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ON SYMMETRICAL O-H-O HYDROGEN BONDS (1)

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Résumé. — Plusieurs liaisons d'hydrogène avec des longueurs de liaison H-O-H d'environ 2,4 Å sont maintenant connues. Parmi celles-ci, certaines ont été examinées par diffraction neutronique et par d'autres moyens avec une précision suffisante pour reconnaître qu'il s'agit de liaison d'hydrogène symétriques avec un maximum de densité simple ou double et symétrique. Les résultats mêmes de diffraction neutronique ne peuvent décider si la distribution a un maximum simple ou double.

Plusieurs expérimentateurs ont rapporté des liaisons cristallographiquement symétriques O-H-O avec des distances d'environ 2,5 — 2,6 Å. Les amplitudes thermiques de quelques-unes d'entre elles ont été étudiées avec soin, et la plupart de ces liaisons longues semblent être vraiment, et non pas statistiquement symétriques. Il semble probable que les liaisons d'environ 2,4 Å sont des distributions avec de simples maxima tandis que les liaisons d'hydrogène plus longues, apparemment symétriques sont des cas de double maxima. Toute évidence obtenue par des études dans l'infrarouge et par résonance magnétique nucléaire qu'il y ait des liaisons O-H-O simples symétriques aussi longues que 2,6 Å devrait être soigneusement vérifiée avant d'être acceptée.

Quelques calculs théoriques de distribution d'hydrogène dans des puits de potentiel simples et doubles montrent que les cas des maxima doubles devraient avoir un effet isotopique prononcé avec une distance O-H-O plus courte que O-D-O tandis que les cas des maxima simples n'auraient pas d'effet isotopique appréciable.

Avec la précision actuelle dans les déterminations de structure, une distribution entre les deux cas semble possible, avec ou sans l'aide de diffraction neutronique. Afin d'illustrer la possibilité d'obtenir des longueurs de liaison avec une précision de 0,01 Å, et cela avec des techniques de routine, mentionnons l'exemple de la structure de l'acide 3-4 furan-dicarboxylique, déterminée avec cette précision, grâce à des données expérimentales, obtenues en 10 jours.

Abstract. — Several hydrogen bonds with O-H-O bond lengths of about 2.4 Å are now known. Some of these have been examined well enough by neutron diffraction and other means to know with reasonable certainty that they are symmetrical hydrogen bonds, with either a single or a symmetrical double distribution peak. Even neutron diffraction results remain ambiguous as to whether the distribution has a single or double maximum.

Several investigators have reported crystallographically symmetrical O-H-O hydrogen bonds with distances of about 2.5 — 2.6 Å. Thermal amplitudes of some of these have been given careful study, and most of these longer bonds appear to be truly, not statistically, symmetrical.

It seems likely that the bonds of about 2.4 Å are distributions with single maxima, while the longer, apparently symmetrical hydrogen bonds are cases of double maxima. IR and NMR evidence that there are O-H-O bonds as long as 2.6 Å with single maxima should be carefully checked before they are accepted.

From some theoretical calculation of hydrogen distributions in double and single wells it can be shown that cases with double maxima have a strong isotope effect with a shorter O-H-O distance than O-D-O distance, while cases with single maxima should show almost no isotope effect. With present accuracy in structure determinations a distinction between the two cases seems possible with or without the use of neutron diffraction. As an example that bond distances reliable to ~ 0.01 Å are now obtainable in nearly routine fashion, the structure of 3, 4-furandicarboxylic acid was determined to about this accuracy with data obtained in ten days.

Introduction. — Since 1948 there have been reports of symmetrical O-H-O hydrogen bonds [1]. The first reports [2, 3] involved rather long distances, and it was easy to suppose, and in better agreement with ideas then prevailing, that these bonds were only statistically symmetrical. The X-ray structure determinations at that time did not eliminate this viewpoint.

In 1951 a very short hydrogen bond (2.42 Å) was found [4], along with an IR spectrum [5] which

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led to a more reasonable expectation that a truly symmetric hydrogen bond had been found. (Since that time a refined structure determination has shown this hydrogen bond, in nickel dimethylglyoxime, to have the distance $2.40 \pm .015$ Å [6].)

