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Weak dihydrogen bond interactions in organic crystals☆

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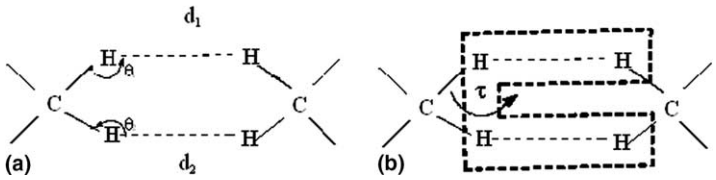
Abstract—Database analysis on H ··· H interactions of the type $CH_2 \cdots H_2C$ and N–H ··· H–N in organic crystals substantiate the occurrence of dihydrogen bonds in the absence of metal atoms.

The existence of H ··· H interactions is observed experimentally and theoretically in Group III hydrides,[1] aminoboranes,[2] aluminoboranes,[2] 1,3,5-trigermanocyclohexane,[3] 1,3,5,7-tetra-*tert*-butyl-*s*-indacene[4] and biphenyl.[5] The dihydrogen bond in transition metal hydrides is strong enough to be considered as a hydrogen bond.[1,6–11] A dihydrogen bond is said to be formed when the hydrogens have a partial charge due to a bonded heavier atom like Al, B, Ge.[12] The serendipitous observation of such a dihydrogen bond interaction involving two hydrogens bonded to carbon atoms in an organic crystal structure led to the present analysis.

The proton–proton non-bonded interactions between hydrogens bonded to sp^3 hybridized carbon in this analysis. Since the hydrogen positions in methyl groups could be grossly in error due to rotation, they were not included in the analysis. A cambridge structural database (CSD)[13,14] search was done of error free organic compounds ($R_{factor} < 0.05$). Disordered structures were excluded from the search, d_1 and d_2 are the distances between the two protons, θ_1 and θ_2 are angles subtended at the hydrogen atoms (Scheme 1(a)). A search was made for distances <2.40 Å and for angles θ_1 and θ_2 ranging from 0° to 180°. The search gave 23 hits from crystal structures (CSD codes: AEHIBQ, AHCDLA, BOBVIX, BOJHOX, BUDCIM, CEMQOA, CUZYEB, DAQVUM, GUFKAT, JOFWEG, JOKNAY, KEBJIK, KEYXOB, MIMDUH, QAMZOT, RUKKUD, SATMUV, TUGFUW, UBUPOW, VOFDEZ, WIQJUB, YEPGOP, YEQBIF). The polar plot (the distance vs angle) in Figure 1a shows an angular preference of 99–150° when the proton distance is between 2.0 and 2.4Å, with a denser distribution around 120°. In the 64–89° region (Fig. 1a), there are 3 hits and they belong to noncentric space groups and the hydrogens are staggered rather than aligned as in other cases. The frequency of the occurrence of distances and angles are shown in Figure 1b. θ_1, θ_2 both have a preference for 100–140° and the distance plot has a clear preference for 2.3–2.4 Å (Fig. 1b).

Considering Scheme 1(b) as a synthon, a further search was done. This synthon essentially has all 4 protons in



Scheme 1.

