for the significant high-order correlation effects while maintaining the small low-order values. At the present time, however, it must be stressed that such a possibility is merely conjecture.

Another possibility which is being investigated as an explanation for the occurrence of the 'hole' in the diffuse scattering is in terms of effects analogous to the 'atomic-size effect' which was first discussed by Warren, Averbach & Roberts (1951) for alloys. This takes account of the fact that a disordered distribution of two types of atoms will relax to alleviate strains caused by their different sizes, by allowing the atoms to shift from their idealized positions. These atomic displacements modify the ordinary substitutional disorder diffuse scattering both by redistributing the original scattering and also by producing additional effects. These effects may be taken account of in the case of alloys using analysis procedures described for example by Hawakawa, Bardhan & Cohen (1975). In particular we note that certain terms in the intensity expression given by these authors have a minimum in the region of Bragg positions. The fact that a molecule has rotational as well as translational degrees of freedom which may be utilized to alleviate size-effect strain means that for molecular crystals the analysis is necessarily considerably more complex than for alloys, and until such an analysis is made this explanation for the presence of the 'hole' cannot be tested.

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A Revision of van der Waals Atomic Radii for Molecular Crystals. II: Hydrogen Bonded to Carbon

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Abstract

The neutron diffraction subset of the Cambridge Structural Database has been used to yield intermolecular non-bonded distances $H \cdots H$, $d_{HH} \leq 3 \cdot 0$ Å, where hydrogen is bonded to carbon. For both sp^2-hybridized and sp^3-hybridized carbon, the non-bonded effective shape of the hydrogen atom appears to be that of a spheroid of revolution about the bond with the shortest radius towards the pole ('polar flattening'). For sp^3-hybridized carbon, the spheroid is centered on the proton; for sp^2-hybridized carbon, on the other hand, the center of the spheroid is 0·42 Å away from the proton towards carbon. The effective radii are shorter in this case than when hydrogen is bound to sp^3-hybridized carbon.

Introduction

Ever since Pauling's pioneering tabulations (1939) and revisions by others (*e.g.* Bondi, 1964), the non-bonded shape of a hydrogen atom in a crystal has been regarded as that of a sphere about the proton of van der Waals radius *ca.* 1·20 Å. Accordingly, it has become routine in crystal structure analysis to

comment on H$\cdots$H distances which are 2·50 Å or less. The Cambridge Structural Database (CSD) (Allen *et al.*, 1979) permits the retrieval of a large number of non-bonded H$\cdots$H distances and hence a detailed analysis of the true effective shape. In this paper, to ensure the greatest possible accuracy in crystal coordinates, we have used data taken solely from the neutron diffraction subset of CSD. It is shown that the effective shape of a non-bonded hydrogen atom is not spherical, and, as a consequence, in certain directions, radii less than 1·20 Å are not unusual.

In a previous paper (Nyburg & Faerman, 1985), we reported on the use of CSD to retrieve non-bonded interatomic contacts, d_{XX}, less than some upper limit, between various types of X atoms, each bound to a single carbon atom. Defining μ as the polar angle, namely the supplement of the angle C–$X\cdots X$ (see explanatory diagram in Nyburg & Faerman, 1985) it was shown that, whereas the effective radii of atoms O and N are given by spheres about the nuclei, for F, S, Cl, Se, Br and I, the effective radii are represented by spheroids of revolution about the C–X bond, having their minor radii in the direction $\mu = 0°$ ('polar flattening'). The retrieval we report here is similarly restricted to those crystal structures where hydrogen is bonded to carbon.

In the previous paper we discussed the question as to whether the shortest non-bonded distances $X\cdots X$, d_{XX}, are influenced by the nature of the atom(s) to which X is chemically bound. Although we did not make an extensive study of this effect we were able to present evidence showing that the shortest distances d_{XX} are, in fact, influenced by the nature of the atom(s) to which X is bound.