Along with the discovery of this very short hydrogen bond came the discovery of a remarkable lowering of the O-H stretching frequency with distance [5], a lowering which was quickly confirmed by several groups of spectroscopists [7, 8, 9]. Also, several other very short hydrogen bonds have been found, and X-ray, spectroscopic, NMR and espe-

cially neutron diffraction studies have tended to show that at least some of these are probably symmetrical. Several of these studies are referred to in Tables I and II. The field has expanded so rapidly in recent years that a review requires a book rather than a paper, and it is fortunate that several lengthy reviews are available [10, 11, 12].

For some time it appeared reasonable to believe that the very short hydrogen bonds from, say, 2.40 to ~ 2.45 Å were symmetrical, while the longer bonds were probably at best statistically symmetrical. The careful neutron diffraction study of potassium diphenylacetate at two temperatures provides, however, rather strong evidence that the hydrogen bond in KH diphenylacetate may be symmetrical, with the hydrogen centered in a single potential well, even though the O-H-O distance is 2.54 ± 0.02 Å [13].

There is now considerable data, much of it due to Speakman and his collaborators [14], for crystallographically symmetrical hydrogen bonds in a large group of acid salts, varying in distance from 2.61 or even 2.69 Å (in KH bis-p-hydroxy benzoate) to 2.41 Å (NaH diacetate). For the very long bonds it is unlikely that the hydrogen is in a centered distribution, and the possibilities of symmetrical double wells along with statistical averaging have been considered, especially by Hadzi, *et al.* It is unfortunate that neutron diffraction results, particularly for the short O-H-O bonds,

are rather insensitive to the difference between distributions with single and double maxima for hydrogen or deuterium because of the relatively large thermal amplitude of hydrogen or deuterium along the bond [13, 15].

In order to try to differentiate between double maxima and single maxima symmetric hydrogen bonds, Hadzi has looked for and apparently found transitions in the far infrared (near 120-150 cm^{-1}) corresponding to transitions between the lowest symmetrical and asymmetric vibrational levels for double maxima hydrogen bonds, as well as doublets for the transition to the next symmetric and asymmetric levels [16]. Blinc and Hadzi have also found hydrogen bonds with shorter and longer relaxation times in NMR spectra which they ascribe to double maxima and single maximum hydrogen bonds, respectively [17]. In a summary [18], Blinc, Hadzi and Novak (hereafter BHN) cite evidence for four types of hydrogen bonds: A. Symmetrical, single maximum, B. Symmetrical or asymmetric double-maximum with low barrier, C. Symmetrical or asymmetric double maximum with a high barrier, D. Asymmetric single maximum. Though this must be correct in general, BHN reach the surprising conclusion that single maximum symmetric hydrogen bonds may exist for O-H-O distances as long as 2.61 Å, and the less surprising conclusion that symmetrical double maxima may exist for distances as short as 2.48 Å.

TABLE I

TYPE-A HYDROGEN BONDS ACCORDING TO BHN

COMPOUND	ν OH	ν OD	O-H-O, Å	REFERENCES	
				DISTANCE	ν
KH Maleate	1 700	1 420	2.44	[14]	[19]
NaH Diacetate	1 700	1 320	2.41	[13]	[19]
KH Dibenzoate	1 700	1 390	2.50	[13]	[19]
KH Diphenylacetate	1 715	1 370	2.54	[13, 12]	[19]
KH Malonate	1 663	1 330	unk.	—	[19]
KH Glutamate	1 650	1 320	»	—	[19]
KH Succinate	1 700	1 330	»	—	[19]
KH Adipate	1 700	1 400	»	—	[19]
KH Fumarate	1 675	1 370	»	—	[19]

In Table I the information on type A-hydrogen bonds is reproduced. It can be seen (Table II) that BHN have accepted very few of the very short hydrogen bonds as symmetric, and that their evidence for long (2.50 Å or greater) hydrogen bonds with single maxima is limited to three compounds.

Apparently the IR and NMR methods used by BHN in assigning the nature of hydrogen bonds leave in doubt the character of many very short hydrogen bonds [18] (see Table II). One wonders

whether enough cases have been examined to generalize. In other cases other observations are capable of providing very good evidence for symmetrical single-maximum hydrogen bonds for distances near 2.4 Å.

