Supporting Information for:

C–H···S Hydrogen Bonding Interactions

Hazel A. Fargher,† Tobias J. Sherbow,† Michael M. Haley,* Darren W. Johnson,* and Michael D. Pluth*

Department of Chemistry and Biochemistry, Materials Science Institute, Knight Campus for Accelerating Scientific Impact and Institute of Molecular Biology, University of Oregon, Eugene, Oregon, 97403-1253, United States

haley@uoregon.edu, dwj@uoregon.edu, pluth@uoregon.edu

Table of Contents Page

1. Parameters for Searches.

All non-metal bound HB Acceptor contacts with D–H HB Donors

The CCDC Conquest Program[1] was used to identify all D–H···A contacts in crystal structures in the Cambridge Structural Database[2] up to November 2019. D–H···A---NM contacts were identified when A was bound (by any bond order) to 1, 2, and 3 other non-metal (NM) elements. D–H···A---NM contacts in which A did not have a free lone-pair (such as sulfur trioxide) were excluded. Contacts in which A is not bound to any element were determined by searching for all D–H···A contacts and excluding instances when A was bound to another element.

The Draw function of the Conquest program allows the user to restrict contact distances and angles. D···A contacts were defined between 0 and 5 Å. Intramolecular D···A contacts were separated by 4 to 999 bonds. Inter- and intramolecular H···A contacts were defined between 0 and 4 Å. Intramolecular H···A contacts were separated by 4 to 999 bonds. Both D–H···A and NM---A···H angles were defined between and including 90 and 180°. Placing distance and angle restrictions which include H meant that contacts in which the H atom is not located were excluded. Searches were conducted for each donor and acceptor pair of interest. Both organic and organometallic structures were allowed. No further filters were applied. After the search was completed, contact distances and angles were downloaded into Microsoft Excel spreadsheets.

Assessing the importance of crystal structure quality

Structures with serious disorder issues and poor R factors were not excluded in the search parameters. Given the large number of contacts (>423,000 C–H contacts were identified with S, for example), it was not feasible to investigate whether the disorder was near or far from the interaction site for each individual structure. To evaluate if the presence of individual structures with disorder and high R factors significantly impacted conclusions from the data, an additional search of the CSD for C–H···S contacts from exclusively well-resolved crystal structures was performed. In this search in Conquest, structures with disorder and/or R factors > 0.05 were excluded. Figure S1 shows a comparison of weighted 3D histograms of all C–H···S contacts (Fig. S1a) and C–H···S contacts from only well-resolved structures (Figure S1b). Exclusion of disordered structures decreased the number of contacts by roughly half, however, there is no other discernable difference in the weighed heat maps, and therefore no change in the conclusions from the data. We expect that most structures in these searches used riding models with calculated hydrogen positions and H-U_{iso} values rather than direct hydrogen atom location and refinement. In cases with strong / short C–H···S interactions, the use of the riding model may result in a shorter C–H and thus longer C–H···S interaction than if the hydrogen atom was refined explicitly, which would lead to a more conservative estimate of the C–H···S interactions.

Alkyl and aryl C-H HB donor specific searches

Alkyl C–H HB donors were specified by requiring that the C donor formed four single bonds with NM elements. Aryl C–H HB donors were specified by using the benzene ring stamp in the Draw function.

3D Histograms

All weighted and unweighted 3D histograms were plotted in MATLAB using the heatmap function.