In the present study, we show that the effective radii of a hydrogen atom bonded to carbon are affected by the state of hybridization of the carbon atom, hydrogen atoms bonded to an sp^2-hybridized carbon atom having somewhat shorter effective radii than hydrogen atoms bonded to sp^3-hybridized carbon. Using a far smaller data set, this difference was noticed more than 20 years ago by Bondi (1964).

Data retrieval

To ensure that hydrogen bonding was not influencing the results, if two hydrogen atoms, each bonded to carbon, had an interatomic distance $d_{HH} \leq 3·0$ Å, both were eliminated from the retrieved data if either also had a distance $\leq 2·3$ Å from an oxygen atom of another molecule (Taylor & Kennard, 1982). In fact, few such hydrogen atoms had to be eliminated (and these did not have short d_{HH} distances).

Unlike the earlier survey, from which a significant number of distances d_{XX} had to be eliminated for either structural reasons (disorder, *etc.*) or for factual errors in the data, no eliminations were required in this survey, although it was feasible to check only relatively few of the original structural references which give rise to the shortest recorded H$\cdots$H distances.

The procedure adopted was as set out in the first paper (Nyburg & Faerman, 1985). Neutron diffraction structural data were retrieved for the following six connectivities:
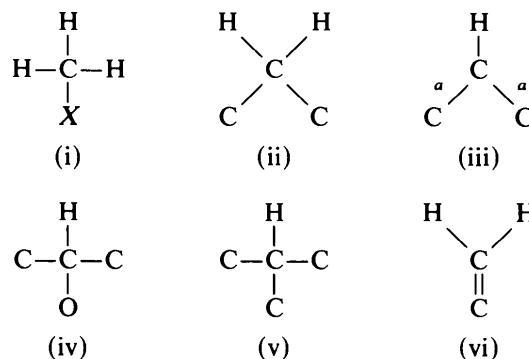
where a indicates any type of bond (otherwise the bonds were exactly as written). From these retrieved data, non-bonded distances $d_{HH} \leq 3·0$ Å were recovered. The numbers of retrieved reference codes (REFCODES) and d_{HH} distances (bracketted) for the first four connectivities were: (i) 78 (500), (ii) 20 (79), (iii) 88 (418) and (iv) 22 (44).* For connectivities (v) and (vi) only 5 and 4 REFCODES, respectively, were retrieved, too few to warrant obtaining any d_{HH} values. Because of the paucity of data we were able to make shape analyses of connectivities (i) and (iii) only.

If one assumes that the effective non-bonding radius r_X is a function of μ, then strictly, this dependence can only be found by halving the shortest contacts d_{XX} when $\mu_1 = \mu_2$. Such cases are fairly rare, being generally confined to those cases where the midpoint of the vector H$\cdots$H is a crystallographic center or diad axis. If the requirement for exact equality in the μ's is relaxed say to $|\mu_1 - \mu_2| \leq 10°$, much of the potentially available data still remains unused. We found, as previously, that the most useful initial plots were those in which d_{HH} was plotted against the smaller of the two values. Such scatterplots for connectivities (i), (ii) and (iii) are given in Figs. 1(a), (b) and (c), respectively.

Our aim in this, as in the previous paper, is to describe the envelopes of shortest contact by as simple curves as possible, namely by those having a smooth, monotonic dependence of d_{HH} on μ and a smooth,

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* A full list of references for the REFCODES has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43011 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

monotonic dependence of $(\partial d_{HH}/\partial\mu)$ on μ. We recognize that the actual dependence of d_{HH} on μ could well be less simple, but the curves we describe are such as to ensure that any d_{HH} distance in a crystal structure which is shorter than that prescribed by the boundary curve must be regarded as unusually short on the basis of currently available data. For such genuinely short non-bonded contacts it might well be worth seeking a structural explanation.

