

# Covalent Nature of the Strong Homonuclear Hydrogen Bond. Study of the O—H---O System by Crystal Structure Correlation Methods<sup>1</sup>

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**Abstract:** All cases of strong ( $2.50 \leq d(\text{O} \cdots \text{O}) \leq 2.65 \text{ \AA}$ ) and very strong ( $d(\text{O} \cdots \text{O}) < 2.50 \text{ \AA}$ ) O—H---O hydrogen bonds whose geometries are known from accurate neutron or X-ray diffraction studies are reviewed and classified in chemical classes belonging to three fundamental types: (A) —O—H---O—, or *negative charge assisted hydrogen bonding*, (–)CAHB; (B) =O---H<sup>+</sup>---O=, or *positive charge assisted hydrogen bonding*, (+)CAHB; and (C) —O—H---O=, where the two oxygens are interconnected by a system of  $\pi$ -conjugated double bonds, or *resonance-assisted hydrogen bonding*, RAHB. An empirical model is discussed where the hydrogen bond energy is expressed as  $E_{\text{HB}} = E_{\text{COV}} + E_{\text{EL}} + E_{\text{REP}}$ ,  $E_{\text{COV}}$  being the energy of the covalent three-center-four-electron O—H---O bond, and  $E_{\text{EL}}$  and  $E_{\text{REP}}$ , the electrostatic attraction and interoxygen repulsion energies, respectively. By means of a detailed analysis of bond and contact distances, it is shown that, while the O---O distance is shortened from 2.80 to 2.40 Å, the hydrogen bond is transformed from a dissymmetrical O—H---O electrostatic interaction to a covalent and symmetrical O--H--O bond. It is suggested that such behavior is common to all *homonuclear* hydrogen bonds (O—H---O, N—H---N, F—H---F), while *heteronuclear* ones (e.g. N—H---O) can only give weaker bonds of mostly electrostatic nature.

In spite of the great number of papers, books, and reviews<sup>2</sup> published on the hydrogen bond, the chemical factors determining its strength remain widely unknown if exception is made for the role played by the electronegativities of the hydrogen bond donor and acceptor atoms. This rather paradoxical situation is better stressed by the case of homonuclear linear or nearly linear (say, having the O—H—O angle  $\geq 165^\circ$ ) O—H---O bonds. They display a practically continuous distribution of  $d(\text{O} \cdots \text{O})$  contact distances ranging from 2.36 to 3.69 Å (this last value being only a van der Waals cutoff and not the physical limit of the hydrogen bond interaction), and they are somewhat loosely referred to<sup>3a-d</sup> as very strong ( $< 2.50 \text{ \AA}$ ), strong (2.50–2.65 Å), medium (2.65–2.80 Å), or weak ( $> 2.80 \text{ \AA}$ ). However, we do not have any general rule able to predict, except by sheer analogy, which chemical species will be able to form the strongest (that is the shortest<sup>4</sup>) hydrogen bonds.

So far the prevalent opinion has been that very strong O—H---O bonds can only occur because of severe intramolecular strain or in connection with protonated oxyanions —O—H---O— or solvated protons =O---H<sup>+</sup>---O=<sup>2d</sup>. Moreover, the fact that the strongest bonds often occur as a charge-

assisted phenomenon has, in some way, supported the idea that all hydrogen bonds are essentially electrostatic in nature irrespective of their strength, in touch with the results of previous theoretical studies<sup>5</sup> indicating that this is most probably true in the case of weak or medium range bonds.

It has been recently shown,<sup>1</sup> however, that there is a further class of strong or very strong hydrogen bonds which cannot be accounted for by electric charges or steric hindrance, but is due to the fact that the neutral donor and acceptor atoms are connected by a system of  $\pi$ -conjugated double bonds; such a bond has been referred to as RAHB (resonance-assisted hydrogen bonding).<sup>1a</sup>

(4) (a) There has been considerable discussion on the direct relationship between hydrogen bond strength and length, particularly for very short bonds, and most recently Jeffrey and Saenger (ref 2d, p 51) remarked that there is no direct experimental evidence for it. In the present paper  $d(\text{O} \cdots \text{O})$  is employed as indicator of O—H---O length, and it might be wondered whether it is also an indicator of its strength. The following points are to be stressed. (i) For linear weak and medium bonds all quantum-mechanical and empirical<sup>6</sup> calculations indicate that there is a functional dependence between O---O distance and hydrogen bond energy, the latter increasing almost exponentially while  $d(\text{O} \cdots \text{O})$  tends to its minimum. (ii) The effect of the O—H—O angle can be evaluated from empirical energy fields<sup>6</sup> (with respect to the linear bond, the energy of the bent bonds are reduced to a 90% for O—H—O =  $165^\circ$ , 60% for O—H—O =  $149^\circ$ , and less than 10% for O—H—O =  $110^\circ$ ). (iii) For very short O—H---O bonds, calculations become difficult because of uncertainties in the value of the interoxygen repulsion energy and we must rely on experiments. Recent measurements of pulsed electron-beam mass spectrometry in the gas phase have shown<sup>4b</sup> that the largest association enthalpies are found for compounds of the classes O—H---O<sup>–</sup> and O<sup>–</sup>—H<sup>+</sup>---O for which the shortest nearly linear O—H---O bonds are observed (see Table 1 and Charts 1 and 2): for example, HCOO<sup>–</sup>—HOOC<sup>+</sup>, 36.8; CH<sub>3</sub>COO<sup>–</sup>—HOOC<sup>+</sup>CH<sub>3</sub>, 29.3; (CH<sub>3</sub>)<sub>2</sub>SO<sup>–</sup>—H<sup>+</sup>—OS(CH<sub>3</sub>)<sub>2</sub>, 30.8 kcal mol<sup>–1</sup>. (iv) Last but not least, it is shown in the following of this paper that very short linear hydrogen bonds must be considered three-center-four-electron covalent bonds for which the usual dependence of bond energy on internuclear distance is to be expected. It may be so suggested that the strength-length relationship can be considered to hold for all linear or nearly linear (O—H—O  $\geq 165^\circ$ ) O—H---O bonds, which include almost all intermolecular and a part of intramolecular bonds. In intramolecular bonds closing six-membered rings (see Chart 3), the O—H—O angle is typically in the range  $149 \pm 5^\circ$ ; such bonds are to be considered as having a hydrogen bond energy some 40% lower than it would be expected if the bond were linear. For small angles, hydrogen bonds start fading irrespective of the observed  $d(\text{O} \cdots \text{O})$  distance. (b) Meot-Ner (Mautner), M. J. Am. Chem. Soc. 1984, 106, 1257. Meot-Ner (Mautner), M.; Sieck, L. W. J. Am. Chem. Soc. 1986, 108, 7525.

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(1) Evidence for Resonance-Assisted Hydrogen Bonding. 4. (a) Part 1: Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. J. Am. Chem. Soc. 1989, 111, 1023. (b) Part 2: Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. J. Am. Chem. Soc. 1991, 113, 4917. (c) Part 3: Gilli, G.; Bertolasi, V.; Gilli, P.; Ferretti, V. *Acta Crystallogr., Sect. B* 1993, 49, 564. (d) Gilli, G.; Bertolasi, V. In *The Chemistry of Enols*; Rappoport, Z., Ed.; John Wiley & Sons: New York, 1990; Chapter 13.