For example, nickel and palladium dimethylglyoximes are very nearly isostructural, but the former has a hydrogen bond of 2.40 Å, and an apparent molecular symmetry of D_{2h} , while the latter has a hydrogen bond of 2.59 Å, and an apparent molecular symmetry of only C_{2h} [6]. If

TABLE II
OTHER SHORT HYDROGEN BONDS

COMPOUND	O-H-O, Å	REFERENCE
Ni dimethylglyoxime	2.40 ± 0.015	[6]
Acetamide hemihydrochloride	2.40 ± 0.02	[20]
RbH bis p-nitrobenzoate	2.43 ± 0.02	[14, e]
KH Maleate	2.44 ± 0.02	[15]
NH ₄ H disalicylate	2.45 ± 0.02	[14, d]
HCoO ₂	2.45 ⁽²⁾ (2.36)	[21]
Maleic acid	2.46 ± 0.02	[22]
KH ₂ PO ₄ ⁽³⁾	2.48 ± 0.01	[23]
NH ₄ H ₂ PO ₄ ⁽³⁾	2.49 ± 0.02	[24]
HCrO ₂	2.49 (O-H-O) ; 2.55 (O-D-O) ± 0.02 ⁽⁴⁾	[25, 35]
Oxalic acid dihydrate	2.49 ± 0.02	[26, a]
HNO ₃ ·3H ₂ O	2.49 ± 0.02	[26]
αAlOOH (boehmite)	2.47 ± 0.07	[27]

⁽²⁾ Based on calculations from the isomorphous HCrO₂ structure, assuming Co-O is 0.03 Å < Cr-O. Authors give 2.36 Å, but had very little data.

⁽³⁾ Structure shows well must be asymmetric.

⁽⁴⁾ Structure shows evidence for single-maximum symmetric hydrogen bond and double maximum symmetric deuterium bond.

these symmetries, obtained from well refined X-ray data, are correct, then the hydrogen bond is symmetric in the former, asymmetric in the latter. The IR spectra of the two crystals support rather

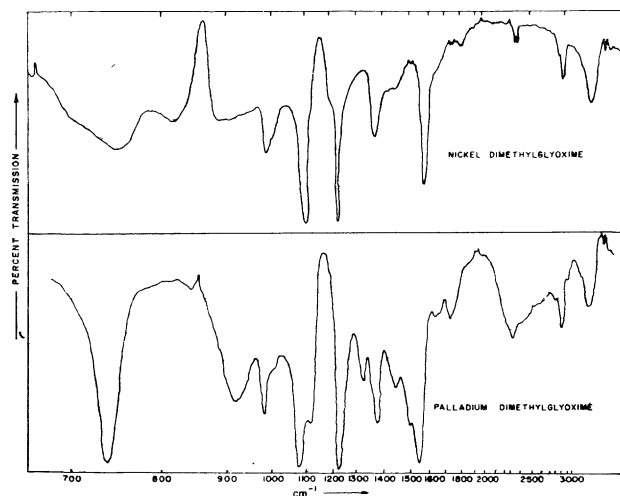


FIG. 1. — Infrared transmission spectra for nickel dimethylglyoxime (above) and palladium dimethylglyoxime [27]. It is to be noted that many of the single peaks in the nickel compound split into doublets or multiplets for the palladium compound. The X-ray structures [6] suggest that this arises from a change in molecular symmetry from D_{2h} to C_{2h}.

dramatically a lower symmetry for the palladium compound, as shown in figure 1 [27]. It is to be noted that longer distances, not inherently different fields, cause this difference.

Since far infrared spectra present some difficulties in interpretation, and suffer from the fact that the corresponding transitions for O-D-O have not yet been observed, since most unit cells contain more than one equivalent O-H-O so that a strictly molecular interpretation is too simple, and since the way in which crystalline interactions may affect relaxation processes is not fully understood, it would be well to have another method for checking the conclusions reached by IR and NMR.

Moreover, these methods have led to certain conclusions which should be well checked before they are accepted. For example, since all free O-H bonds give comparable stretching and bending frequencies, and show other signs of similarity, it would be surprising if they did not follow some such treatment as that made by Schroeder and Lippincott [28], so that potential wells are better correlated with O-H-O distances than suggested by recent work [17, 18, 19].