Keywords: Proton ··· proton interaction; Weak dihydrogen bond; Occurrence of dihydrogen bonds; N–H ··· H–N interaction.
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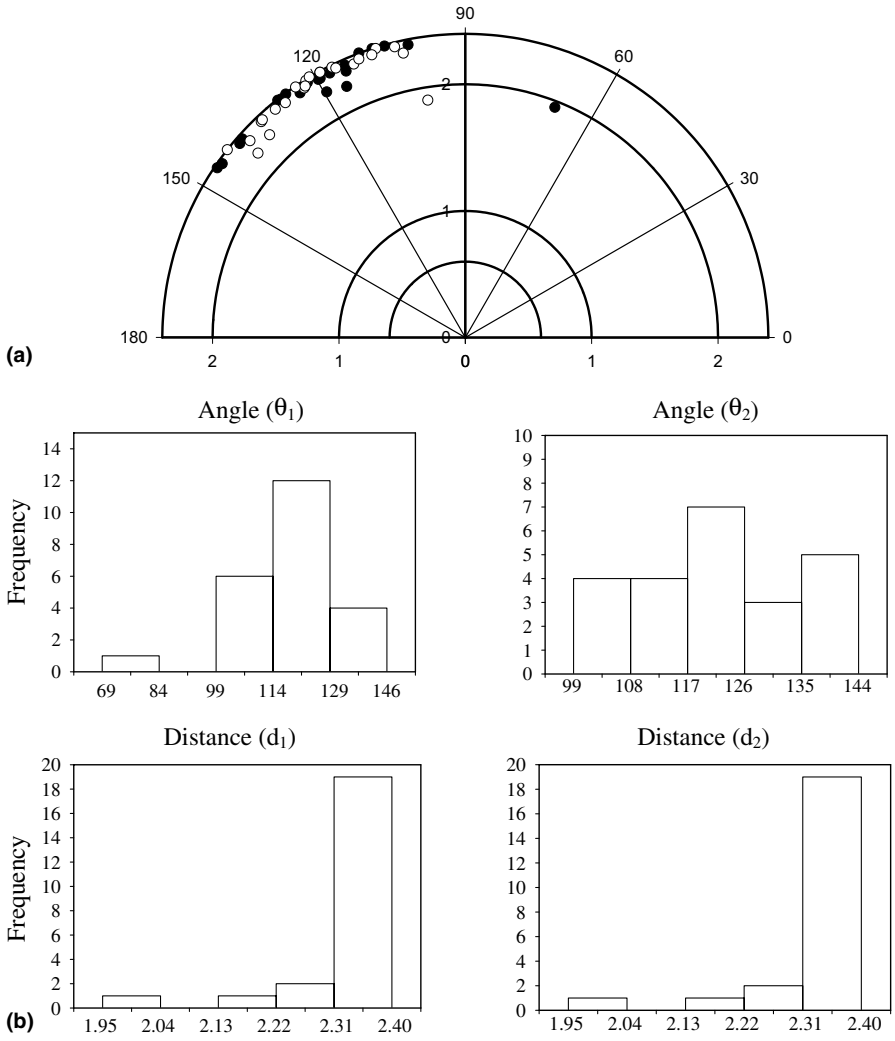


Figure 1. (a) Polar plot showing the H ⋯ H in $CH_2 \cdots H_2C$ type contacts. Shaded circle is d_1 and θ_1 and open circle is d_2 and θ_2. (b) The frequency plot for the angles (θ_1 and θ_2) (°) and distance (Å) between the H ⋯ H in $CH_2 \cdots H_2C$ type contacts.

one plane. A virtual torsion angle (τ) was constructed for the four protons (bold dotted lines). The CSD search using these parameters gave 19 out of 23 hits from the earlier search and four structures had $\tau > 0$ (nonplanar) out of which three cases were noncentric and one centric. In 82.6% of the cases the protons lie in the same plane (i.e., τ is close to 0°, Fig. 2) and in these cases the hydrogens are related by a center of symmetry. It is not clear whether the formation of a dihydrogen bond in this case is due to the presence of a center of symmetry or vice versa.

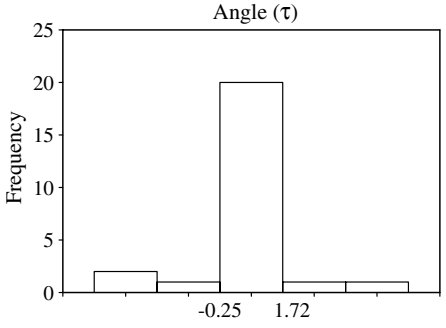
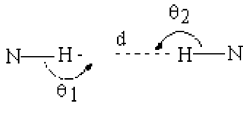


Figure 2. The frequency plot for the virtual torsion angle (°) of the H ⋯ H nonbonded interaction in the $CH_2 \cdots H_2C$ type.