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These new findings seem to require a revision of our ideas on the origins of the strong hydrogen bond and the formulation of a new model able to take into account both resonance and charges as possible causes of its strength. The present paper is devoted to developing this model for the case of the O—H...O bond, a system which has been chosen because (i) its homonuclearity permits avoidance of the complications introduced by the different donor and acceptor electronegativities, (ii) it is probably unique for the wide range of strengths and lengths of the bonds formed, and (iii) the pertinent structural information is detailed and often very accurate. The paper is divided in two main parts, the first outlining the model employed and the second showing that all structural data available do conform to the model itself.

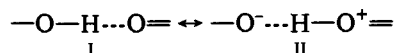
### An Empirical Model for the Strong O—H...O Hydrogen Bond

The most general semiempirical treatments for the hydrogen bond have been proposed by Lippincott and Schroeder<sup>6a</sup> and Reid;<sup>6b</sup> they are very similar and will be used here as a starting point for the discussion. In both models the hydrogen bond potential energy,  $E_{HB}$ , is the sum of three terms, that is

$$E_{HB} = E_{COV} + E_{EL} + E_{REP} \quad (1)$$

Calling  $r$  the O—H distance and  $R$  the O...O contact distance, the repulsion term assumes the negative exponential form,  $E_{REP} = Ae^{-bR}$  ( $A$  and  $b$  empirical constants), while the electrostatic one is expressed as  $E_{EL} = -B/R^m$ , where  $B$  is another empirical constant to be determined and the exponent  $m$  can be given a value in between 1 (in which case the interaction between the two oxygens is considered monopolar electrostatic) and 6 (when the interaction is considered to be dipole-dipole or dispersive).

A mathematical expression for the covalent part is obtained by assuming that, as far as such a covalent term is concerned, the hydrogen bond is a linear three-center-four-electron O—H...O covalent bond whose wave function is a linear combination  $\Psi = a_1\Psi_I + a_2\Psi_{II}$  of its VB resonance forms, that is



Since both O—H and H—O<sup>+</sup> bonds can be described by Morse-like functions,  $E_{COV}$  may be obtained by overlapping two of such curves reciprocally shifted by the O...O distance,  $R$ , as shown in Figure 1.<sup>7</sup> The upper curve concerns the O—H bond and the depth of its minimum corresponds to the accepted value of the O—H bond dissociation energy, i.e.  $D = 118 \text{ kcal mol}^{-1}$ , while the lower curve is representative of the H—O<sup>+</sup> bond, characterized by a dissociation energy  $D^*$ , which must be smaller than  $D$  because of the destabilization induced in II by the positive charge; it can be written as  $D^* = cD$  ( $0 \leq c \leq 1$ ). We do not know the correct value of  $c$  to be used; Lippincott and Schroeder,<sup>6a</sup> in their parametrization of the O—H...O bond, assumed a value of  $c = 0.65$  for the relatively weak bond in water, and Reid<sup>6b</sup> maintained, for reasons to be discussed later, that it must be increased for the strongest hydrogen bonds to the value of 1.0.

It must be stressed that  $c$  strongly affects the calculated values of  $E_{COV}$ , particularly for very short bonds. Actually the quantity  $\Delta E = -[E_{COV}(c = 1.0) - E_{COV}(c = 0.65)]$ , which represents the energy gain in the covalent part of the hydrogen bond that can be obtained by using  $c = 1.0$  instead of  $c = 0.65$ , increases almost linearly from 8 to 33 kcal mol<sup>-1</sup> as  $R$  decreases from 3.0 to 2.5 Å and remains as large as 30–37 kcal mol<sup>-1</sup> in the range  $2.39 \leq R \leq 2.55$  Å, typical of strong or very strong hydrogen bonds. Values of  $E_{COV}(c = 1.0)$  and  $E_{COV}(c = 0.65)$  are reported in

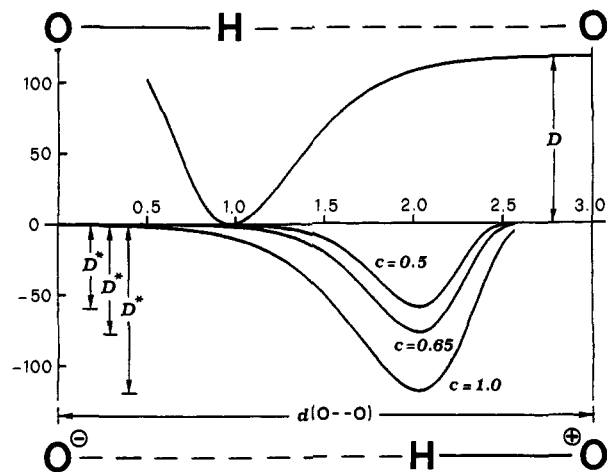


Figure 1. Covalent part of the hydrogen bond energy,  $E_{COV}$ , can be calculated by overlapping two Morse-like functions shifted by the O...O distance,  $R$ . The upper curve concerns the O—H bond and the lower one the H—O<sup>+</sup> bond of the resonant forms I and II having bond dissociation energies  $D$  and  $D^* = cD$ , respectively. Curves corresponding to three different values of  $D^*$  are shown.

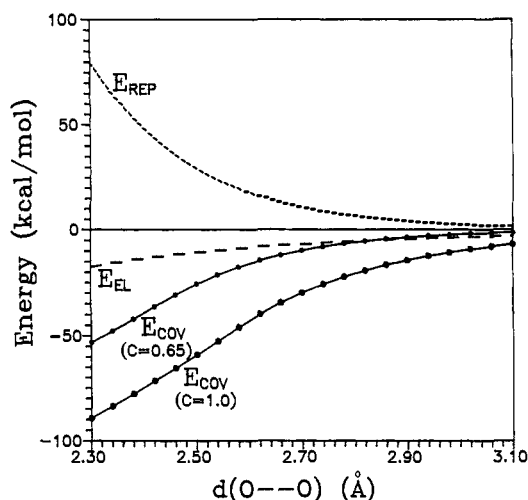


Figure 2. Energy components of the linear O—H...O hydrogen bond,  $E_{COV}$ ,  $E_{EL}$ , and  $E_{REP}$  of eq 1, calculated as functions of  $R = d(\text{O} \cdots \text{O})$ . The term  $E_{COV}$  is calculated for two different values of the constant  $c$  (0.65 and 1.00).

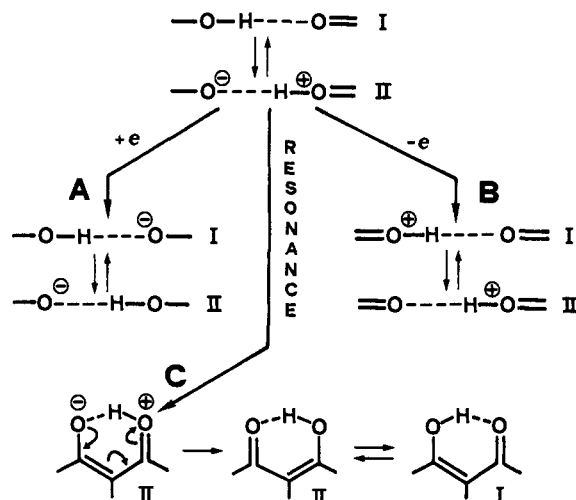
Figure 2 as a function of  $R$  together with the corresponding values of  $E_{EL}$  and  $E_{REP}$  calculated by the use of the Reid's parameters.<sup>6b,8</sup> This plot can be used as a base for our qualitative model. The basic idea is that, because of the steep increase of the repulsion term with the decreasing inter-oxygen distance, very short  $d(\text{O} \cdots \text{O})$  values can be attained only by taking advantage of the energy difference  $\Delta E = -[E_{COV}(c = 1.0) - E_{COV}(c = 0.65)]$  or, in other words, that the increase of  $c$  beyond its value of 0.65 is the factor controlling the formation of short and very short hydrogen bonds. If, conversely, such value cannot be exceeded, only relatively long and weak bonds can be formed, such as those characterized by  $R = 2.77 \pm 0.07$  Å in alcohols and saccarides<sup>9a,b</sup> or some 2.75 Å in the polymorphs of ice.<sup>9c</sup> This hypothesis on the nature of the strong O—H...O bond was originally suggested by Reid in 1959<sup>6b</sup> but has been widely overlooked so far, mainly because the

