Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information:

Controlling achiral and chiral conformations of benzyl alcohol by ortho-halogenation, collisional relaxation and dimerisation

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Contents

List of Figures

List of Tables

1 Theoretical results

1.1 Keywords

Tab. S1: Applied keywords in ORCA 5.0.3[S1] for electronic structure optimisations (superscript ES), single point calculations (SP), reaction path optimisations (RP), transition state searches (TS) and relaxed scans (RS).

Level of approximation	Applied keywords
B97-3c^{ES}	B97-3c abc Opt
B3LYP-D3(BJ)/def2-TZVP^{ES}	B3LYP D3BJ def2-TZVP abc defgrid3 UseSym VERYTIGHTSCF TIGHTOPT FREQ
B3LYP-D3(BJ)/def2-QZVP^{ES}	B3LYP D3BJ def2-QZVP abc defgrid3 UseSym VERYTIGHTSCF TIGHTOPT FREQ
DLPNO-CCSD(T)/aug-cc-pVQZ^{SP}	DLPNO-CCSD(T) TightPNO aug-cc-pVQZ aug-cc-pVQZ/C TIGHTSCF additional for structures including iodine: Basis sets: aug-cc-pVQZ-PP aug-cc-pVQZ-PP/C ECP: SK-MCDHF-RSC
NEB-CI/B97-3c^{RP}	NEB-CI B97-3c abc
NEB-CI/B3LYP^{RP}	NEB-CI B3LYP D3BJ def2-TZVP abc defgrid3 VERYTIGHTSCF
TS-B97-3c^{TS}	B97-3c abc defgrid3 UseSym OptTS VERYTIGHTSCF TIGHTOPT FREQ
TS-B3LYP-D3(BJ)/def2-TZVP^{TS}	B3LYP D3BJ def2-TZVP abc defgrid3 UseSym OptTS VERYTIGHTSCF TIGHTOPT FREQ
TS-B3LYP-D3(BJ)/def2-QZVP^{TS}	B3LYP D3BJ def2-QZVP abc defgrid3 UseSym OptTS VERYTIGHTSCF TIGHTOPT FREQ
Relaxed Scan^{RS}	B97-3c abc defgrid3 TIGHTOPT

1.2 Influence of isotope masses on ORCA frequency calculations

There are small effects from the choice of masses in the harmonic frequency calculations - table S2 exemplifies the influence of the used atom masses on the calculated OH stretching frequencies and IR intensities in ORCA 5.0.3[S1]. The calculated OH stretching wavenumbers and IR intensities of the homochiral dimer Tg-G'g (Hom) are shown. For the purposes of this work, the used masses have a negligibly small influence on the wavenumber and on the IR intensity. For OH wavenumbers, the dominant effect is the mass used for H. This work uses the default ORCA option for all calculations.

Tab. S2: Comparison between calculated OH stretching wavenumbers and intensities using different isotope mass options in ORCA 5.0.3[S1] for the atoms in the homochiral dimers. The default option uses an abundance weighted isotope mass which is not the most logical choice in particular for H, while the keyword "Mass2016" uses the mass of the most abundant isotopes. D is short for H-bond donor and A short for H-bond acceptor. The mass change in H from the default ($1.008\,00\,\mathrm{g\,mol^{-1}}$) to the Mass2016 value ($1.007\,83\,\mathrm{g\,mol^{-1}}$) has a small, but larger effect on OH than the halogen isotope mass due to the local mode character.

Isotope	**ORCA option**	M $\mathrm{g\,mol^{-1}}$	ω_D $\mathrm{cm^{-1}}$	I_D $\mathrm{km\,mol^{-1}}$	ω_A $\mathrm{cm^{-1}}$	I_A $\mathrm{km\,mol^{-1}}$
$^{35/37}$Cl	default	35.45300	3618.11	424	3778.43	38
^{35}Cl	Mass2016	34.96885	3618.44	424	3778.77	38
^{37}Cl	Cl M=36.96590	36.96590	3617.94	424	3778.43	38
$^{79/81}$Br	default	79.90000	3615.00	435	3762.93	44
^{79}Br	Mass2016	78.91834	3615.32	435	3763.27	44
^{81}Br	Br M=80.91690	80.91690	3614.91	435	3763.01	44
^{127}I	default	126.90000	3615.10	445	3746.49	51
^{127}I	Mass2016	126.90447	3615.42	446	3746.83	51

1.3 Monomer coordinates

The xyz files for the Cl monomer structures (fig. 5 in the main publication) are listed in table S3, table S4 and table S5.