In the previous survey, the boundary curves giving the shortest contacts $X\cdots X$ for various atoms X, were drawn by eye, and were in each case, based on a spheroid of revolution about the nucleus of X. The initial boundary curve for the scatterplot of Fig. 1(a) was drawn in this way. For the scatterplot of Fig. 1(b) there were too few data points to allow a curve to be drawn with any confidence. However both scatterplots refer to hydrogen bound to sp^3-hybridized carbon and the curve from scatterplot (a) has been copied onto scatterplot (b). For the scatterplot of Fig. 1(c) we found the most convincing boundary curve to be based on a spheroid of revolution whose center is displaced $-0\cdot83$ Å in the $\mu = 0$ direction. This corresponds to the spheroid representing the effective radii, r_H, having its center $0\cdot42$ Å away from the proton towards the carbon nucleus.

To be of greatest use in structural crystallography, it is important that the shortest possible non-bonded contacts between a pair of atoms can be expressed as the sum $d = r(\mu_1) + r(\mu_2)$. To ensure this, we produced additivity scatterplots in which observed distances d_{HH} are plotted (horizontally) against calculated distances obtained from the above sum. In any such plot, if the function $r(\mu)$ has been correctly described, all the data points should lie below a line of unit slope through the origin. We found such plots to be very useful in refining initial spheroid parameters obtained from the d_{HH} vs μ scatterplots. Additivity scatterplots based on refined

parameters for hydrogen bonded to sp^3-hybridized carbon and to sp^2-hybridized carbon are given in Figs. 2(a) and (b), respectively.* The refined parameters thus obtained were used to construct the final boundary curves which are drawn on the scatterplots of Figs. 1(a) and (c).

The boundary curve for hydrogen bonded to sp^2-hybridized carbon [Fig. 1(c)] appears to differ significantly from that for sp^3-hybridized carbon [Fig. 1(a)] having shorter effective radii at all μ values between 0 and 80°. This is clearly shown by copying the boundary curve from Fig. 1(c) to Fig. 1(a).

The spheroid parameters obtained from these procedures are given in Table 1. The shortest contact radii, $r(\mu)$, at intervals of 10° in μ, in the range $0 \le \mu \le 90°$, are listed in Table 2. The reliability of these radii is difficult to assess, but we feel they are probably reliable to $0\cdot02$ Å.

We obtained scatterplots of d_{HH} vs the torsion angle $C-H\cdots H-C$ for the data of Figs. 1(a) and (c). No functional relation could be detected except that, as might be expected, the shorter d_{HH} distances do not occur so frequently at the smaller torsion angles. (To take an extreme case, if $\mu = 90°$ and the torsion angle is zero, the two C–H bonds will be parallel and side-by-side, a virtually impossible occurrence).

The results presented above were obtained entirely from neutron diffraction data and they should not strictly be applied without modification to structural data obtained by X-ray diffraction. We retrieved each of the two C–H bond lengths per d_{HH} distance both from the neutron diffraction data used above and from those same structures which had also been analysed by X-ray diffraction. These lengths were, for connectivities (i) and (iii) respectively: neutron,

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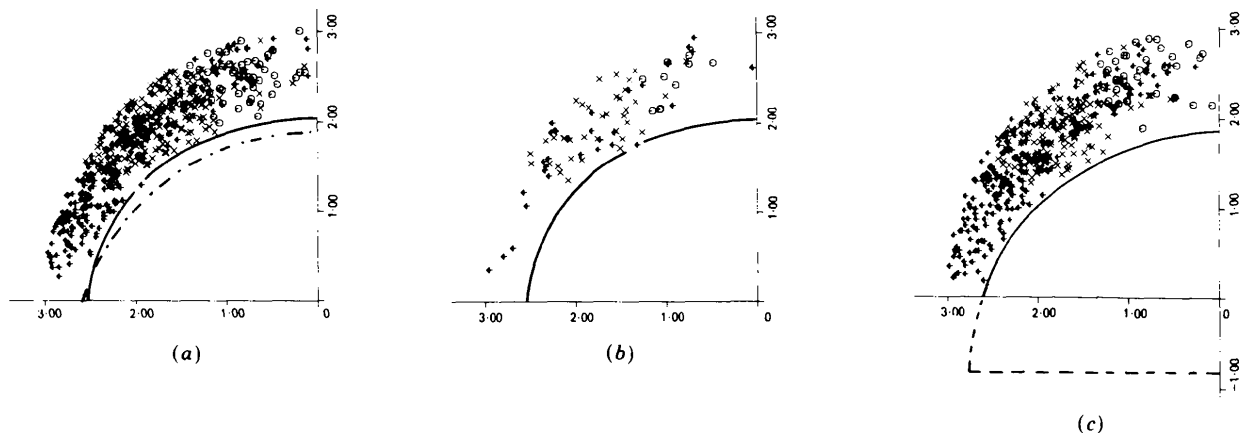* The one obvious outlier in Fig. 2(a) is discussed in the Appendix.