(6) (a) Lippincott, E. R.; Schroeder, R. *J. Chem. Phys.* 1955, 23, 1099. Schroeder, R.; Lippincott, E. R. *J. Phys. Chem.* 1957, 61, 921. (b) Reid, C. *J. Chem. Phys.* 1959, 30, 182.

(7) The general equation<sup>6a</sup> is  $E_{cov} = V(\text{O—H}) + V(\text{H—O})$  with  $V(\text{O—H}) = D[1 - \exp(-n\Delta r^2/2r)]$  and  $V(\text{H—O}) = D^*[1 - \exp[-n^*(R - r - r^0)^2/2(R - r)]] - D^*$ . The variables  $r$ ,  $R$ ,  $D$ , and  $D^* = cD$  have been defined in the text,  $\Delta r = r - r^0$  is the stretching or compression of the bond from its equilibrium length  $r^0$ ,  $n = k^0 r^0/D$  (where  $k^0$  is the bond force constant), and  $n^* = cn$ .

(8) Parameters used are as follows:  $E_{EL} = -2595/R^6$  and  $E_{REP} = 7.87 \times 10^6 e^{-5.0R}$ . Though such parametrization probably underestimates  $E_{REP}$ , particularly for the smallest  $R$  values, the plot in Figure 2 can be considered accurate enough for a qualitative model.

(9) (a) Kroon, J.; Kanters, J. A.; Van Duijneveldt-Van de Rijdt, J. G. C. M.; Van Duijneveldt, F. B.; Vliegthart, J. A. *J. Mol. Struct.* 1975, 24, 109. (b) Ceccarelli, C.; Jeffrey, G. A.; Taylor, R. *J. Mol. Struct.* 1981, 70, 255. (c) For ice Ih, see ref 16.



**Figure 3.** Three ways for making equivalent the two resonant forms I and II: (A) by adding an electron, (B) by removing an electron, and (C) by connecting the two oxygens by a chain of conjugated double bonds.

author could support it only by the infrared evidence (essentially  $\nu(\text{OH})$  stretching frequencies) available at the time. We will try to show hereafter that this hypothesis is supported on the grounds of the large number of accurate structural data collected on the geometry of the  $\text{O}-\text{H}\cdots\text{O}$  bond by neutron or X-ray crystallographic methods and made available by the Cambridge Structural Database.<sup>10</sup>

#### Experimental Verification of the Model

When  $c$  tends to 1,  $D^* = cD$  must tend to  $D$ , and the two resonance forms I and II will become energetically (or chemically) equivalent. Figure 3 shows that there are only three ways for obtaining such chemical equivalence: (A) by adding an electron, which produces the  $\text{O}-\text{H}\cdots\text{O}^-$  situation present in the bond between conjugated acid and basic moieties of acid salts; (B) by removing an electron and generating the situation where a proton is captured by two oxygens, for instance those belonging to two carbonyls or two  $N$ -oxide groups or two water molecules; (C) by connecting the two oxygens by a chain of conjugated double bonds as it happens, for example, in the  $\beta$ -diketone moiety shown in Figure 3 (this situation corresponds to that already described as RAHB<sup>1</sup> and could be realized by resonant chains of any length interconnected by intramolecular<sup>1b</sup> or intermolecular<sup>1c</sup> hydrogen bonds).

It is useful to note here that, though the three cases are chemically different, all produce a final situation where the two covalent bonds connecting the oxygens to their neighboring atoms become identical (single bonds in A, double bonds in B, and a 1:1 mixture of single and double bonds in C). The proof of the validity of the proposed hypothesis is therefore reduced to verifying the three following conditions:

**Condition 1.** All strong (short) hydrogen bonds belong to one of the three classes found.

**Condition 2.** Their length (measured, for instance, by the value of the  $\text{O}\cdots\text{O}$  contact distance) is correlated with a geometrical descriptor measuring how much the two covalent bonds formed by the oxygens with the non-H atoms are similar (or different).

The required geometrical descriptor can be found by considering the ground state of the fragment as a mixture of the canonical forms I and II according to  $\lambda\text{I} + (1 - \lambda)\text{II}$ , where the coupling parameter  $\lambda$  assumes the values of 1.0, 0.0, and 0.5 depending on whether the fragment geometry is that of I, II, or an exact

(10) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* 1979, 35, 2331.

mixture of the two forms, respectively. Writing I as  $\text{X}-\text{O}-\text{H}\cdots\text{O}=\text{X}$ , it is obtained<sup>1a</sup> that  $\lambda = [1 + Q/Q^0]/2$ , where  $Q = [d(\text{X}-\text{O}) - d(\text{X}=\text{O})]$  for the experimental bond distances, while  $Q^0$  is the same quantity for the standard pure single and double bonds.<sup>11</sup>

A final consideration concerns the mathematical form of the relationship linking  $r = d(\text{O}-\text{H})$  with  $r^* = d(\text{H}-\text{O})$  and, for linear  $\text{O}-\text{H}\cdots\text{O}$  bonds, with  $R = d(\text{O}\cdots\text{O})$ . Symmetrical three-center-four-electron  $\text{X}\cdots\text{Y}\cdots\text{X}$  bonds are known<sup>12a,b,3d</sup> to follow the bond number conservation rule  $n_1 + n_2 = 1$ , where  $n_1$  and  $n_2$  are the bond numbers of the  $\text{X}-\text{Y}$  and  $\text{Y}\cdots\text{X}$  bonds, respectively, and  $n$  is defined according to the Pauling formula<sup>12c</sup>  $\Delta d = -C \log_{10} n$ . It is easy to show that the relationships to be fulfilled by a linear homonuclear  $\text{O}\cdots\text{H}\cdots\text{O}$  system must be, for any  $r$ ,

$$r^* = r^0 - C \log_{10}(1 - 10^{-(r-r^0)/C}) \quad (2)$$

$$R = r + r^* \quad (3)$$

where  $r^0$  is the  $\text{O}-\text{H}$  distance in the absence of hydrogen bonding and  $C$  is a constant which can be calculated as  $C = [R_{\text{min}}/2 - r^0]/\log_{10} 2$ ,  $R_{\text{min}}$  being the shortest possible  $\text{O}\cdots\text{O}$  distance occurring when the proton is centered. Accordingly, only two values,  $r^0$  and  $R_{\text{min}}$ , can control the functional form of the  $r^*$  vs  $r$  and  $R$  vs  $r$  relationships, which leads to the third condition.

