Supplementary Material (ESI) for Chemical Communications

Is there any Bona Fide Example of O–H...F–C Bond in Solution? The Cases of $HOC(CF_3)_2(4\text{-}X\text{-}2,6\text{-}C_6H_2(CF_3)_2)$ (X = $Si(i\text{-}Pr)_3$, CF_3)

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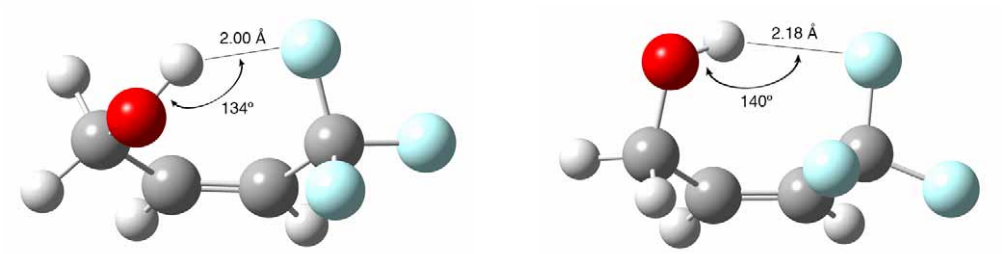
The calculations were carried out with the Gaussian 03 (Revision B.01) suite of programs: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

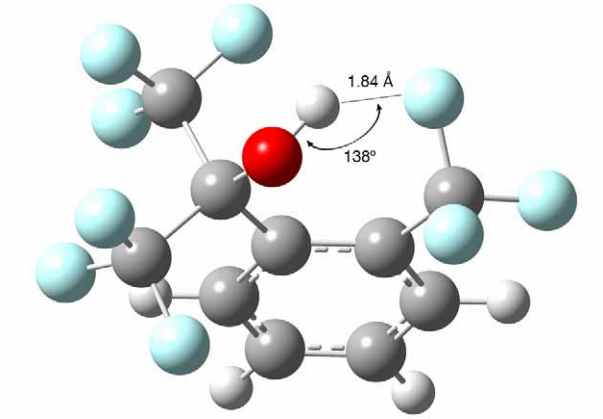
A 6-31G(d,p) basis set was used in all calculations.[1] Full optimizations without symmetry constraints have been carried out at the MP2 level for the model compound *cis*-$CH_2OH\text{-}CH{=}CH\text{-}CF_3$ (**2**).[2,3] The same minima and transition states were reached for that simplified model when a DFT method (B3LYP) was employed. Therefore the calculations were performed at the B3LYP level for the more complex model compounds **3** and **4**.[4,5] To assure that a small basis set is not the cause of the hydrogen bond missing in model compound **4**, the calculations were also performed in that case with 6-31+G†[6] and 6-311++G(d,p) basis set. In both cases the hydrogen bond couldn't be found as discussed in the main text.

[1] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
[2] M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett*, 1990, **166**, 281.
[3] M. Head-Gordon, T. Head-Gordon, *Chem. Phys. Lett.*, 1994, **220**, 122.
[4] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
[5] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
[6] G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193.

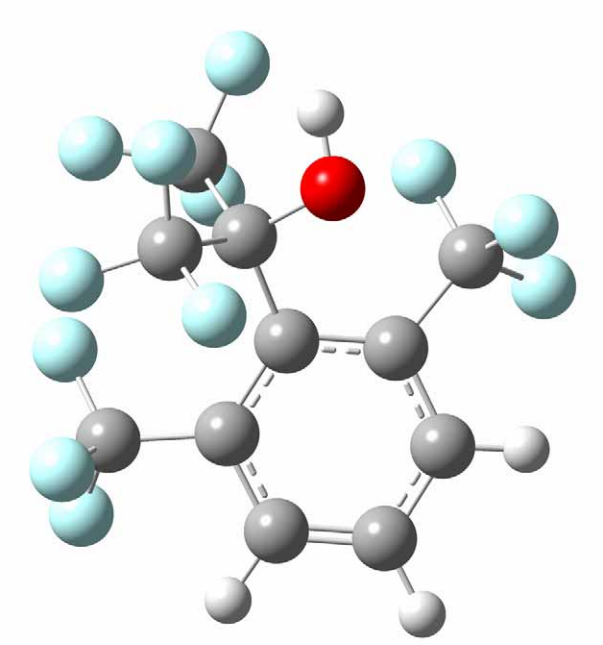
Geometries of the minima and transition states.



Geometries for model compound *cis*-CH_2OH-CH=CH-CF_3 (**2**), *left:* local minimum, *right:* transition state connecting the two symmetrical minima



Local minimum for compound $HOC(CF_3)_2(2\text{-}C_6H_4(CF_3))$ (**3**)



Minimum found for compound $HOC(CF_3)_2(2,6\text{-}C_6H_3(CF_3)_2)$ (**4**)

Table S1. Cartesian coordinates of the MP2/6-31G(d,p) optimized structure of the model compound *cis*-CH_2OH-CH=CH-CF_3 (**2**).