In this paper a different method of attack on finding whether symmetrical hydrogen bonds have single or double maxima is suggested. It arose from attempts to understand the abnormal isotope effect in hydrogen bonds discovered by Robertson and Ubbelohde [26].

The isotope effect in strong hydrogen bonds. — It has been found that in the case of many strong hydrogen bonds the substitution of D for H causes an increase in the O-H-O distance, sometimes by as much as 0.06 Å, whereas generally substituting D for H causes a contraction of about a tenth of this amount when hydrogen is in a single potential well [29]. A comparatively recent review contains most of the known data on this effect [24]. It is noteworthy that this abnormal isotope effect has not been found or is very negligible for several O-H-O hydrogen bonds with distances 2.70 Å or larger, although there have been several careful studies looking for the effect [24]. The effect seems to be at a maximum in the range of about 2.56 to 2.49 Å. It is unknown for the very short hydrogen bonds near 2.4 Å, but serious attempts to find the effect in these bonds appear not to have been made. It is significant that there is no abnormal effect in KFDF⁽⁵⁾ [24]. Other than these observations, no direct dependence of the size of the effect on the length of the O-H-O distance has been observed. Observations, however, have been

⁽⁵⁾ This result has now been made much more precise by recent work on NaF.HF and NaF.DF where

$$F-H-F > F-D-F$$

by 0.0046 Å [36].

limited to examining lattice constants and inferring the effect from these measurements, since until rather recently it has been impossible to determine positional parameters with the accuracy required. A few of the hydrogen bonds, such as the one in oxalic acid dihydrate [26, *a*] involve only one lattice parameter and a rather direct inference, but others require more indirect inferences, and this may have led to the lack of good correlation of distance with effect.

Several attempts have been made to explain this abnormal isotope effect [24, 30], but these are, I now believe, only partly correct, in spite of earlier expressions of support [31]. Another explanation which I have favored for some years is given here.

If the molecular or crystal symmetry is correct, then when two oxygens of an O-H-O hydrogen bond approach each other the potential energy curve should have a symmetric double well of the type obtained from adding two Morse or Lippincott potentials for single O-H bonds. The height of the barrier should then decrease rapidly as the O...O distance decreases. At the same time the number of vibrational levels below the barrier will decrease, and the separation of symmetric and asymmetric levels will increase. If, as we assume, the problem is one dimensional, the symmetric level will be the ground state vibrational level. At sufficiently short O...O distances there will be at most one symmetric (and possibly one asymmetric) vibrational level below the barrier. This level will lie deeper in the well for D than for H, and at various distances the H and D distributions will resemble those shown in figure 1 [32]. It is to be noted that as the lowest hydrogen level approaches the top of the barrier the difference between D and H distributions can become marked, so that hydrogen has considerably more density than deuterium in the center of the double well. In this case, whether a covalent, ionic or combined sort of interaction is assumed between H and O, the hydrogen density at the center will attract both oxygens and lead to a shortening of the bond, while deuterium will have a lower density in the center of the bond and less effect. Hence, it is in just that region where the difference in hydrogen and deuterium density differs most that the abnormal isotope effect should be largest, with the O-H-O distance smaller than the O-D-O distance in this region. The readjustments of distances will provide a lower barrier for hydrogen, a higher barrier for deuterium, enhancing still further the difference in H and D density in the center of the bond.

Unfortunately it is not certain just what sort of interaction to assume between hydrogen and oxygen at these distances, and thus it is difficult to make the treatment quantitative. But if all the assumptions implied in the use of the Lippin-

cott potential are made [28], then it can be seen that different O...O distances are obtained by this method by adjusting A in the term for the repulsive force between oxygens, $A e^{-bR}$, and B in the electrostatic potential term, $-B/R^m$, which comes from the fractional negative charges on oxygen atoms and the fractional positive charge on the hydrogen atom.

Adjusting B is physically reasonable, since it is observed that the strongest hydrogen bonds are formed when O-H is a good proton donor and :O is a good proton acceptor. This probably means, at least in part, that there is a higher coulomb term for such bonds, increasing B and shortening the O...O distance.