**Condition 3.** The most accurate neutron data on the hydrogen bond geometries must conform to eq 2 and, if the bond is linear or nearly linear ( $\text{O}-\text{H}\cdots\text{O}$  angle  $\geq 165^\circ$ ), also to eq 3. Possible discrepancies are to be interpreted as deviations from a complete covalency due to the electrostatic contribution.

#### Crystal Data Retrieval

Crystallographic data were retrieved from the Cambridge Crystallographic Database<sup>10</sup> (1993 release) on the basis of a search for neutron and X-ray organic and organometallic structures containing inter- or intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds with  $d(\text{O}\cdots\text{O}) \leq 2.69$  Å and having crystallographic discrepancy index  $R < 0.07$ , average standard deviations  $\sigma(\text{C}-\text{C}) < 0.008$ , no disorder in the group of interest, and refined hydroxyl protons. In the case of intermolecular bonds, only associations of identical molecules were taken into account (for example, cases of water bridges connecting two molecules were excluded). Likewise, cases where the two  $\text{O}-\text{H}\cdots\text{O}$  oxygens were further solvated were not examined. The search can be considered essentially exhaustive as far as the neutron data of short hydrogen bonds are concerned. X-ray data of good quality have been mainly used to cover the chemical classes for which neutron information was inadequate. For each  $\text{O}-\text{H}\cdots\text{O}$  bond, individual values of  $d(\text{O}\cdots\text{O})$  and  $\lambda$  were calculated; they have been deposited as supplementary Table S1 and are summarized in Table 1. The final  $\lambda$  vs  $d(\text{O}\cdots\text{O})$  scatter plot is shown in Figure 4.

In view of the low accuracy of X-ray determined  $\text{O}-\text{H}$  distances, only neutron data were used for the scatter plots  $d(\text{O}-\text{H})$  vs  $d(\text{H}\cdots\text{O})$  or  $d(\text{O}\cdots\text{O})$  in Figures 5 and 6. Only linear or nearly linear bonds were selected ( $\text{O}-\text{H}\cdots\text{O}$  angles  $\geq 165^\circ$ ); complete data have been deposited as supplementary Table S2. A few neutron structures of inorganic compounds (hydrogen phosphates and sulphates) have been added to show that the present discussion is not confined to organic molecules. However, since  $\lambda$  values cannot be easily calculated for tetrahedral ions, these data were used only for drawing Figures 5 and 6.

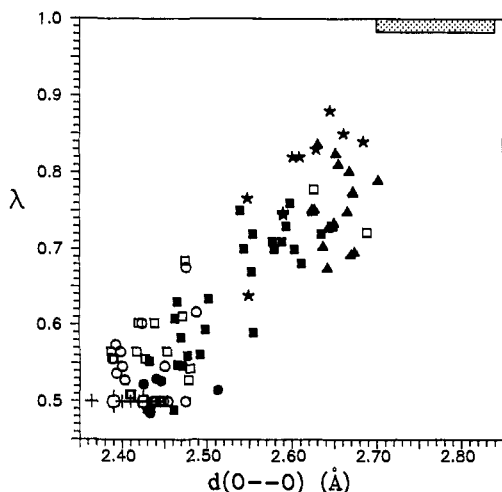
(11) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *Chem. Soc., Perkin Trans. 2*, 1987, S1. (b) In  $\beta$ -diketone enols  $\text{O}=\text{C}-\text{C}=\text{C}-\text{OH}$ ,  $Q$  (and  $Q^0$ ) can be calculated<sup>1a</sup> with greater accuracy by taking into account also  $\text{C}-\text{C}$  distances, that is,  $Q = [d(\text{C}=\text{O}) - d(\text{C}=\text{O}) + d(\text{C}-\text{C}) - d(\text{C}=\text{C})]$ .

(12) (a) Bürgi, H. B. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 460. (b) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* 1983, 16, 153. (c) Pauling, L. *J. Am. Chem. Soc.* 1947, 69, 542.

**Table 1.** Summary of Chemical Classes Where Strong Hydrogen Bonding Occurs<sup>a</sup>

class <sup>b</sup>	HB	sample	<i>d</i> (O...O) range	$\lambda$ range	chemical schemes	
					formula	ref
A1a. carboxylic acid-carboxylates	i	9N, 4X	2.44-2.49	0.50-0.68	A1.1, A1.2	15a,b
A1b. carboxylic acid-carboxylates	I	7N	2.39-2.42	0.53-0.60	A1.3, A1.4	15c,d
A2a. metal oximes	I	6N, 3X	2.39-2.48	0.56-0.61	A2.1	15e
A2b. metal glyoximes	I	5X	2.44-2.69	0.54-0.78	A2.2	15f
A3. alcohol-alcoholates	i	1N, 1X	2.39-2.43	0.5 <sup>c</sup>	A3.1	15g
A4. water-hydroxyl	i	2X	2.41-2.44	0.5 <sup>c</sup>	A4.1	15h
A5. inorganic acid salts	i	9N	2.36-2.43	n.c. <sup>d</sup>	A5.1, A5.2	15i,j
B. O...H...O	i	3N, 4X	2.36-2.43	0.5 <sup>c</sup>	B.1-B.4	15k-n
C1a. $\beta$ -diketone enols	I	1N, 10X	2.43-2.55	0.51-0.72	C1.1	15o
C1b. $\beta$ -diketone enols	i	2N, 14X	2.46-2.65	0.56-0.76	C1.2	15p
C2. $\beta$ -keto ester or ketoamide enols	i	1N, 9X	2.55-2.69	0.64-0.88	C2.1	15q
C3. $\delta$ -diketone enols	I	2X	2.42-2.44	0.52-0.53	C3.1	15r
C4. $\zeta$ -diketone enols	I	4X	2.43-2.51	0.51-0.53	C4.1	15s
C5a. carboxylic acids (chains)	i	1N, 6X	2.62-2.70	0.74-0.84	C5.1	15t
C5b. carboxylic acids (dimers)	i	4N, 6X	2.62-2.67	0.68-0.83	C5.2	15u
D. alcohols and saccharides	any		2.77 $\pm$ 0.07	1.0		9

<sup>a</sup> Class D is reported for comparison. HB = i(inter), I(intra). Sample = number of neutron (N) and X-ray (X) structures considered.  $\lambda$  is defined in the text. The *d*(O...O) range is in Å. <sup>b</sup> A1.1 = KH bis(trifluoroacetate); A1.2 = KH succinate; A1.3 = imidazolium maleate; A1.4 = pyridine-2,3-dicarboxylic acid; A2.1 = bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride; A2.2 =  $\alpha$ -bis(1,2-benzoquinone dioximato)palladium(II); A3.1 = Na<sub>3</sub>H<sub>3</sub> bis[tris(glycolato)aluminatate(III)]; A4.1 = tetrakis(ethylenediamine-*N,N'*)( $\mu^2$ -hydroxo-aqua-*O,O'*-dinitrodicobalt(III) triperchlorate); A5.1 = Na<sub>2</sub>H(SO<sub>4</sub>)<sub>2</sub>; A5.2 = Sn<sup>II</sup>HPO<sub>4</sub>; B.1 = *trans*-[H(Me<sub>2</sub>SO)<sub>2</sub>][Rh<sup>III</sup>Cl<sub>4</sub>(Me<sub>2</sub>SO)<sub>2</sub>]; B.2 = H bis(pyridine *N*-oxide) tetrachloroaurate(III); B.3 = H bis(*N,N*-dimethylacetamide) tetrachloroaurate(III); B.4 = [V<sup>III</sup>(H<sub>2</sub>O)<sub>6</sub>][H<sub>2</sub>O<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>; C1.1 = 1,3-diphenyl-1,3-propanedione enol; C1.2 = 1,3-cyclohexanedione enol; C2.1 =  $\alpha$ -methyltetric acid; C3.1 = 4-((5-hydroxy-1,3-dimethyl-4-pyrazolyl)methylene)-1,3-dimethyl-2-pyrazolin-5-one; C4.1 = 4,5-diacetyl-2-nitrocyclopentadiene; C5.1 = acetic acid; C5.2 = trichloroacetic acid. <sup>c</sup> Assumed for symmetry. <sup>d</sup>  $\lambda$  not computable.



