

average distance of the atoms of (II) to the molecular plane of (I) is 3.3 Å; minimum [maximum] values are 3.11 Å for O(6) [3.58 Å for O(4)]. The mode of molecular overlap of (I) and (II) within a triad is shown in Fig. 3. These triads are arranged in stacks along *b*, Fig. 4. The molecular overlap between two species (II) of adjacent triads is given in Fig. 5. The molecular planes are parallel by symmetry and the mean [min./max.] distances of the non-H atoms of one species to the molecular plane of the adjacent one are 3.35 Å [3.28 Å for N(10)/3.48 Å for N(12)]. In terms of the usual stacking modes of 1,2-dioximato complexes of the Ni triad (Endres *et al.*, 1977), the title compound is composed of triads of *M-L* form stacked in an *M-L* fashion, with a more pronounced slip of adjacent molecules between triads than within triads. Stacks of triads occur in a Pt(oaoH)₂ species as well (Endres, 1980*b*), but with a pronounced difference: in the Pt compound the stacking pattern corresponds to the *M-M* form in accordance with the greater tendency of Pt complexes to arrange in this form (Endres *et al.*, 1977).

In [Pd(oaoH)(oaoH₂)₂]₂SO₄ which crystallizes simultaneously with the title compound (Endres, 1980*a*), the complex species arrange in stacks of diads where the diads are linked by SO₄²⁻ ions *via* H bridges involving the amino substituents. A similar kind of linking does not occur in the title compound, but the sulfate ion and the water molecules are involved in a network of H bridges to each other and to the complex molecules. Relevant distances and angles are summarized in Table 4. H bridges involving the oxime groups also link

the different complex cations, as is evident from the short distances O(1)–O(6) 2.61 (1) Å involving H(17) with O(6)–H(17) 1.73 (16) Å and an O–H–O angle of 169°, and O(6)–O'(6) 2.57 (12) Å. In the latter case it is not evident where the bridging H comes from, as there should not be an H atom bound to O(6), nor has an H been found in the structure analysis. There might be a statistically occupied site between O(6) and O'(6) together with statistical vacancies at the H(13) or H(17) positions. Similar intermolecular linking has been found in other oaoH₂ complexes (Endres, 1979, 1980*b*).

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Hydrogen-Bond Length in Homomolecular Organic Crystals

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Abstract

A statistical analysis of X-ray data on the intermolecular hydrogen bond (H bond) in organic homomolecular crystals has been carried out. The average lengths obtained for different types of H bonds are compared with those obtained by other authors and with the van der Waals radii of the atoms forming H bonds. It is shown that the H-bond length is determined just by the van der Waals contact between *X* and *Y* atoms, as if the H atom were absent.

The length of the H bond *XH...Y* is usually considered as a distance *R* between atoms *X* and *Y* or as a distance *d* between atoms H and *Y*. We shall use the former description. The distance *d* is known only if the H atom is located. Its position can only be determined with sufficient accuracy by neutron diffraction, whereas the distance *R* is available from normal X-ray analysis. However, as will be shown in this paper, the *R* values are in some respects more informative than the *d* values.

We have carried out a statistical analysis of X-ray data on the intermolecular H bond in organic homo-

molecular crystals, *i.e.* crystals built up of chemically identical molecules. Thus, crystalline hydrates and substances like $R-NH_2 \cdot HCl$ *etc.*, were excluded. As the source for data we used the two volumes by Kitaigorodsky, Zorkii & Belsky (1980, 1982). The data cover the period from 1929 to 1974 inclusively, and more than 4000 crystal structures are described, 1053 of which contain intermolecular H bonds. Here the question arises: which intermolecular contacts should be considered as H bonds? In our investigation only those H bonds were included that were indicated as such by the authors concerned. The crystal structure generally gives clear evidence of the presence or absence of an H bond and there is usually little difficulty in identifying one in an X-ray analysis.

In all, 2220 symmetrically independent H bonds are considered in this paper.