The CSD search was further extended to NH ⋯ HN interactions, which gave 234 hits. Parameters for the search are shown in Scheme 2. The polar plot shows that the hits are in the angular range 60–170°. Both θ_1 and θ_2 have clear preferences for 90–150° and 100–130°, respectively (Fig. 3a), the distance preferences are 2.2–2.4 Å (Fig. 3b). This analysis demonstrates that the protons approach each other with a directional preference and we would like to call them weak dihydrogen bonds. The stabilizing energy of these interactions is expected



Scheme 2.

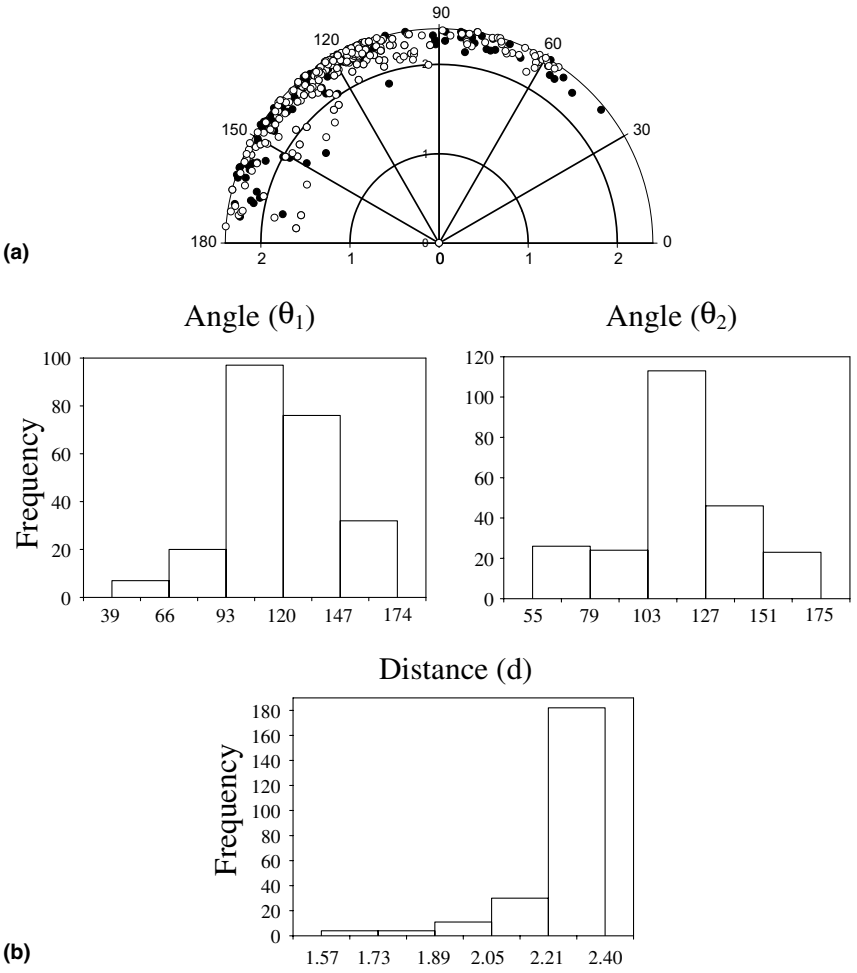


Figure 3. (a) Polar plot showing the NH ··· HN proton interaction (nitrogen atom is in sp^2 hybridization). Shaded circle is d and θ_1 and open circle is d and θ_2. (b) The frequency plot for the angle (°) and distance (Å) for H ··· H nonbonded interactions in NH ··· HN type.

to be between that of a hydrogen bond and a van der Waal's interaction, i.e less than 1 kcal per interaction.

Thus the analysis shows that the weak dihydrogen bonds described here may be a contributing force to the packing of the molecules in the crystal. Unlike strong dihydrogen bonds these interactions do not involve metal atoms for polarization.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.097. CSD data for the Scheme 1(1 page).

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