**Figure 4.** Scatter plot of the coupling parameter  $\lambda$  as a function of the O...O distance (*R*) for all the chemical classes listed in Table 1. Class symbols: A1 = open circles; A2 = open squares; A3 and A4 = larger open circles; B = crosses; C1 = full squares; C2 = stars; C3 and C4 = full circles; C5 = triangles; D = shaded upper right rectangle.

Short and very short hydrogen bonds are actually observed exclusively in connection with a limited number of chemical situations that can be easily reduced to the three main classes A, B, and C outlined in Figure 3. Each class can be further subdivided into more homogeneous chemical classes as shown in Table 1 and illustrated in the PLUTO<sup>13</sup> drawings of Charts 1-3.

A very limited number of structures accomplishing the general conditions given above but being outliers in Figures 4-6 were left out for specific chemical reasons. They include (i) four cases<sup>14a</sup> of carboxylic acid-carboxylates (class A1) where the hydrogen bonds are perturbed by short-range interactions with strongly

(13) Motherwell, W. D. S.; Clegg, W. *PLUTO: Program for Plotting Molecular and Crystal Structures*; University of Cambridge: Cambridge, England, 1978.

(14) (a) KH oxydiacetate: Albertson, J.; Grenthe, I. *Acta Crystallogr., Sect. B* 1973, 29, 2751. KH dicrotonate: McGregor, D. R.; Speakman, J. C.; Lehman, M. S. *J. Chem. Soc. A* 1977, 1740. NH<sub>4</sub><sup>+</sup> tetraoxalato-2H<sub>2</sub>O: Currie, M.; Speakman, J. C.; Curry, N. A. *J. Chem. Soc. A* 1967, 1862. KH bis(dichloroacetate): Hadzi, D.; Leban, I.; Orel, B.; Iwata, M.; Williams, J. M. *J. Cryst. Mol. Struct.* 1979, 9, 117. (b) CaHPO<sub>4</sub>: Catti, M.; Ferraris, G.; Filhol, A. *Acta Crystallogr., Sect. B* 1977, 33, 1223.

and asymmetrically coordinated cations and (ii) the structure of CaHPO<sub>4</sub><sup>14b</sup> (class A5: inorganic acid salts) where the Ca<sup>2+</sup> ion is strictly coordinated to the hydrogen bond bridge.

Finally, data for  $\beta$ -diketone enols (class C1) and  $\beta$ -keto esters (class C2) are taken from our previous papers,<sup>1</sup> and the average values for alcohols and saccharides (class D), from the literature.<sup>9</sup> In this last class of compounds, the hydrogen bond established is unable of modifying the adjacent covalent bond distances and, accordingly, a  $\lambda$  value of 1.0 has been assumed.

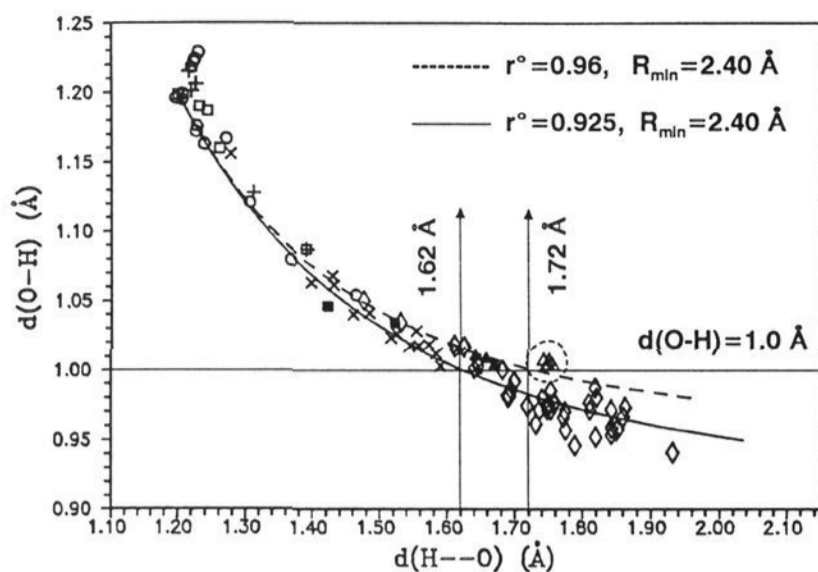
## Discussion

A limited number of chemical classes have been found able to form short ( $2.50 \leq R \leq 2.65$  Å) or very short ( $R < 2.50$  Å) homonuclear O—H...O bonds. They are listed as classes A-C in Table 1 together with their ranges of observed  $\lambda$ , *d*(O...O) values, and the total number of neutron or X-ray crystal structures used in the analysis. Charts 1-3 collect molecular sketches for all the chemical situations encountered.

It is evident that all cases found can be divided in the three main classes underlined in Figure 3 and fulfilling Condition 1, i.e. (A) negative charge assisted hydrogen bonds [(-)CAHB]; (B) positive charge assisted hydrogen bonds [(+)CAHB]; and (C)  $\pi$ -resonance assisted hydrogen bonds [RAHB].

Also Condition 2 turns out to be fulfilled, as shown by the scatter plot of Figure 4: *d*(O...O) distances monotonically shorten

(15) (a) Macdonald, A. L.; Speakman, J. C.; Hadzi, D. *J. Chem. Soc., Perkin Trans. 2* 1972, 825. (b) McAdam, A.; Currie, M.; Speakman, J. C. *J. Chem. Soc. A* 1971, 1994. (c) Hsu, B.; Schlemper, E. O. *Acta Crystallogr., Sect. B* 1980, 36, 3017. (d) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr., Sect. B* 1978, 34, 1149. (e) Schlemper, E. O.; Hamilton, W. C.; La Placa, S. J. *J. Chem. Phys.* 1971, 54, 3990. (f) Kistenmacher, T. J.; Destro, R. *Inorg. Chem.* 1983, 22, 2104. (g) van Koningsveld, H.; Vevema, F. R. *Acta Crystallogr., Sect. C* 1991, 47, 289. (h) Adrdon, M.; Bino, A. J.; Jackson, W. G. *Polyhedron* 1987, 6, 181. (i) Joswig, W.; Fuess, H.; Ferraris, G. *Acta Crystallogr., Sect. B* 1982, 38, 2798. (j) Schroeder, L. W.; Prince, E. *Acta Crystallogr., Sect. B* 1976, 32, 3309. (k) James, B. R.; Morris, R. H.; Einstein, F. W. B.; Willis, A. J. *J. Chem. Soc., Chem. Commun.* 1980, 31. (l) Hussain, M. S.; Schlemper, E. O. *J. Chem. Soc., Dalton Trans.* 1982, 751. (m) Hussain, M. S.; Schlemper, E. O. *J. Chem. Soc., Dalton Trans.* 1980, 750. (n) Cotton, F. A.; Fair, C. K.; Lewis, G. E.; Mott, G. N.; Ross, F. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* 1984, 106, 5319. (o) Jones, R. D. G. *Acta Crystallogr., Sect. B* 1976, 32, 1807. (p) Etter, M. C.; Urbanczyk-Lipkowska, Z.; Jahn, D. A.; Frye, J. S. *J. Am. Chem. Soc.* 1986, 108, 5871. (q) Krog Andersen, E.; Krog Andersen, I. G. *Acta Crystallogr., Sect. B* 1975, 31, 394. (r) Druck, U.; Littke, W. *Acta Crystallogr., Sect. B* 1980, 36, 3002. (s) Ferguson, G.; Marsh, W. C.; Restivo, R. J.; Lloyd, D. *J. Chem. Soc., Perkin Trans. 2* 1975, 998. (t) Jönsson, P.-G. *Acta Crystallogr., Sect. B* 1971, 27, 893. (u) Jönsson, P.-G.; Hamilton, W. C. *J. Chem. Phys.* 1972, 56, 4433.



