Distance Dependence of C–H···O Interactions in some Chloroalkyl Compounds

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1078 C···O non-bonded distances, retrieved from the Cambridge Structural Database for the series $(Cl_{3-n}C_n)C–H\cdots O$ where $0 \leqslant n \leqslant 3$, are found to decrease smoothly with increasing donor group acidity.

C–H···O Hydrogen bonds are directionally specific interactions, often important in determining organic crystal packing.[1—4] Systematic studies of these interactions are, however, difficult since their very weakness precludes the use of many techniques which have been used successfully for stronger hydrogen bonds.[5] This communication deals with the analysis of 1078 C–H···O geometries in crystal structures of 1585 compounds $(Cl_{3-n}C_n)C–H$ where $0 \leqslant n \leqslant 3$, which were retrieved from the Cambridge Structural Database.[6]

This study uses the third version of the Database (63589 entries) which combines bibliographic and connectivity information and which is particularly well adapted to the analysis of intermolecular geometry. The program GSTAT88 further allows extension of connectivity information to *inter*molecular fragments and this feature greatly facilitates the search for structural fragments such as the one shown in Figure 1. For example, the search question for all error-free, not disordered, diffractometer-data crystal structures containing a

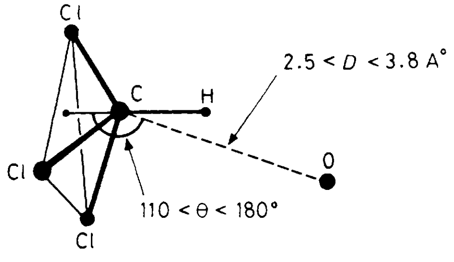

Figure 1. Schematic view of a C–H···O interaction in the compounds $(Cl_{3-n}C_n)CH$ showing chosen limits for distances (D) and angles (θ).

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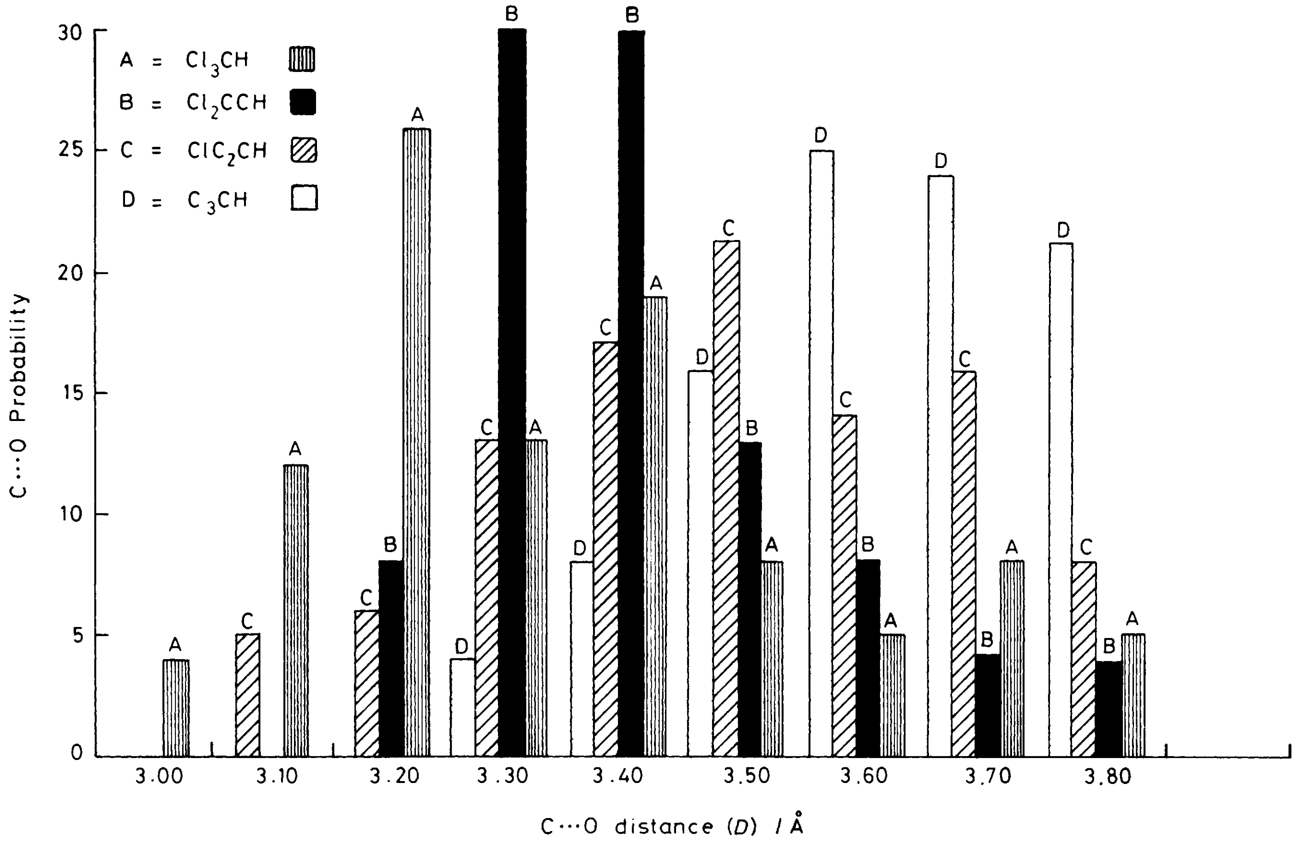

