Some "Very Short" Hydrogen Bonds

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POTASSIUM HYDROGEN BISPHENYLACETATE (KHX_2, where HX = phenylacetic acid) was the first compound in whose structure a crystallographically symmetrical O · · · H · · · O bond was reported.[1] [Trona, $Na_3H(CO_3)_2,2H_2O$, studied independently and at about the same time by Brown *et al.*,[2] has a similar feature.] Using the two-dimensional methods in vogue *ca.* 1947, we found the O · · · O distance across a centre of inversion to be 2·55 Å.[3] No formal assessment of accuracy was made, though it was affirmed that this distance was "almost certainly less than 2·65 Å". Interest in this hydrogen bond has stimulated other work on KHX_2—notably on its infrared spectrum[4] and projections of its neutron-scattering density;[5] and the result 2·55 Å has sometimes been cited without qualification.

Clearly this primitive *X*-ray analysis should now

TABLE

Acid, HX	M	Symmetry of Bond	O · · · H · · ·O (Å with e.s.d.)	Ref.
Acetic	Na	2	2·444 (10) 2·433 (corr.)	8
p-Chlorobenzoic	K	$\bar{1}$	2·457 (10)	9
Trifluoroacetic	K	$\bar{1}$	2·437 (7)	10
Aspirin	K	$\bar{1}$	2·445 (5) 2·437 (corr.)	11
Anisic	K	2	2·450 (10)	12
Phenylacetic	K	$\bar{1}$	2·445 (5)	—
p-Hydroxybenzoic	K	$\bar{1}$	2·458 (7)	—
		weighted mean =	2·446 (3)	

["corr." means that a correction, of possibly questionable validity, has been made for the libration of X.]

be repeated by three-dimensional methods. Dr. Ljubica Monojlović has therefore collected some 1950 counter-intensity data and refined the structure by anisotropic least-squares analysis, with inclusion of H-atoms, to a final R-value of 8·4% ($R' = 0·8\%$). We hope to publish a short account of this work elsewhere. Meantime the revised O · · · H · · · O distance is reported as $2·445 \pm 0·004_5$ Å.

Dr Manojlović is also engaged on a similar redetermination of the structure of KHX_2,H_2O (where HX now = *p*-hydroxybenzoic acid). Some 1260 photographic data, refined to $R = 8·7\%$ ($R' = 1·7\%$), have reduced the value for the intercarboxyl O · · · H · · · O distance from the 2·61 Å reported in 1951[6] to 2·458 ± 0·007 Å.

We now have satisfactory three-dimensional analyses of seven type-A[7] acid salts (MHX_2) and the results, shown in the Table, for the hydrogen bond-lengths agree well.

The Table represents a class of compounds possessing "very short" hydrogen bonds. It is beyond the power of current X-ray methods to exclude all possibility that such structures are really disordered, with the proton occupying alternative sites (perhaps up to 0·1 Å) on either side of the midpoint. But genuinely symmetrical O · · · H · · · O bonding may be suspected.

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