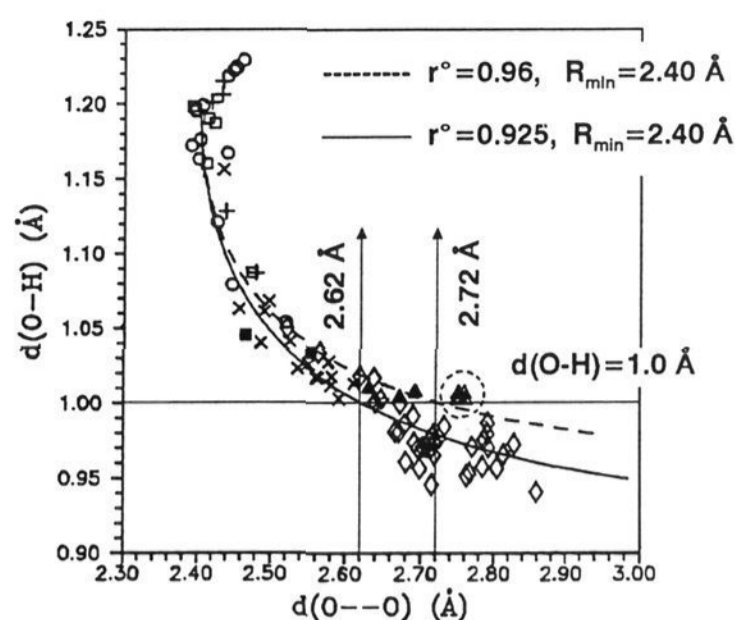
**Figure 5.** Scatter plot of  $r = d(\text{O}-\text{H})$  as a function of  $r^* = d(\text{H}-\text{O})$  for selected neutron diffraction data of  $\text{O}-\text{H}\cdots\text{O}$  bonds with  $\text{O}-\text{H}-\text{O} \geq 165^\circ$  (all standard deviations  $\leq 0.01$  Å). The continuous and dashed curves are interpolations according to eq 2 using  $(R_{\min}, r^\circ)$  values of (2.40, 0.925 Å) and (2.40, 0.96 Å), respectively. Class symbols: A1 = open circles; A2 = open squares; A5 = diagonal crosses; B = vertical crosses; C1 = full squares; C5 = full triangles; Alcohols, saccharides, nonresonant acids and aminoacids = open lozenges; ice Ih = open triangles encircled by a dashed line. Horizontal and vertical lines indicate that a totally covalent  $\text{O}-\text{H}\cdots\text{O}$  bond with  $d(\text{O}-\text{H}) = 1$  Å would have a  $d(\text{H}-\text{O})$  distance of 1.72 Å, which is reduced to the actual value of 1.62 Å by the electrostatic interaction term (see text).

from 2.80 to some 2.40 Å while the coupling parameter  $\lambda$  decreases from 1.0 to 0.5, that is, while the resonance forms I and II become progressively identical and their contributions to the fundamental state equal. This confirms, in agreement with the stated hypothesis, that the degree of covalency in the homonuclear  $\text{O}-\text{H}\cdots\text{O}$  bond is continuously increasing with the shortening of the bond itself and that very short hydrogen bonds are to be considered totally delocalized three-center-four-electron covalent bonds. Since the establishment of such covalent interaction implies bond energies much higher than the simple electrostatic attraction (see Figure 2), this result seems to confirm that very short and very strong hydrogen bonds are the same, at least for the homonuclear case, and that the strength-length relationship<sup>4</sup> must hold for the complete range of  $d(\text{O}\cdots\text{O})$  distances.

Similar considerations arise from the analysis of the scatter plots of  $r^* = d(\text{H}-\text{O})$  or  $R = d(\text{O}\cdots\text{O})$  vs  $r = d(\text{O}-\text{H})$  reported in Figures 5 and 6, respectively. According to Condition 3, it should be possible to fit the experimental points by means of eqs 2 and 3. As a matter of fact, making due allowance of the dispersion of the experimental points, this turns out to be feasible (continuous curves in Figures 5 and 6) by using values of 2.40 and 0.925 Å, respectively, for  $R_{\min}$ , the shortest hydrogen bond  $\text{O}\cdots\text{O}$  contact distance, and  $r^\circ$ , the shortest  $\text{O}-\text{H}$  distance in the absence of hydrogen bonding.<sup>16</sup> While 2.40 Å is a quite reasonable value for  $R_{\min}$  (see Table 1 and Figure 4), that of 0.925 Å for  $r^\circ$  is definitely too short when compared with the gas electron diffraction values<sup>17</sup> of 0.95–0.96 Å. On the other hand, a similar fitting carried out with the values  $R_{\min} = 2.40$  and  $r^\circ = 0.96$  Å gives curves (dashed lines in Figures 5 and 6) which are seen to be too high for long bonds. Such an inconsistency is more apparent than real, however, as can be illustrated by an example. The dashed curves are derived from the application of Pauling equation to a purely covalent three-center-four-electron bond ( $E_{\text{EL}} = 0$  in