2. Supplemental Figures

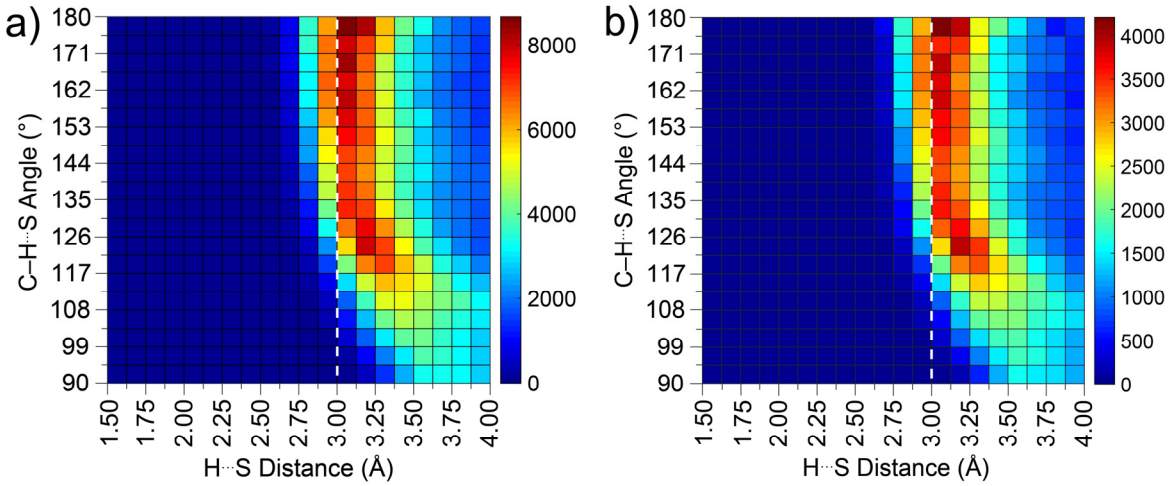

Fig. S1. a) Comparison of weighted 3D histograms of all C–H···S contacts. b) C–H···S contacts from only well-resolved structures (structures with disorder and/or R factors > 0.05 were excluded).