(a)   (b)

(c)

Fig. 1. (a), (b), (c) Polar scatterplots of d_{HH} (Å) vs μ (measured counterclockwise from vertical), for connectivities (i), (ii) (both sp^3-hybridized carbon) and (iii) (sp^2-hybridized carbon), respectively. The smaller value of μ_1, μ_2, is that plotted. The larger μ value is designated according to its magnitude: 0–30°, circles; 30–60°, crosses; 60–90°, arrows. The boundary curve appropriate to scatterplot (a) (full line) has been copied to (b) and that for (c) (full line) copied to (a) (broken line).

Table 1. *Spheroid parameters for hydrogen bonded to carbon*

Carbon hybridization	Major axis a (Å)	Minor axis b (Å)	Displacement of center c (Å)
sp^3	1.26_3	1.00_6	0.0
sp^2	1.38_3	1.35_2	0.42

$1.063\ (36)$, $1.076\ (10)$ Å; X-ray, $0.997\ (84)$, $1.015\ (19)$ Å, where brackets enclose standard deviations from the means. Thus when comparing H$\cdots$H distances from X-ray structural data with those given here, we recommend using proton positions estimated by increasing C–H lengths by, say, 6%.

Discussion

The results presented in this survey show clearly that the non-bonded effective shape of a hydrogen atom bound to carbon is of the same form as those reported earlier for other atoms, namely, that of a polar-flattened spheroid of revolution about the bond.

Based on currently available data, the effective radii for hydrogen bound to sp^2-hybridized carbon appear to be significantly shorter than those bound to sp^3-hybridized carbon. One possible cause is that sp^2-hybridized carbon is necessarily part of a local or extended π-MO system. Such systems will have larger polarizabilities than those containing only single bonds and accordingly, larger, attractive dispersion energies. This could account for the generally shorter distances, d_{HH}, in these cases.

Although, for hydrogen bound to sp^2-hybridized carbon, we propose a spheroid centered on the C–H bond 0.4 Å towards the carbon atom, such a shape does not differ greatly, in the range $0 \le \mu \le 90°$ from one having a smaller parameter b but centered closer to, or on, the proton. Our method is not sensitive

Table 2. *Shortest non-bonded* H$\cdots$H *radii,* $r_H(\mu)$ (Å)

μ (°)	C–H$\cdots$H (°)*	r_H for carbon hybridization	
		sp^3†	sp^2§
0	180	1.01	0.94
10	170	1.01	0.94
20	160	1.03	0.96
30	150	1.05	0.98
40	140	1.09	1.01
50	130	1.13	1.06
60	120	1.18	1.11
70	110	1.22	1.17
80	100	1.25	1.24
90	90	1.26	1.32

* Angle C–H$\cdots$H is $180° - \mu$.

† $r = ab[a^2 \cos^2 \mu + b^2 \sin^2 \mu]^{-1/2}$.

§ r is the positive root of $(a^2 \cos^2 \mu + b^2 \sin^2 \mu)r^2 + 2a^2 cr \cos \mu + a^2(c^2 - b^2) = 0$.

enough to categorically rule out this latter possibility, although the derived radii $r(\mu)$ will not be affected greatly in any case.