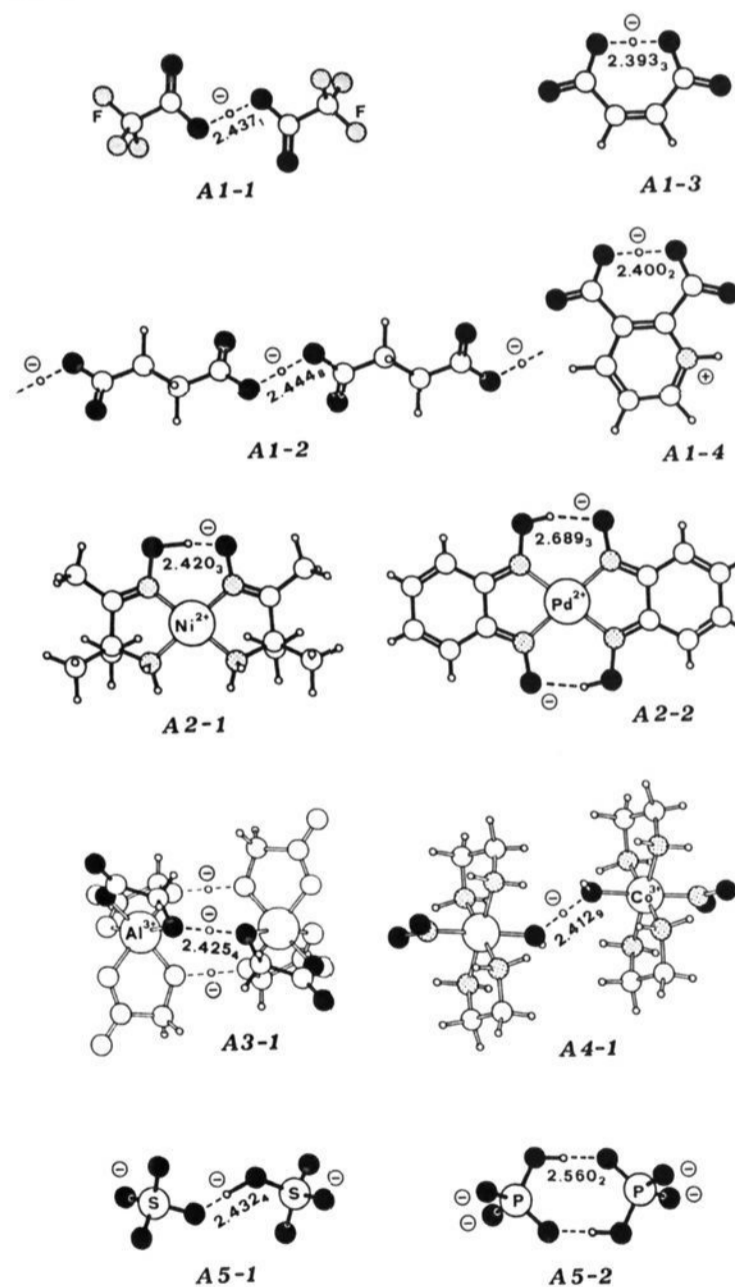
(16) The open triangles encircled by dashed lines in Figures 5 and 6 represent the results of neutron diffraction studies on ice Ih at three different temperatures (60, 123, and 223 K): Kuhs, W. F.; Lehmann, M. S. *Nature (London)* **1981**, *294*, 432. Kuhs, W.; Lehmann, M. S. *J. Phys. Chem.* **1983**, *87*, 4312. It is interesting to remark that ice displays longer  $\text{O}-\text{H}$  distances for given  $\text{H}-\text{O}$  or  $\text{O}\cdots\text{O}$  distances than most other compounds, probably because of its 4-fold connectivity.

(17) Vajda, E.; Hargittai, I. *J. Phys. Chem.* **1992**, *96*, 5843. Portalone, G.; Schultz, G.; Domenicano, A.; Hargittai, I. *Chem. Phys. Lett.* **1992**, *197*, 482.



**Figure 6.** Scatter plot of  $r = d(\text{O}-\text{H})$  as a function of  $R = d(\text{O}\cdots\text{O})$  for selected neutron diffraction data of Figure 5. The continuous and dashed curves are interpolations according to eq 3 using  $(R_{\min}, r^\circ)$  values of (2.40, 0.925 Å) and (2.40, 0.96 Å), respectively. Class symbols are as in the caption of Figure 5. Horizontal and vertical lines have the same meaning as in Figure 5 but referred to  $d(\text{O}-\text{H})$  and  $d(\text{O}\cdots\text{O})$  distances (see text).

### Chart 1



eq 1); their interpolation for a  $\text{O}-\text{H}\cdots\text{O}$  bond with  $r$  equal to, say, 1 Å gives  $r^* = 1.72$  (Figure 5) and  $R = 2.72$  Å (Figure 6), which would be the correct  $d(\text{H}-\text{O})$  and  $d(\text{O}\cdots\text{O})$  distances if the hydrogen bond were totally covalent. These values, however, will be further decreased by the contribution of the  $E_{\text{EL}}$  electrostatic attraction term and are in fact reduced to the corresponding values of 1.62 and 2.62 Å, which can be interpolated, still for  $r = 1$  Å, on the close continuous curves.

Chart 2

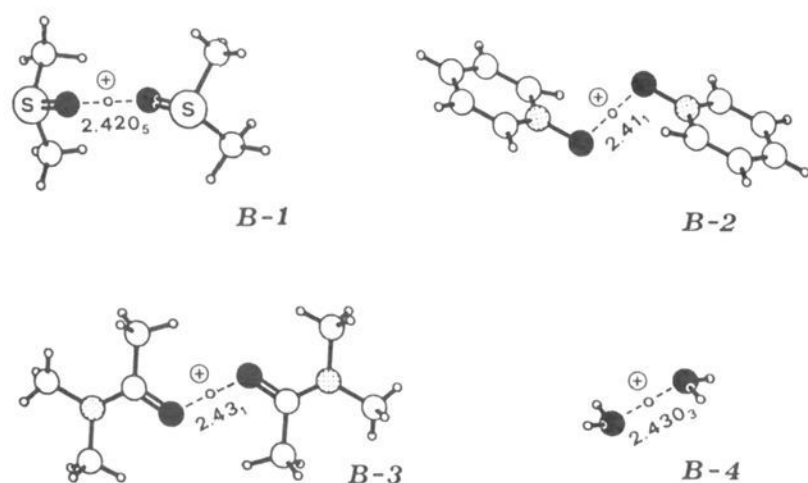
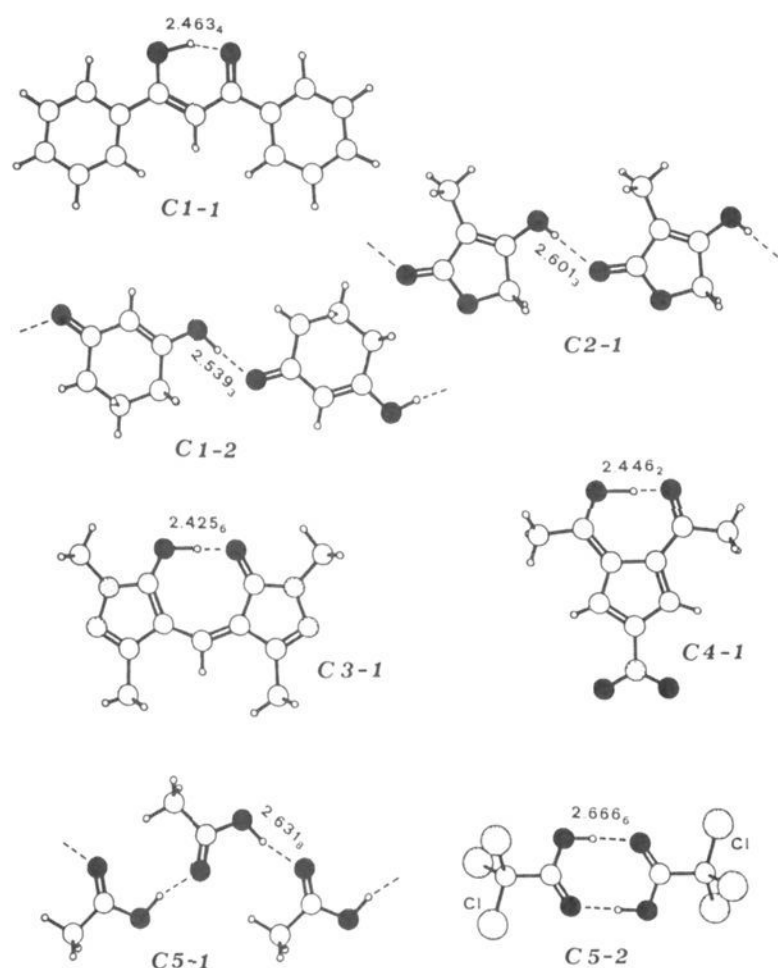


Chart 3



The example can be generalized by saying that, for any specific  $r$  value, the dashed curves represent the contribution of the covalent term ( $E_{cov}$ ) to the geometry of the hydrogen bond (that is, its value of  $r^*$  in Figure 5 and of  $R$  in Figure 6), while the horizontal displacements between the dashed and the continuous curves are a measure of the further contribution given by the electrostatic attraction term ( $E_{EL}$ ). Such horizontal displacements are rather large for long hydrogen bonds which, accordingly, can be considered mostly electrostatic in nature, but rapidly decrease for shorter bonds and, when  $R = d(O\cdots O)$  becomes smaller than 2.45–2.50 Å (see Figure 6), the dashed and continuous curves are seen to converge, indicating that the hydrogen bond can be considered essentially covalent.