The distribution of structures by numbers of H bonds which one molecule forms is as follows: number of H bonds (number of structures): 2(494), 4(265), 6(102), 8(119), 10(34), 12(23), 14(4), 16(1), 24(1). In addition we found ten crystal structures in which symmetrically unrelated molecules formed different numbers of H bonds.

We came across seven bonds of the type $X-H \cdots Y$ (X -bifurcated) and 31 bonds of type $X-H \cdots Y$ (Y -bifurcated). Each of these systems was considered as two bonds.

The statistical data obtained were represented as histograms, one of which is shown in Fig. 1. The form of the histograms is close to the normal distribution and we therefore performed least-squares calculations to fit Gaussian curves to the histograms. In this way we obtained the estimated mean \bar{R} , the standard deviation σ and the parameter Q which characterizes the goodness of fit.

Table 1 contains our statistical data and the analogous data of Pimentel & McClellan (1960, 1971).

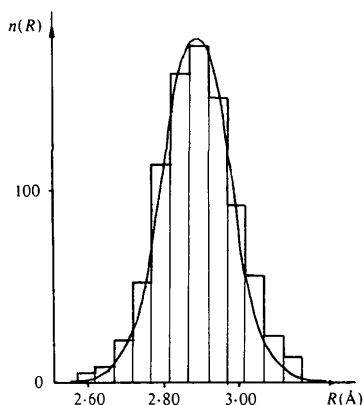


Fig. 1. Histogram showing the distribution of $NH \cdots O$ bond lengths.

The number of bonds (n) shows that only $OH \cdots O$, $OH \cdots N$, $NH \cdots O$, $NH \cdots S$ and $NH \cdots N$ bonds are common in organic homomolecular crystals. Other types of bonds (in particular bonds with halogen atoms) are very rare. It is of interest that the $OH \cdots S$ bond is more rare than $NH \cdots S$. It perhaps occurs because the former cannot compete with the possible $OH \cdots O$ bond formation; on the other hand the $NH \cdots S$ bond often successfully competes with the $NH \cdots N$ bond. Naturally we could determine the Gaussian curves only for rather common H-bond types.

The data of Pimentel & McClellan, unlike our data, contain characteristics of both organic and inorganic substances and also those of crystalline hydrates. It should be remarked that the results of Pimentel & McClellan mainly relate to the ions of halogens. H bonds formed by such ions can differ considerably from those in homomolecular crystals where the halogen atoms play the part of substituents in molecules. Of course statistical estimations are reliable only if n is great. In some cases our data practically coincide with those of Pimentel & McClellan (\bar{R} for $OH \cdots O$, $OH \cdots N$), but there are also noticeable discrepancies (\bar{R} for $NH \cdots O$ and especially for $NH \cdots N$). In Table 1 the most reliable values are boxed; only these values are used in the following discussion.

In the literature are other statistics, for example some concise work by Donohue (1952). We may mention also the statistics of Hamilton & Ibers (1968) based on neutron diffraction experiments; these data almost coincide with the data of Pimentel & McClellan (except \bar{R} values for $NH \cdots F$, 2.8 Å, and $NH \cdots Cl$, 3.3 Å). A special study (Donohue, 1969) is devoted to the $NH \cdots S$ bond; Donohue's data give an \bar{R} value equal to 3.48 Å (estimated mean for 37 bonds).

Table 1. Statistical data for H-bond length (X-ray analysis)

Type of H bond	Pimentel & McClellan (1960, 1971)		Kuleshova & Zorkii (present work)			
	n	\bar{R} (Å)	n	\bar{R} (Å)	σ (Å)	Q (%)
$OH \cdots O$	165	2.71*	1019	2.72	0.15	17.3
$OH \cdots N$	21	2.80	115	2.79	0.10	22.8
$OH \cdots S$	18	3.31	4	3.23	—	—
$OH \cdots F$	13	2.72	1	3.00	—	—
$OH \cdots Cl$	56	3.12	2	3.10	—	—
$OH \cdots Br$	41	3.28	1	3.26	—	—
$NH \cdots O$	106	2.94*	883	2.89	0.14	5.1
$NH \cdots N$	37	3.10	114	2.98	0.16	23.8
$NH \cdots S$	76	3.39	53	3.42	0.11	11.3
$NH \cdots F$	10	2.92	3	3.08	—	—
$NH \cdots Cl$	84	3.23	3	3.23	—	—
$NH \cdots Br$	51	3.37	2	3.39	—	—

* The average distances obtained from data of Pimentel & McClellan for different classes of compounds.