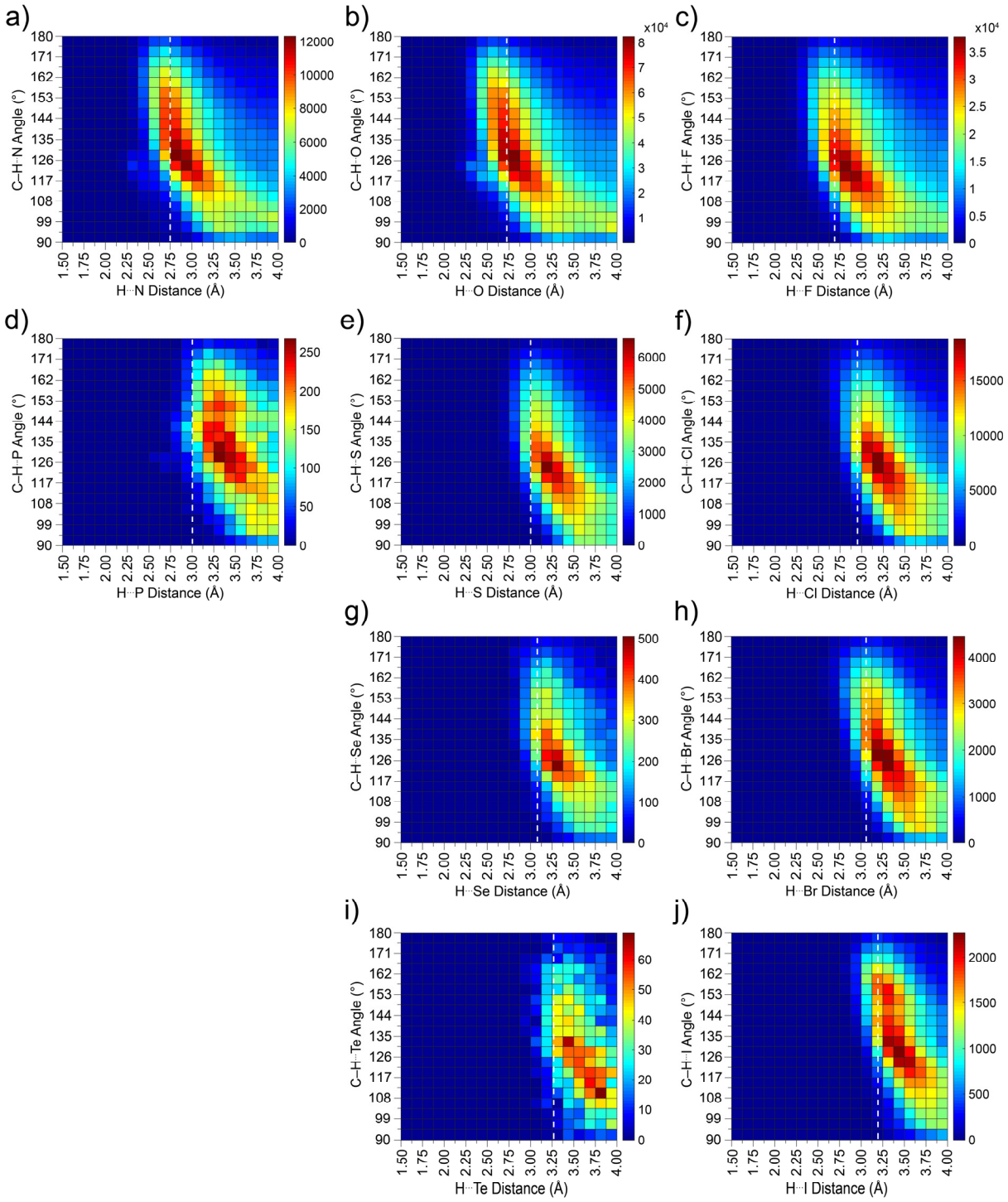

Fig. S2. Unweighted histograms of H···Acceptor distance (Å) vs. C–H···Acceptor contact angle (°). The dashed white line is the sum of the van der Waal radii of C and the Acceptor. C–H···Acceptor contacts with a) N, b) O, c) F, d) P, e) S, f) Cl, g) Se, h) Br, i) Te, j) I.