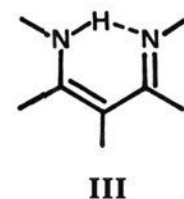
The increased degree of covalency causes a remarkable lengthening of the O—H bond, and all the shortest hydrogen bonds ( $2.39 \leq R \leq 2.44$  Å; Figures 5 and 6) display more or less perfectly centered protons typical of the symmetrical O—H—O geometry. The possibility of achieving such final symmetry seems to play a crucial role in the establishment of very strong O—H—O bonds. Conversely, the role played by acid–base properties seems to be almost irrelevant because O—H—O complexes as different as carboxylic acid–carboxylates (class A1), oxime–oximates (class A2), and alcohol–alcoholates (class A3) give comparably short O—H—O bonds ( $2.39 \leq R \leq 2.43$  Å; Table 1). Likewise, O—H<sup>+</sup>—O (class B) interactions have

O—O distances in the restricted range 2.36–2.43 Å, irrespective of the electron donor properties of the linked molecules.

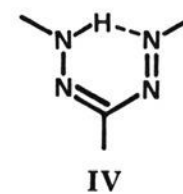
It seems reasonable to assume that, if such symmetry is broken and the two resonant forms I and II can no longer be equivalent, the covalent contribution will be decreased or lost and the hydrogen bond will be reduced to a weaker electrostatic interaction. Symmetry is certainly broken in the heteronuclear X—H—Y ( $X \neq Y$ ) bond, and this suggests the not trivial conclusion that *homonuclear and heteronuclear hydrogen bonds must have different properties, in particular as their covalent part is concerned, while different homonuclear hydrogen bonds ( $X = Y$ ) should display similar behavior.*<sup>18</sup>

Verification of this hypothesis by extended comparison of O—H—O, N—H—N, and N—H—O bonds is in progress in our laboratory, and preliminary results seem to show that it is not manifestly unfounded. In a recent book<sup>19a</sup> Jeffrey and Saenger remark that “Unlike the O—H—O bonds, there are no examples for strong N—H—O hydrogen bonds.” This statement, though perhaps too conclusive, is clearly consistent with the idea of a hindered covalency occurring in heteronuclear hydrogen bonds. This hindering is more convincingly proved by neutron diffraction studies<sup>19b</sup> on the N—H—O system, showing that the N—H bond can be only slightly stretched by hydrogen bond formation (from 1.01 to 1.06 Å) in spite of the strong electronegativities of the donor and acceptor atoms involved.

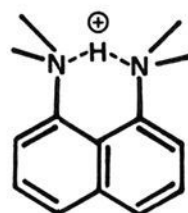
The situation is reversed in the homonuclear N—H—N bonds which, not differently from the O—H—O bonds, can give very short resonance-assisted (N—N distances of 2.65<sup>20a</sup> in enaminimine III and 2.57 Å<sup>20b</sup> in *cis*-formazan IV) or positive charge



III



IV



V



VI

assisted hydrogen bonds (N—N distances of 2.54–2.65 Å and 2.53–2.60 Å in *proton sponges* of aromatic V or intrabridgehead VI type<sup>20c,d</sup>) displaying elongated N—H bonds and even centered protons. Likewise difluoride anions are well-known to form homonuclear F—H—F bonds which are extremely short (F—F distances of 2.264 Å in NaHF<sub>2</sub>, 2.265 Å in NaDF<sub>2</sub>,<sup>21a</sup> and 2.277 Å in KHF<sub>2</sub><sup>21b</sup>) and have essentially symmetrical proton or deutron positions. Interestingly, these very difluoride anions were used

(18) It is interesting to remark that not only heteronuclearity weakens the hydrogen bond but also heteromolecularity does. For instance, the gas-phase dissociation enthalpy<sup>4b</sup> of HCOO—HOOCH is 36.8 kcal mol<sup>-1</sup> while those of HCOO—HOH and HCOO—HOCH<sub>3</sub> are 16.0 and 17.6 kcal mol<sup>-1</sup>, respectively; analogously, the enthalpy of H<sub>2</sub>O—H<sup>+</sup>—OH<sub>2</sub> is 31.6 and that of (CH<sub>3</sub>)<sub>2</sub>O—H<sup>+</sup>—OH<sub>2</sub> 24.0 kcal mol<sup>-1</sup>. In general, Meot-Ner (Mautner) and co-workers<sup>4b</sup> were able to show that the dissociation enthalpies of many O—H—O and O—H<sup>+</sup>—O hydrogen bonds linearly decrease with the increasing differences of proton affinities ( $\Delta PA$ ) of the two linked molecules, which is in perfect agreement with our previous conclusions.

(19) (a) Reference 2d, Chapter 7, p 128. (b) Olovsson, I.; Jönsson, P.-G. In ref 2c, Chapter 8, p 412.

(20) (a) Furmanova, N. G.; Kompan, O. E.; Strutchkov, Yu. T.; Michailov, I. E.; Oleckhnovich, L. P.; Minkin, V. I. *Zh. Strukt. Khim.* **1980**, *21*, 98. (b) Cunningham, C. W.; Burns, G. R.; McKee, V. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1429. (c) Staab, H. A.; Saupe, T. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 865. (d) Alder, R. W. *Tetrahedron* **1990**, *46*, 683.

(21) (a) McGraw, B. L.; Ibers, J. A.; *J. Chem. Phys.* **1963**, 2677. (b) Ibers, J. A. *J. Chem. Phys.* **1964**, *40*, 402.

by Coulson<sup>22</sup> as a base for the suggestion that hydrogen bonds between very electronegative donor and acceptor atoms resemble covalent bonds, at variance with those implying weakly electronegative atoms which are primarily electrostatic. Present findings seem to confirm this early hypothesis, extending it to the other homonuclear N—H...N and O—H...O hydrogen bonds.

**Acknowledgment.** We thank the Ministero Università e Ricerca Scientifica e Tecnologica, Italy, for financial support within the

(22) Coulson, C. A. *Valence*; Oxford University Press: Oxford, U.K., 1952. McWeeney, R. *Coulson's Valence*; Oxford University Press: Oxford, U.K., 1979.

scheme of its 40% program and the Cambridge Crystallographic Data Centre for having made available their most recent programs and given hospitality to P.G.

**Supplementary Material Available:** Tables S1 and S2 reporting references and O—H...O geometrical parameters of all crystal structures used in the present analysis (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.