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H···H van der Waals distance in cooperative O—H···O—H···O hydrogen bonds determined from neutron diffraction data. Addendum

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Abstract. Experimental evidence supporting the paper by Steiner & Saenger [*Acta Cryst.* (1991), B47, 1022-1023] is presented. In cooperative $O_1—H_1\cdots O_2—H_2\cdots O_3$ hydrogen bonds, short $H_1\cdots H_2$ contacts (<2.2 Å) are only observed in a specified range of polar contacting angles. It is shown that the shortest allowed $H_1\cdots H_2$ separation trigonometrically determines the shortest allowed non-bonding separation $H_2\cdots O_1$.

Introduction. In Steiner & Saenger (1991), hereafter SS91, we determined the shortest possible $H_1\cdots H_2$ separation in cooperative $O_1—H_1\cdots O_2—H_2\cdots O_3$ hydrogen bonds in carbohydrates, $d_{\rm HH,min} \simeq 2.05$ Å. The same value of $d_{\rm HH,min}$ has also been found for inorganic crystal structures (Baur, 1972). In SS91, we reported some observations without giving the experimental evidence which we now present in this contribution.

Method. The same sample was used as in SS91 (23 carbohydrate and cyclodextrin neutron crystal structures); the parameters analyzed are defined [according to Nyburg & Faerman (1985)] in the inset of Fig. 1. (Note that in Fig. 1 of SS91, the polar angle μ_2 was defined incorrectly.) Bond lengths $d_{\rm OH}$ were not corrected for thermal vibration and minor components of three-center and four-center hydrogen bonds were not considered.

Results and discussion. In SS91, the directionality of the short $H_1\cdots H_2$ contacts in $O_1—H_1\cdots O_2—H_2$ was described as roughly 'head-to-side'. A closer look at this directionality is given by the scatterplot of μ_2 *versus* μ_1 (Fig. 1). Short contacts are only observed in certain ranges of μ_1 and μ_2 ($\sim 20 < \mu_1 < 55$, $100 < \mu_2 < 135°$). Short 'perfect' head-to-side contacts ($\mu_1 \simeq 0$, $\mu_2 \simeq 90°$) do not exist because the axis $O_1—H_1$ would then point *exactly* in the direction of H_2 and not to the acceptor atom O_2. For all short H···H contacts, μ_2 substantially exceeds 90°.

It has been found empirically that the non-bonding distance $H_2\cdots O_1$ is limited to values ≥ 3.0 Å (Savage & Finney, 1986); we interpreted this without direct proof from $H_1\cdots H_2$ van der Waals repulsions in SS91. It is obvious from the inset of Fig. 1 that $d_{H_2\cdots O_1}$ is determined trigonometrically by $d_{\rm OH}$, $d_{\rm HH}$ and μ_1 $\{d_{H_2\cdots O_1} = [d^2_{\rm OH} +$