Center Number	Atomic Number	X	Y	Z
1	6	1.199706	1.270870	0.053663
2	6	-0.139126	1.225969	0.113190
3	6	2.210029	0.166583	-0.107065
4	6	-1.005816	0.012615	0.013298
5	8	1.770130	-1.144727	0.177736
6	9	-2.292251	0.386213	-0.184333
7	9	-0.672380	-0.780965	-1.054689
8	9	-0.980987	-0.772752	1.107351
9	1	1.645899	2.259850	0.110832
10	1	-0.696937	2.143351	0.241653
11	1	2.643748	0.247837	-1.113434
12	1	3.023948	0.363551	0.592831
13	1	1.144112	-1.405455	-0.507245

Table S2. Cartesian coordinates of the MP2/6-31G(d,p) transition state connecting the two symmetrical minima for the model compound *cis*-CH_2OH-CH=CH-CF_3 (**2**).

Center Number	Atomic Number	X	Y	Z
1	6	1.161659	1.261620	-0.178724
2	6	-0.170173	1.186790	-0.329874
3	6	2.070929	0.185175	0.362797
4	6	-1.003147	-0.002815	0.021926
5	8	1.924294	-1.087934	-0.262644
6	9	-2.297512	0.354274	0.174857
7	9	-0.968499	-0.947132	-0.965901
8	9	-0.608143	-0.609645	1.160058
9	1	1.631754	2.191344	-0.478753
10	1	-0.724132	2.008917	-0.761963
11	1	3.105126	0.510580	0.234910
12	1	1.893991	0.071606	1.436079
13	1	1.210684	-1.041069	-0.906991

Table S3. Cartesian coordinates of the B3LYP/6-31G(d,p) optimized structure of the model compound $HOC(CF_3)_2(2\text{-}C_6H_4(CF_3))$ (**3**).

Center Number	Atomic Number	X	Y	Z
1	6	-1.883504	-0.518321	0.148881
2	6	-0.711639	0.252392	0.083361
3	6	0.521439	-0.442736	-0.012374
4	6	0.526366	-1.844851	-0.011389
5	6	-0.649587	-2.582300	0.071287
6	6	-1.863119	-1.910309	0.148264
7	6	-0.883355	1.795090	0.091548
8	6	1.895102	0.198218	-0.108223
9	8	0.281054	2.536339	0.310735
10	6	-1.484260	2.269033	-1.268233
11	6	-1.803745	2.251261	1.271663
12	9	2.855639	-0.709663	-0.374417
13	9	1.968637	1.105823	-1.136919
14	9	2.265238	0.834801	1.013297
15	9	-0.552598	2.069988	-2.229460
16	9	-2.594956	1.607610	-1.632798
17	9	-1.772967	3.577525	-1.243768
18	9	-1.457924	1.620165	2.404328
19	9	-3.108959	1.983008	1.027671
20	9	-1.706200	3.565850	1.479195
21	1	-2.840119	-0.020535	0.210261
22	1	1.474092	-2.361908	-0.082123
23	1	-0.610070	-3.666891	0.070510
24	1	-2.798476	-2.458102	0.207949
25	1	0.877593	2.418853	-0.441856

Table S4. Cartesian coordinates of the B3LYP/6-31G(d,p) optimized structure of the model compound $HOC(CF_3)_2(2,6\text{-}C_6H_3(CF_3)_2)$ (**4**).

Center Number	Atomic Number	X	Y	Z
1	6	0.000000	0.000000	0.000000
2	6	0.000000	0.000000	1.381435
3	6	1.195334	0.000000	2.116911
4	6	2.453049	-0.070927	1.458725
5	6	2.428922	0.088191	0.039817
6	6	1.216300	0.094632	-0.658428
7	6	0.878661	0.116474	3.609803
8	9	0.287882	-1.008318	4.065745
9	6	3.794005	-0.370828	2.199870
10	6	4.284334	0.830120	3.111124
11	9	3.448289	1.878015	3.044252
12	6	3.632473	0.329331	-0.872163
13	9	4.510845	1.267906	-0.331538
14	9	-0.021527	1.117266	3.783558
15	9	1.905497	0.401124	4.419132
16	6	3.732222	-1.746561	2.953351
17	9	2.785480	-1.843042	3.895555
18	8	4.857512	-0.686774	1.287999
19	9	4.911283	-2.003581	3.533143
20	9	3.484340	-2.703766	2.043871
21	9	4.326909	-0.758057	-1.212503
22	9	3.232336	0.893998	-2.034264
23	9	4.448437	0.484317	4.391870
24	9	5.483323	1.280358	2.668742
25	1	1.233514	0.191553	-1.735201
26	1	-0.930666	-0.020832	-0.556654
27	1	-0.940000	0.018402	1.919934
28	1	5.313596	0.141600	1.084722