Complete statistical studies of the OH...O bond have been performed for crystalline hydrates (Ferraris & Franchini-Angela, 1972; Brown, 1976) and for molecular crystals (Kroon, Kanters, van Duijneveldt-van de Rijdt, van Duijneveldt & Vligenthart, 1975). Their data give \bar{R} values equal to 2.81, 2.73 and 2.77 Å respectively.

A measure of the types of potential donor and acceptor atoms occurring in the crystals ought to be given, whenever the frequency of occurrence of certain types of H bonds is considered. Among 1053 substances under consideration we found 1485 H atoms belonging to OH groups and 1108 H atoms belonging to NH or NH₂ groups. Respectively 1142 and 1058 of them take part in H-bond formation. The analogous data for acceptor atoms are summarized in Table 2.

It is of interest to compare the R values with the van der Waals radii of the atoms forming the H bonds.* Such a comparison was made by Pimentel & McClellan (1960, 1971). They compared R with the sum of van der Waals radii $\sum R_v$ introduced by Pauling (1940) and drew the conclusion that the $\sum R_v - R$ value usually varies from 0 to 0.25 Å. Only for H bonds involving N and S atoms does this value have a small negative magnitude. Almost all these exceptions could be eliminated by accepting a radius of 1.65 Å for N.

On the other hand, elsewhere it was noted that in the analysis of H-bond geometrical characteristics special attention should be paid not to the R distance but to the d distance, which is considerably shorter than the sum of the van der Waals radii (Hamilton & Ibers, 1968; Rahim & Barman, 1978) or the $2\sqrt{(R_H R_Y)}$ value, where R_H and R_Y are the van der Waals radii of the corresponding atoms (Zefirov, 1976).

In the present work we infer that the equilibrium H-bond length is determined just by the contact

* A survey of the different systems of van der Waals radii has been given by Zefirov & Zorkii (1974).

Table 2. The frequency of occurrence of potential acceptor atoms in crystals (n_1)

Acceptor atom	n	n_1	n/n_1 (%)
O*	1445	1899	76.1
O†	457	1485	30.8
N‡	222	389	57.1
N§	7	1108	0.6
S	57	172	33.1
F	4	49	8.2
Cl	5	145	3.4
Br	3	96	3.1

* O= or -O-.

† -OH.

‡ $\begin{array}{c} | \\ \text{N} \\ | \end{array}$, -N= or N≡.

§ $\begin{array}{c} > \\ \text{N} \\ > \end{array}$ or -NH₂.

between the X and Y atoms, the d distance (for a linear H bond) being simply the difference between R and the length of the X -H covalent bond. It should be noted, however, that here we are dealing with comparatively weak H bonds which are present in organic homo-molecular crystals.

Like Pimentel & McClellan we have compared the \bar{R} and $R_X + R_Y$ values (Table 3), where R_X and R_Y are the van der Waals radii given by Kitaigorodsky (1971). In this table the comparison of \bar{R} and $2\sqrt{(R_X R_Y)}$ is also presented; here R_X and R_Y are the statistical van der Waals radii obtained by Zefirov & Zorkii (1974, 1976) (we also used as preliminary estimated values R_F 1.4 Å and R_{Br} 2.1 Å). It was shown by these authors that the average length of the intermolecular atom-atom contacts is nearer to $2\sqrt{(R_X R_Y)}$ than to $R_X + R_Y$. Both $|\bar{R} - R_X - R_Y|$ and $|\bar{R} - 2\sqrt{(R_X R_Y)}|$ are always small; their values are not more than 0.2 Å, and the situation is close to that shown in idealized form in Fig. 2.

