04.6-3   BOND VALENCE VS. O...O DISTANCE IN HYDROGEN BONDS. By G. Ferraris and G.Ivaldi, Dipartimento di Scienze della Terra, Università di Torino,via S. Massimo 24,10123 Torino,Italy.

On principle the bond valence (bond strength) donated to the acceptors through the hydrogen bond (S_d) should be equal to the bond valence received by the donor from coordination bonds (S_r), in the case of a water molecule. For OH⁻ groups the relation $S_r - 1 = S_d$ holds.
Since accurate location of the hydrogen atom can be obtained from neutron diffraction work only, the necessity of using bond-valence vs. O...O, instead than vs. H...O, curves is apparent. Plots of S_r, calculated with Brown and Wu's [Acta Cryst. B32, 1957 (1976)] method, vs. O...O bond length have been obtained from published experimental data on O...O hydrogen bonds donated by H_2O and OH⁻. The decrease of the hydrogen bond length with increasing S_r agrees with the recent report by Ferraris et al. [Acta Cryst. B42, 258 (1986)] which used average values for bond lengths and Pauling's bond strengths p. The dispersion of the experimental points indicates that the calculated bond valences can explain the bond lengths only on the average. Anyway, average curves interpolating the experimental points of the plots could be useful to estimate S_d as a function of the O...O hydrogen bond length.
A comparison of the experimental plots with the theoretical curves given by Brown [Acta Cryst. A32,24 (1976)],shows that these curves underestimate S_d for water molecules when O...O>2.8 A. For shorter hydrogen bonds, the O...O length of the hydrogen bond obtained by Brown (quoted paper) as "minimum non-bonded O...O distance" does better fit the experimental plots.

| piperR$_2$O$_2$ .nH$_2$O	I	II	III	IV	V
piperR$_2$	1	2	3	4	5
n	8	4	4	4	8
Space group	Pnma	P$\bar{1}$	P$\bar{1}$	P2$_1$/c	C2/m
a, Å	12.327(2)	7.778(1)	6.558(1)	9.159(3)	12.961(4)
b, Å	9.804(1)	7.915(2)	7.134(2)	12.390(4)	11.533(4)
c, Å	17.443(4)	8.919(2)	11.610(3)	8.339(4)	7.907(1)
α, °	90	106.25(2)	73.23(2)	90	90
β, °	90	99.56(1)	78.08(2)	97.38(3)	98.37(2)
γ, °	90	108.80(2)	72.67(2)	90	90
z	4	1	1	2	2
$2\theta_{max}$, °	65	55	65	56	60
No. $|F_o|$	3032	1749	2651	1827	1192
R	0.056	0.049	0.055	0.035	0.045
Site symmetry of piperR$_2$O$_2$	m	$\bar{1}$	$\bar{1}$	$\bar{1}$	2/m
Crystal structure	3-D network	layer	composite layer	layer	3-D network
Water H ordering	partial	partial	complete	complete	partial

1. Taken from the M.Phil. thesis of Chun-Kiu Kwok, June, 1987.
2. Emilio Sol Morera, Quim. e ind. 71, 303 (1929);
    C.N. Ionescu, St. Geroszkowski, A. Serper, M. Ionescu, A. Sorescu, D. Panaitescu and A. Hacig, through Chemical Astracts 52,398i (1958); G.M. Bennett and E. Glynn, J. Chem. Soc., 211 (1950).

04.6-4   SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF HYDRATED N,N'-DIARYL- AND N,N'-DICYCLOHEXYL-PIPERAZINE N,N'-DIOXIDES.[1] By Chun-Kiu Kwok and Thomas C.W. Mak, Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong.

piperR$_2$

1 R = phenyl

2   o-tolyl

3   p-tolyl

4   p-chlorophenyl

5   cyclohexyl
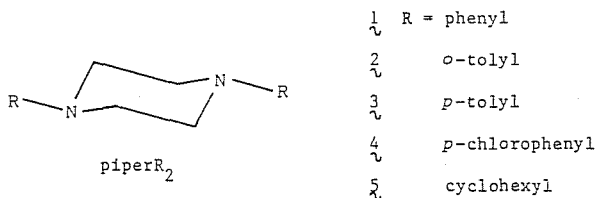
A series of heterocyclic di-tertiary amines of general formula piperR$_2$ (compounds 1 - 5) and their hydrated N,N'-dioxides piperR$_2$O$_2$.nH$_2$O (compounds I - V) have been synthesized according to the following scheme.[2]

$$2RNH_2 + 2BrCH_2CH_2Br \xrightarrow{130-140\ °C} piperR_2$$

$$piperR_2O_2.nH_2O \xleftarrow[HOAc,\ H_2O_2(30\%)]{50-70\ °C}$$
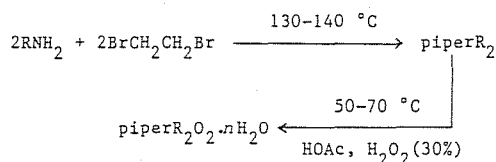
The structures of N,N'-dioxide hydrates I - V have been determined by X-ray crystallography using MoKα radiation. The results are summarized in the following table.