03(1)						
D(3)	0.599(7)	1/4	0.26(2)						

Table 2. Hydrogen bond distances (Å) and angles (°) with e.s.d.'s in DIDAC.

N···Cl	3.146(4)	$O(2^{ii})\cdots Cl$	3.052(6)	$\angle D(1^{iv})\cdots Cl\cdots D(1^{v})$	144(4)
$N-D(1^{iv})$ [a]	0.84(8)	$O(2^{ii})-D(3^{ii})$	0.90(8)	$\angle D(3^{ii})\cdots Cl\cdots D(3^{ii})$	120(5)
$Cl\cdots D(1^{iv})$	2.37(8)	$Cl\cdots D(3^{ii})$	2.15(8)	$\angle D(1^{iv})\cdots Cl\cdots D(3^{ii})$	99(1)
$\angle N-D(1^{iv})\cdots Cl$	154(7)	$\angle O(2^{ii})-D(3^{ii})\cdots Cl$	179(8)		

[a] The superscripts are in accordance with Ref. 1.

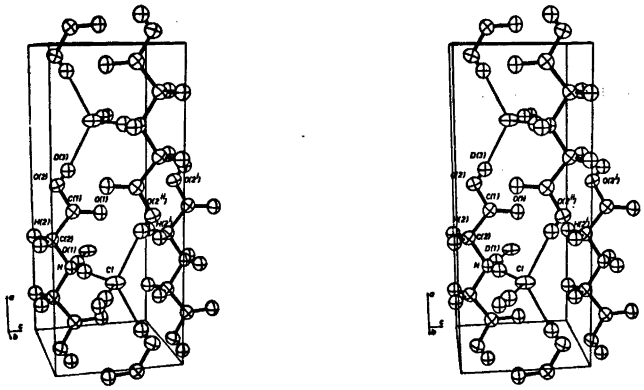

Fig. 1. A stereoscopic pair of drawings showing the structure of DIDAC.

Five cycles of refinement in the space group $Pm2_1n$ did not improve R, R_w or the e.s.d.'s, and it was concluded that a centrosymmetric model well describes the structure of DIDAC.

IDAC and DIDAC are closely isostructural. Positively charged iminodiacetic acid ions, $[C_4H_4D_4NO_4]^+$, with the symmetry *mm* are connected by hydrogen bonds N–D···Cl and O–D···Cl forming zigzag shaped layers. These layers are stacked in the **c**-direction and the forces between the layers are of van der Waals type. The structure is shown in Fig. 1. The dimensions of the positively charged iminodiacetic acid ion are not significantly different in DIDAC and IDAC.

Isotope effects on the hydrogen bond lengths in solids are well-known.[3] By comparing Table 4c in Ref. 1 with Table 2 in this paper, there are no such effects observed within the limits of error. However, the unit cell dimensions in DIDAC are 0.030 (2), 0.017 (2), and 0.017 (2) Å smaller for the **a**, **b**, and **c** parameters, respectively, as compared to IDAC. It is reasonable to assume that these discrepancies are due

to differences in the hydrogen bond systems. Since the N···Cl bond is situated in the mirror plane at $x = 1/4$ (and $x = 3/4$) it cannot influence the **a** parameter. For similar reasons the O···Cl bond cannot influence the **b** parameter. Therefore both types of hydrogen bonds might be shortened on deuteration and this could explain the difference in the stabilities of IDAC and DIDAC.

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Note on the Crystal Structure of a Mixed Nb-Zr-Oxide

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In our studies on the ZrO_2-Nb_2O_5 system [1] we have observed a phase with the approximate composition $(Nb,Zr)O_{2.46}$. Powder data (Table 1) show that this is identical with that first found by Trunov *et al.*,[2] who suggested the formula $ZrO_2.(5-7)Nb_2O_5$. The same phase has later been studied by Allpress and Roth [3] who thought it to be a polymorph of $Nb_{24}ZrO_{62}$ which they called β-$Nb_{24}ZrO_{62}$. Stephenson *et al.*[4] have also investigated the phase, formulating it as $ZrO_2.16Nb_2O_5$ and proposing a structure.

Since we failed to prepare the phase "$(Nb,Zr)O_{2.46}$" in a pure form, we are unable to give accurate data on its composition. Weissenberg photographs $h0l - h3l$ have been taken from single crystals of the oxide and the relative intensities of the reflections measured visually. The Patterson projection $P(u,p,w)$ as well as the Harker sections $(u,0,w)$ and $(u,\frac{1}{2},w)$ have been calculated and these clearly show "$(Nb,Zr)O_{2.46}$" to be closely related to other monoclinic niobium-rich oxides with $b = 3.82$ Å (*cf.* H-Nb_2O_5[5]), but with a more complicated crystal structure. The Patterson projection indicates that the structure is built up of blocks with ReO_3-structure extending infinitely in the y-direction and 3 or 4 MeO_6-octahedra in each of two directions in the xz plane. The best explanation of the Patterson distributions is that each unit cell contains two 4×4, two 4×3, two 3×4, and two 3×3 blocks. The blocks are fitted together in a way analogous to that in H-Nb_2O_5 and leave space for some tetrahedrally surrounded metal atoms (probably two). We have calculated structure factors for several proposed structures built up from the blocks mentioned above, using the metal positions derived from known structures. For the best of these models the agreement between observed and calculated structure amplitudes was satisfactory except for some of the weaker reflexions. We have also made similar calculations based on the crystal structure proposed by Stephenson *et al.* These give approximately the same agreement as that for the best of our models.

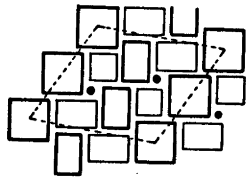

Fig. 1. Idealized projection of the most favoured of our proposed structures for "$(Nb,Zr)O_{2.46}$". The full circles represent metal atoms in tetrahedral positions.

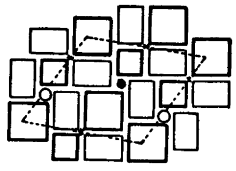

Fig. 2. Idealized projection of the structure of $ZrO_2.16Nb_2O_5$ proposed by Stephenson *et al.* The filled circle represents a metal atom in a tetrahedral position, the open circles are empty positions and intersecting shear planes are marked with a cross.

The main difference between our (Fig. 1) and Stephenson's (Fig. 2) proposals is that the latter introduces two new forms of block junctions and that the former employs only known block junctions. In Stephenson's model, corners of