If one wishes to infer the form of an atom–atom type potential from the effective non-bonded radii it must always be borne in mind that other non-bonded atoms in the crystal, in the immediate vicinity of those of interest, play a part in governing the shape, but this contribution is generally small. Thus, to a first approximation, one can ignore the effect of these other atoms. In this respect, the idea that the effective center of atom–atom interactions between hydrogen atoms might not be located on the protons, is not new. Starr & Williams (1977) showed that the repulsive part of the potential between hydrogen atoms in H_2 molecules is best represented by spheres centered 0.16 Å inwards towards the molecular midpoint. This, however, is only part of the potential and no guarantee that the effective shape, which is governed by the sum of the repulsive and attractive potentials, will necessarily have the same functional form as that of the repulsive term alone.
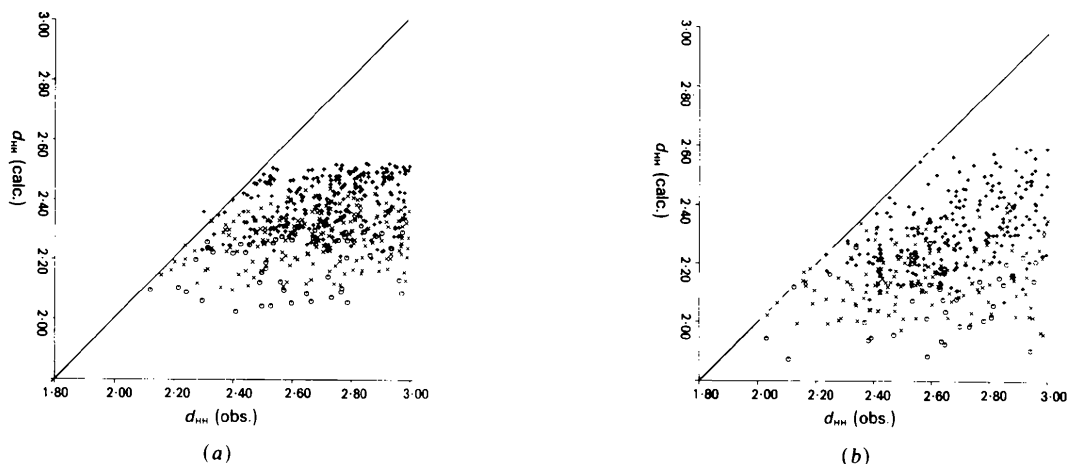

(a)   (b)

Fig. 2. Additivity scatterplots of d_{HH} (observed) vs d_{HH} (calc.) $[=r(\mu_1)+r(\mu_2)]$ with $r(\mu)$ taken from the equations of Table 2: (a) connectivity (i) (sp^3-hybridized carbon); (b) connectivity (iii) (sp^2-hybridized carbon).

For C-H bonds, Williams & Starr (1977) recommend the use of an atom-atom potential for hydrogen which is spherical about a point offset 0·07 Å towards carbon along the bond. Their justification appears to be based to some extent on the fact that the effective scattering center for X-ray diffraction lies away from the nucleus along the bond, whereas for neutrons the center is at the nucleus. In our case the cause of off-centering, if genuine, must be sought elsewhere, since all the data used were obtained by neutron diffraction.

APPENDIX

We have examined the crystallographic data which give rise to the solitary outlier of Fig. 2(a), corresponding to an observed d_{HH} of 2·30 Å compared to a calculated possible minimum, based on the appropriate μ values, of 2·36 Å. This distance is H(311)···H(532) in a crystal structure of a rhodium complex containing bulky trimethylphosphite ligands (HRHMOP11; Brown, Williams, Sivak & Muetterties, 1980). The difference between the observed and predicted minimum is three times σ, 0·02 Å, given by the authors for H···H distances in

this structure which contains an exceptionally large number of non-bonded H···H contacts, $d_{HH} \leq$ 3·0 Å, 64 in all. We have examined the geometry of the two methyl groups containing the two hydrogen atoms in question. There is no firm evidence for any compression effect. Although H(311) has the shortest C-H bond length of its methyl group, 1·03 Å (the others are 1·07 and 1·09 Å), and a slightly enlarged H(311)-C(31)-H(321) bond angle, 114·7°, H(532) shows no corresponding effects within its methyl group. This short contact is thus unexplained, but is clearly of somewhat marginal statistical significance.

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