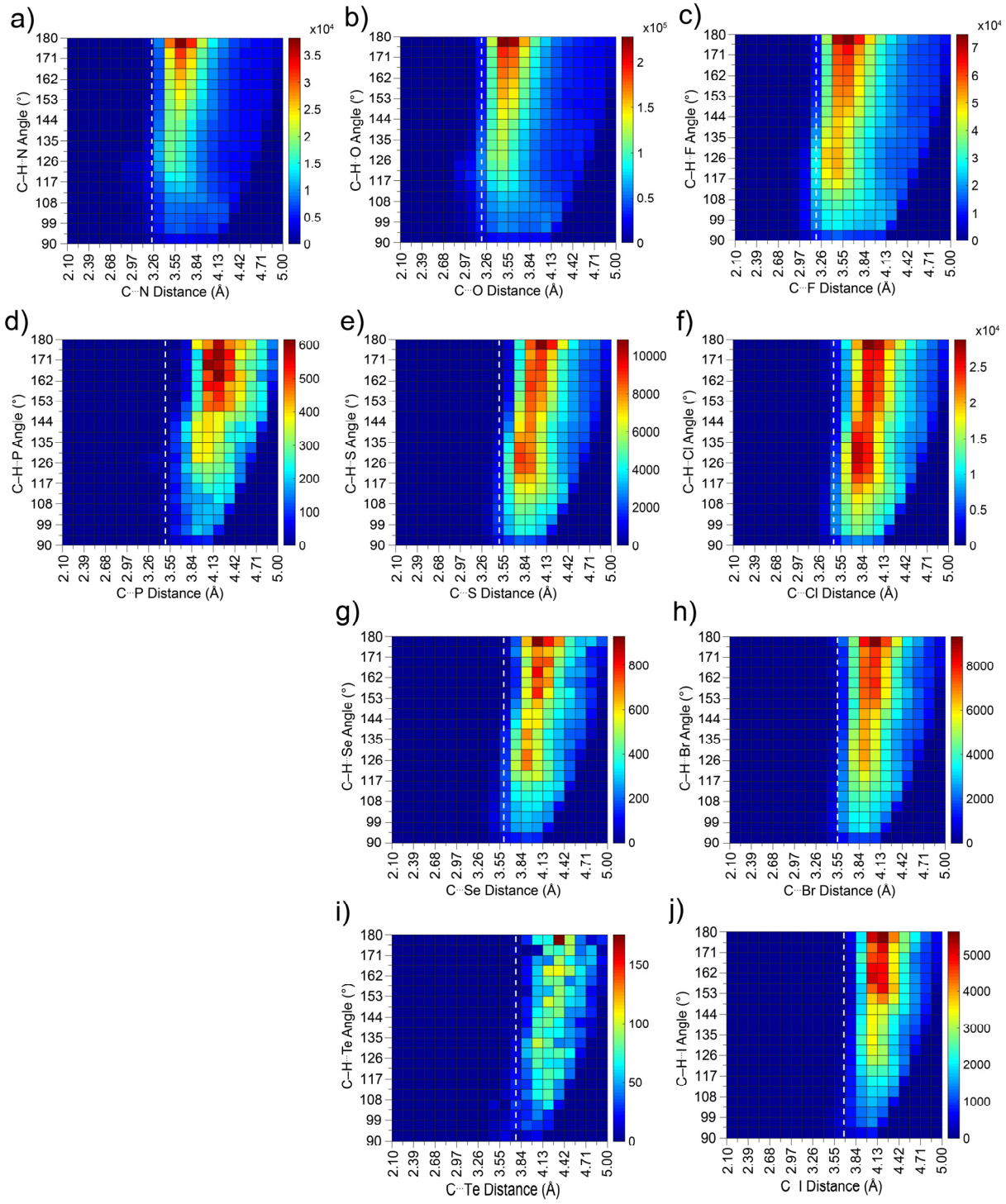

Fig. S3. Cone corrected histograms of C···Acceptor distance (Å) vs. C–H···Acceptor contact angle (°). The dashed white line is the sum of the van der Waal radii of C and the Acceptor. C–H···Acceptor contacts with a) N, b) O, c) F, d) P, e) S, f) Cl, g) Se, h) Br, i) Te, j) I.

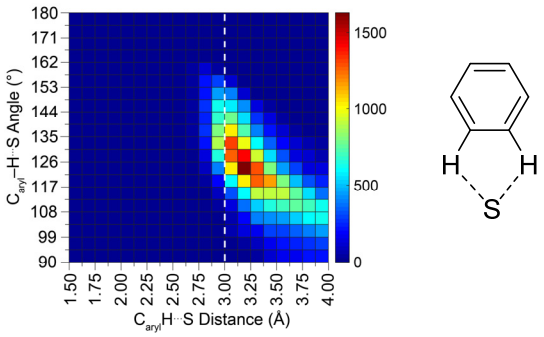

Fig. S4. Cone corrected histograms of C–H···S contacts with S bifurcated between two adjacent aryl C–H HB donors on the same ring.

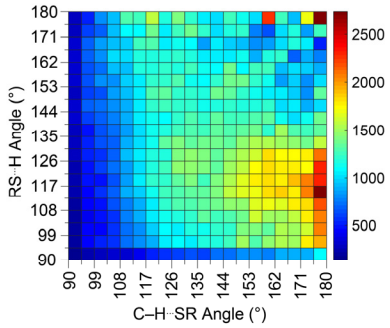

Fig. S5. Bi-weighted 3D histograms of C–H···S contacts when S is bound to only one other non-metal atoms.

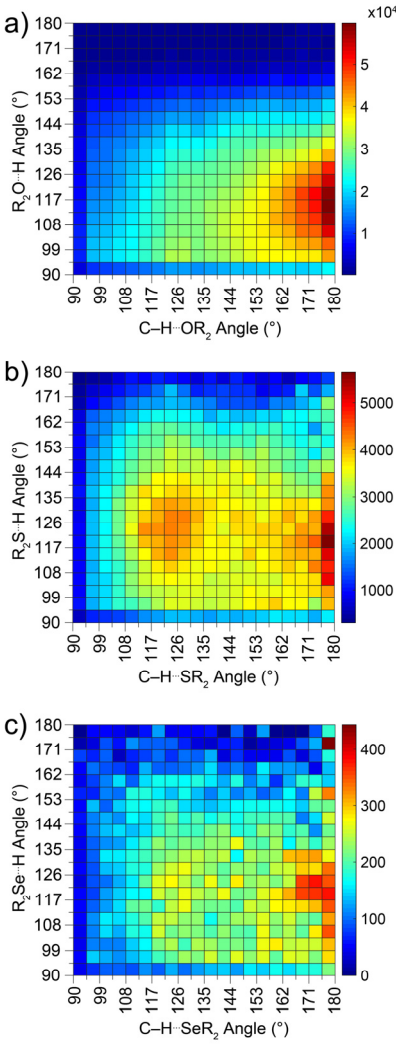

Fig. S6. Bi-weighted 3D histograms of C–H···A contacts when A is bound to two other non-metal atoms for a) O, b) S, and c) Se.