Figure 2. Histogram of C · · · O distances for the four compound categories. The populations are expressed as probabilities to facilitate comparison. The bars at, say 3.40 Å, represent contacts between 3.30 and 3.40 Å.

Cl_3C–H molecule, with a non-bonded contact to an oxygen atom within the *D* and θ ranges shown in Figure 1, yielded 100 such contacts. Restricting the search to the specified θ range ensures that the C · · · O contact is of the C–H · · · O type. Similar queries were framed for the Cl_2CC–H and ClC_2C–H fragments, but these were modified so that compounds containing carbon electron-withdrawing substituents such as –COR, –COOR, and –CN in the α-position were excluded. This procedure resulted in 23 and 87 C–H · · · O contacts for these respective fragments. The very large number of anticipated hits for the C_3C–H fragment justified a contraction of the search question to include only non-metal atom containing compounds and more stringent error limits. Even so, 868 C–H · · · O contacts in the specified range were obtained after removing structures with electronegative α-substituents as above. These computer-generated lists of compounds were also scanned manually and no obviously inappropriate compounds were found.

Figure 2 is a graphical representation of the results. The mean C · · · O distances for Cl_3CH, Cl_2CCH, ClC_2CH, and C_3CH approaching oxygen are 3.32, 3.40, 3.46, and 3.59 Å respectively, and the four probability histograms are neatly offset from each other according to the number of chlorine atoms bonded to the C–H group. The figure convincingly shows that the more acidic the donor group, the shorter the C · · · O distance. This observation indicates that C–H · · · O interactions are electronically similar to the stronger N–H · · · O and O–H · · · O hydrogen bonds where such distance dependence is well substantiated.[5,7] The range of θ (130—170°) for these contacts does not differ significantly for these four groups of compounds. Satisfyingly, many of the C–H · · · O distances in the excluded compounds such as $RCO(Cl_2)C$–H and NC(Cl)(C)C–H are among the shorter ones in their respective groups.

What is noteworthy is that these systematic gradations in C · · · O distances for different types of very weakly acidic C–H groups extend to well beyond the 'conventional' van der Waals limit. Such an observation is further confirmation that the C–H · · · O contact is not really a van der Waals interaction but is primarily electrostatic in nature,[1,8,9] falling off much more slowly with distance. Accordingly, it may be expected that even 'long' C–H · · · O bonds are sufficient to define stable crystal packings in the absence of stronger interactions.

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