As for the comparison of \bar{R} and $2\sqrt{(R_X R_Y)}$, it is conditional on our abandoning the model in which the van der Waals spheres come into contact. Thus, the H-bond $XH...Y$ length approximately coincides, on average, with the length of the $X...Y$ contact, as if the H atom were absent.

The physical meaning of this rather unexpected situation becomes clear if we turn to *ab initio* calculations concerning the redistribution of electron density stimulated by H-bond formation. Such calcu-

Table 3. Length of H bond and van der Waals radii (Å)

Type of H bond	\bar{R}	$R_X + R_Y$	$\bar{R} - R_X - R_Y$	$2\sqrt{(R_X R_Y)}$	$\bar{R} - 2\sqrt{(R_X R_Y)}$
OH...O	2.72	2.72	0.00	2.58	0.14
OH...N	2.79	2.93	-0.14	2.78	0.01
OH...S	3.31	3.38	-0.07	3.08	0.23
OH...F	2.72	-	-	2.69	0.03
OH...Cl	3.12	3.14	-0.02	3.13	-0.01
OH...Br	3.28	3.31	-0.03	3.29	-0.01
NH...O	2.89	2.93	-0.04	2.78	0.11
NH...N	2.98	3.14	-0.16	3.00	-0.02
NH...S	3.42	3.59	-0.17	3.32	0.10
NH...F	2.92	-	-	2.90	0.02
NH...Cl	3.23	3.35	-0.12	3.38	-0.15
NH...Br	3.37	3.52	-0.15	3.55	-0.18

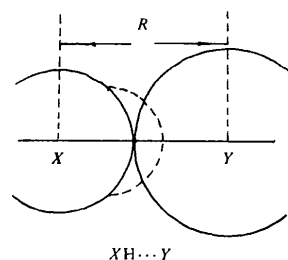


Fig. 2. H bond and van der Waals radii.

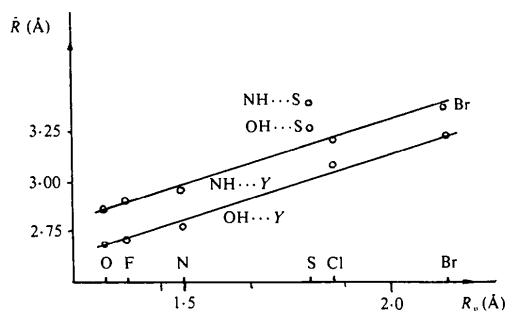


Fig. 3. The dependence of the H-bond length on R_y .

lations were carried out by Yamabe & Morokuma (1975) for three systems: water dimer, formaldehyde-water, cyclopropanone-water. The maps obtained show a considerable shift of electron density from the H atom to the O-H bond and to the other part of the water molecule. Evidently, for this reason, in the formation of the $XH\cdots Y$ bond there is no repulsion between H and Y atoms, and the distance \bar{R} is determined by the contact of the X and Y atoms.

Fig. 3 shows the dependence of \bar{R} on R_y . It is remarkable that H bonds involving S atoms deviate from the linear dependence. Another notable observation is that the difference $\Delta\bar{R} \approx 0.18$ Å between $NH\cdots Y$ and $OH\cdots Y$ bonds is much larger than the difference Δr between NH and OH bond lengths (0.05 Å). $\Delta\bar{R}$ for $XH\cdots O$, $XH\cdots F$ and $XH\cdots N$ bonds is very close to the difference in optimum distance $X\cdots Y$, i.e. to $\Delta[2\sqrt{(R_x R_y)}] \approx 0.2$ Å. At the same time $\Delta\bar{R}$ for $XH\cdots S$, $XH\cdots Cl$ and $XH\cdots Br$ bonds is close to 0.1 Å while $\Delta[2\sqrt{(R_x R_y)}] \approx 0.25$ Å. This may be because the statistical data for these bonds are not quite sufficient.

In the analysis described above we did not consider the degree of H-bond linearity. Inclusion of this factor

leads to a more complicated model of the H bond but does not change the basic findings.

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