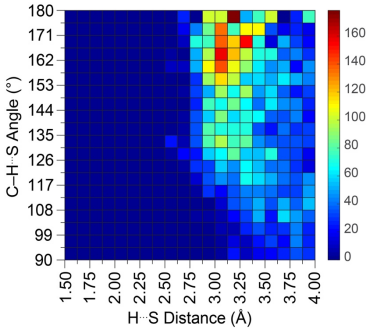

Fig. S7. Cone corrected histograms of C–H···S-M of with group 1 metals of the periodic table.

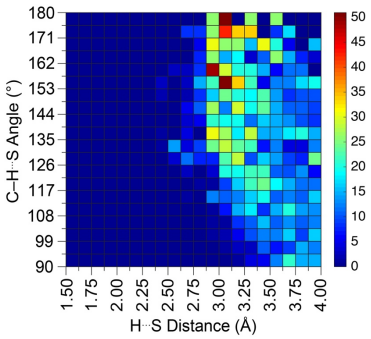

Fig. S8. Cone corrected histograms of C–H···S-M of with group 3 metals of the periodic table.

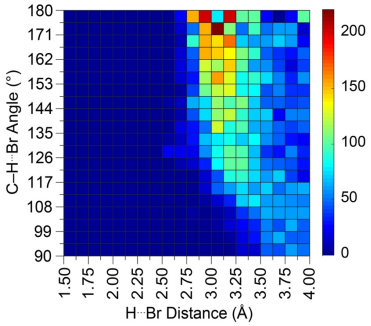

Fig. S9. Cone corrected histograms of C–H···S-M of with group 4 metals of the periodic table.

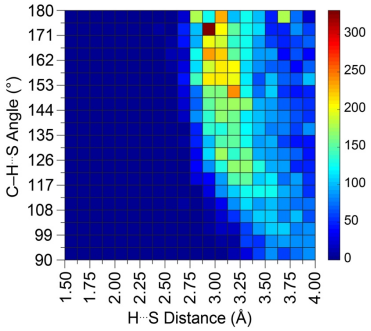

Fig. S10. Cone corrected histograms of C–H···S-M of with group 5 metals of the periodic table.

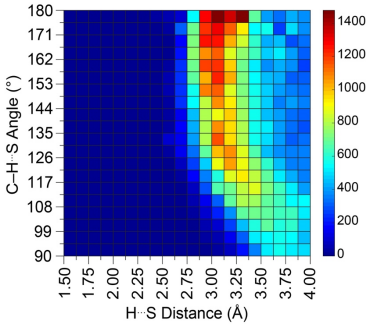

Fig. S11. Cone corrected histograms of C–H···S-M of with group 6 metals of the periodic table.

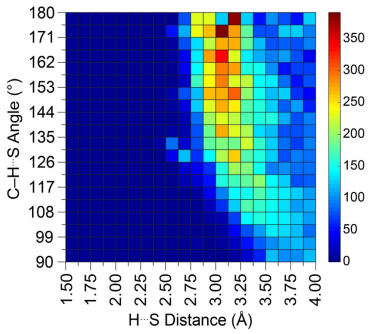

Fig. S12. Cone corrected histograms of C–H···S-M of with group 13 metals (excluding B, a nonmetal) of the periodic table.

3. References.

1. Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr. Sect. B: Struct. Sci.* **2002,** *58*, 389-397.
2. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Crystallogr. Sect. B: Struct. Sci.* **2016,** *72*, 171-179.
3. Pauling, L. C., *The Nature of the Chemical Bond*. Cornell University Press: Ithaca, NY, 1st ed.,1939; 2nd ed., 1940, 3rd ed., 1960.
4. Lau, N.; Pluth, M. D. *Curr. Opin. Chem. Biol.* **2019,** *49*, 1-8.
5. Hisaki, I.; Sakamoto, Y.; Shigemitsu, H.; Tohnai, N.; Miyata, M.; Seki, S.; Saeki, A.; Tagawa, S. *Chem. Eur. J.* **2008,** *14*, 4178-4187.