By making $D = D^*$ (D , the O-H bond dissociation energy) and $n = n^*$ [21], the Lippincott treatment is converted to the symmetrical double well case. After finding $\partial V/\partial R$ (R is the O...O distance) and setting it equal to zero for hydrogen, it is found that the same equilibrium O...O distance will not apply to deuterium, since D (dissociation energy) is involved and this is not equal for O-H and O-D by the difference in the zero-point energies. Very roughly one finds that the O-D-O distance should be about 1.5% larger than the O-H-O distance, or about 0.04 Å for bonds 2.5 Å, which is about the right order of magnitude for the effect. Unfortunately other features of this treatment appear to be incorrect, probably because A and B are tied together artificially [21], so that a quantitative treatment is still to be sought. Nevertheless, qualitatively it appears that the isotope effect can be understood in terms of this model.

An especially interesting case in this respect is HCrO₂, where the evidence is that the O-H-O bond is symmetric with hydrogen centered in a single well, while the O-D-O bond is so much longer, about 0.05 Å, that a well with double maxima is formed [25]. A similar study of HCoO₂, where the hydrogen bond is about 0.05 Å shorter [21], would be of interest. It may be that both HCoO₂ and DCoO₂ will be symmetrical with a much lower isotope effect.

It is to be noted that in the critical region, as the symmetric vibrational level for hydrogen nears the top of the barrier, the asymmetric level will be above the barrier. This may well make interpretation of the far IR spectra difficult to interpret in terms of the model used by Hadzi, *et al.* The HCrO₂ data also seem difficult to understand if symmetric single well potentials are possible over a wide range of O...O distances.

When the O...O distance becomes so short that all vibrational levels for both hydrogen and deuterium are above the barrier, for all practical purposes there is a single, symmetrical well. Now the isotope effect should again become normal, with

deuterium somewhat better centered in the well than hydrogen. This appears to be the case for KFHF and KFDF, as noted ⁽⁶⁾.

The model thus accounts for the general aspects of the abnormal isotope effect. (Clearly when the barrier is very high, as it will be for the longer O...O distances, both H and D will have an insignificant density at the center of the maximum, and there will be no significant isotope effect for long hydrogen bonds.) It would appear probable that similar arguments would explain the isotope effect in the slightly asymmetric double well problems with a low barrier.

Method for distinguishing between single and double well distribution in short hydrogen bonds.

— It is evident that the isotope effect will provide an answer to the problem of whether a short, symmetric hydrogen bond has a single or double distribution. If the isotope effect is present, then there is a double well with a sufficient barrier to cause a split in the distribution function of either hydrogen or deuterium. If there is none, then the well is effectively a single well. The method should not be used for hydrogen bonds above about 2.7 Å, for these presumably cannot be single symmetric-well hydrogen bonds, and yet no appreciable isotope effect is to be expected.

Use of this method is quite demanding on the quality of the X-ray structure determination. Hydrogen bond distances must be reliable to about ± 0.005 Å. The requirements for obtaining such reliabilities have been set forth by Cruickshank [33].

With the advent of single crystal counter diffractometers capable of taking three-dimensional data, and large computers, these requirements are not beyond present day techniques which can almost be made routine. As an example, the structure of 3, 4-furandicarboxylic acid has been determined in the laboratory at Ames by Mr. D. E. Williams using a G. E. goniostat, and scintillation counter, and scanning both maxima and neighboring background [34]. The intensities were carefully corrected for absorption and hot radiation streak errors. It took about ten days to collect data for 980 independent reflections. No data were rejected, and all reflections were measured just once. The structure refinement proceeded smoothly to $R = 0.047$ for all reflections, using the Busing and Levy full matrix least squares refinement and standard deviations. Standard deviations of bond distances at the end of the refinement were ~ 0.003 Å. The molecule contains a mirror plane on which the hydrogen of the intramolecular hydrogen bond must lie (fig. 2), and the hydrogen of the intermolecular hydrogen bond lies at a center of symmetry. A careful analysis of the