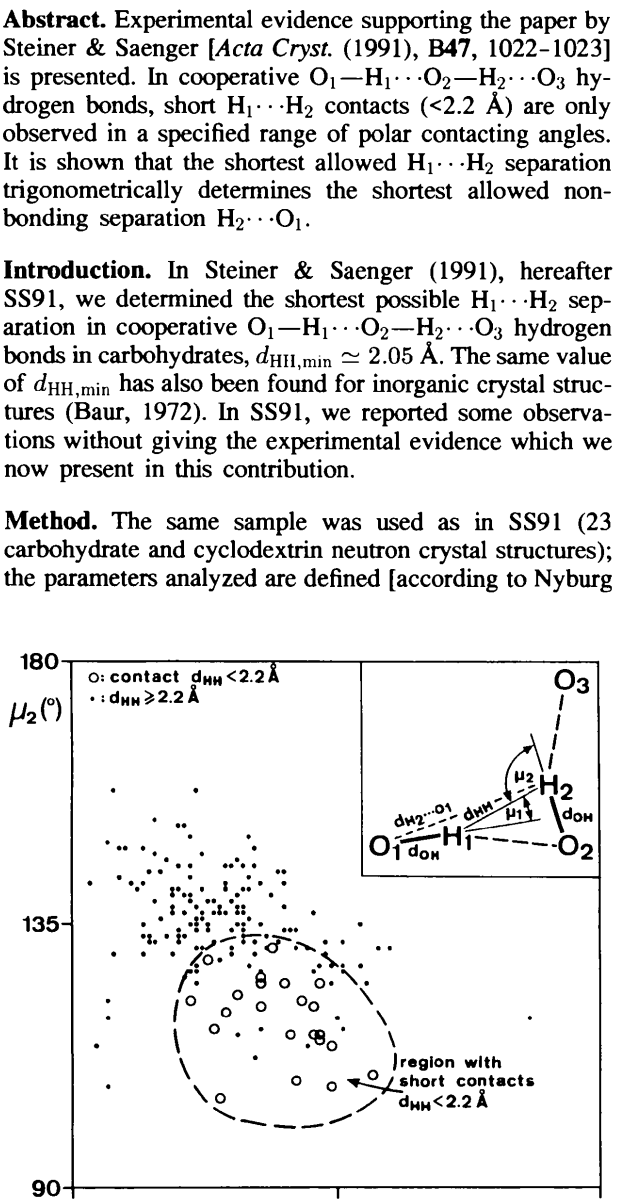

Fig. 1. Scatterplot of μ_2 *versus* μ_1 for *all* $O_1—H_1\cdots O_2—H_2$ hydrogen bonds; open circles indicate contacts $d_{\rm HH} < 2.2$ Å and dots $d_{\rm HH} \geq 2.2$ Å. The inset defines the analyzed parameters.

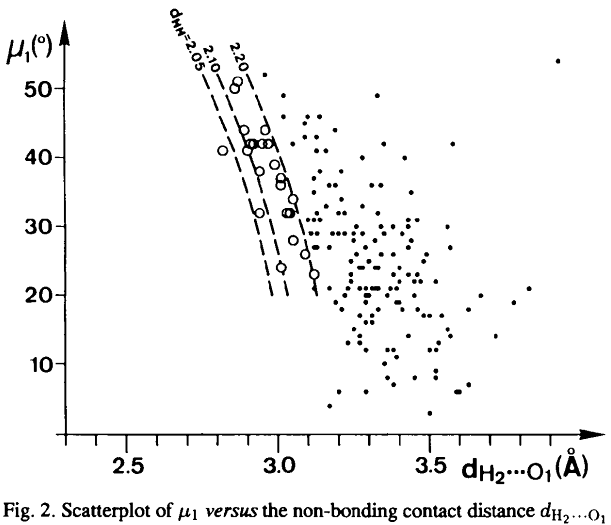

Fig. 2. Scatterplot of μ_1 *versus* the non-bonding contact distance $d_{H_2\cdots O_1}$ for *all* $O_1—H_1\cdots O_2—H_2$ hydrogen bonds; open circles indicate contacts $d_{\rm HH} < 2.2$ Å and dots $d_{\rm HH} \geq 2.2$ Å. The theoretical curves for $d_{H_2\cdots O_1} = f(d_{\rm HH}, \mu_1)$ are based on $d_{\rm OH} = 0.97$ Å and are shown as dashed lines.

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$d^2_{\mathrm{HH}} - 2d_{\mathrm{OH}}d_{\mathrm{HH}}\cos(180° - \mu_1)]^{1/2}$; $d_{\mathrm{OH}} \simeq 0.97$ Å)}. If the existence of a minimal value $d_{\mathrm{HH,min}} \simeq 2.05$ Å is accepted for μ_1 in the range 20–55°, this defines a minimal value $d_{\mathrm{H_2\cdots O_1,min}} = f(\mu_1)$ for the same range of μ_1. Fig. 2 shows the scatterplot of μ_1 *versus* $d_{\mathrm{H_2\cdots O_1}}$ which demonstrates that the shortest $\mathrm{H_2\cdots O_1}$ separations actually coincide with the $\mathrm{H_2\cdots H_1}$ van der Waals contacts and that non-bonding $\mathrm{H_2\cdots O_1}$ contacts may become shorter (down to 2.8 Å) with increasing μ_1.

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