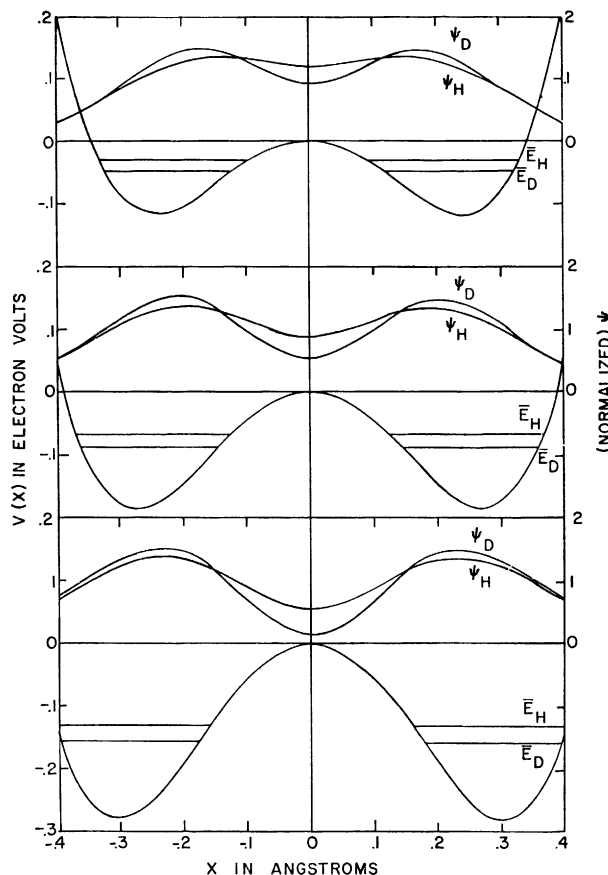


FIG. 2. — Hydrogen and deuterium levels and distributions in symmetrical double well [32]. V is assumed to have the form $-Ax^2 + Bx^4$. From top to bottom the curves represent approximately the expected potential curves for bond lengths 2.50, 2.55 and 2.60 Å.

thermal parameters strongly suggests that the symmetry is real, not statistical. (Even thermal analysis of the furan hydrogen appears to be significant.) The intramolecular hydrogen bond of 2.544 Å and the intermolecular hydrogen bond of 2.652 Å are both in an interesting range for test by this method, and the sensitivity seems to be quite sufficient to make this test meaningful. Unfortunately, we are awaiting a fresh supply of the acid before the deuterated crystals can be made.

Tests are contemplated on several suitable hydrogen bonds where highly accurate distances appear to be obtainable.

Discussion

DR IBERS. — Faites-vous la distinction entre une fonction potentiel symétrique et une fonction à double minimum dans laquelle l'état fondamental est au-dessus de la barrière ?

⁽⁶⁾ See footnote on p. 489.

Comme vous le savez, Snyder et moi-même avons trouvé dans HCrO_2 que l'état fondamental l'était au-dessus de la barrière (symétrique) tandis que dans DCrO_2 ($\text{ODO} = \text{OHO} + 0,06 \text{ \AA}$) la liaison est asymétrique. Ainsi cela cadre bien avec vos idées. $\text{HCrO}_2 - \text{DCrO}_2$ est juste dans la zone de transition entre symétrique et asymétrique, et montre un effet isotopique très grand.

Pr RUNDLE. — Si les états fondamentaux de H ou de D sont au-dessus des barrières, alors dans la mesure où cela concerne ce traitement, il n'y a aucune barrière et la distribution H a un pic unique. Peut-être la terminologie devrait-elle être modifiée en disant « distribution à pic unique » au lieu de « puits de potentiel unique ». Votre cas

intéressant paraît être un bon exemple mais constitue peut-être un cas extrême de l'effet que ce traitement réclame.

Dr YANNONI. — Quels sont les angles de liaison dans les liaisons hydrogène internes ?

Pr RUNDLE. — Ils ont les valeurs normales de liaisons d'hydrogène.

Nous apprenons avec stupeur la mort subite du Professeur R. E. RUNDLE, qui ne laisse que des amis. Le Professeur RUNDLE était un des grands spécialistes américains des liaisons chimiques. La mort a interrompu cruellement une brillante carrière scientifique. (Cf. Physics Today, 1964, 17, 124).

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