Tab. S3: xyz coordinates for Cl G'g at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-0.26356394161413	2.55986789658523	0.38918593290787
C	0.79330883391519	1.67960319390225	0.57869819596818
C	-1.49946842199014	2.07591900092384	-0.01823714476380
H	1.75819397651596	2.05569162735164	0.89099191308363
C	0.64804980654549	0.30886979891708	0.37366528184901
C	-1.67469683693171	0.71522379209413	-0.23439519179916
H	-2.62801699907890	0.32130718147868	-0.55259977080197
C	-0.60561043558444	-0.14433310528653	-0.03587133580298
H	-0.12179957547987	3.61792634182667	0.55619923837629
C	1.81085653617864	-0.62903983842819	0.58066105902757
H	2.63033071860540	-0.08644239919690	1.04653632910369
H	1.51870881259062	-1.43918609472764	1.25479101680001
O	2.33469361613215	-1.15406265216531	-0.63467107750411
H	1.67500574337499	-1.74052097179955	-1.01688052691498
H	-2.32925903445702	2.75110639186627	-0.17077633179049
Cl	-0.85810000791810	-1.85849917232778	-0.31902910648024

Tab. S4: xyz coordinates for Cl Tg at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-0.09003758677876	2.45775345492351	0.00092862736373
C	0.90972292802244	1.49466186226011	0.04749704058780
C	-1.42300760906610	2.07324080337745	-0.04854862492717
H	1.94760890585187	1.78801946184497	0.10084693005809
C	0.60662693243082	0.13530559351958	0.04253447763974
C	-1.75263589387483	0.72443313426295	-0.04614619456897
H	-2.78273051873216	0.40316918052768	-0.07931063329415
C	-0.74075413930195	-0.22256677870864	0.00095650290541
H	0.17341401980437	3.50580790220178	0.00698730790658
C	1.69547278293382	-0.91395853450950	0.09157077892117
H	1.66728983436190	-1.42342113830185	1.05557886469699
H	1.50217011857752	-1.67566728099788	-0.66808762360990
O	3.00661814598101	-0.39038823810023	-0.03376521729313
H	3.14478198044050	-0.10878534091576	-0.94167391632035
H	-2.20782381567952	2.81510211443626	-0.08579380573214
Cl	-1.18755374723000	-1.91650732649196	0.01879935899581

Tab. S5: xyz coordinates for Cl Tt at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-0.06279399695562	2.45159890586220	-0.00317602415922
C	0.93024600224593	1.48061017871958	0.00748042227990
C	-1.40069109430308	2.08117123352762	-0.01565072811524
H	1.97184224167443	1.76038460446624	0.01716120748863
C	0.61007663166593	0.12519375542965	0.00594215878585
C	-1.74449124172957	0.73596877755484	-0.01737707157947
H	-2.77801845291238	0.42457905835364	-0.02695785983318
C	-0.74070967094168	-0.22014966137311	-0.00660657105602
H	0.21080944871053	3.49708062902527	-0.00175186380777
C	1.67515974693176	-0.93679490362115	0.01735607898366
H	1.53789842988232	-1.57337904745093	0.89777959577379
H	1.55300300897641	-1.57717506930959	-0.86252786585000
O	2.95954860380586	-0.32991694483273	0.02701106904131
H	3.62342024445683	-1.02169996874639	0.03747756268070
H	-2.17851418626149	2.83131067028230	-0.02404813949439
Cl	-1.19961734928992	-1.91132774984138	-0.00887015127111

1.4 Electronic energy of the monomers

Supplementary to fig. 7 in the main publication the electronic energy order of the B, Cl, Br and I monomers at B3LYP-D3(BJ)/def2-QZVP and DLPNO-CCSD(T)/aug-cc-pVQZ//B3LYP-D3(BJ)/def2-QZVP level can be found in fig. S1.

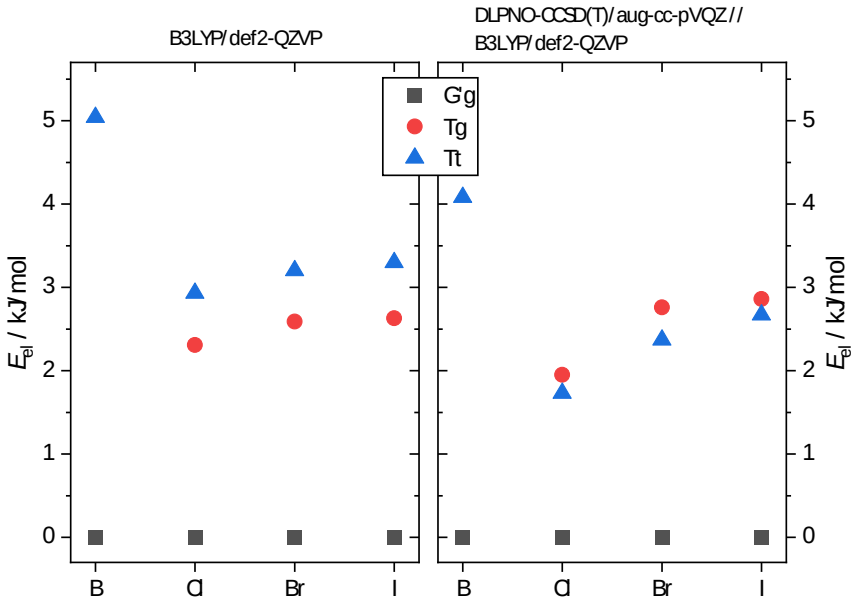
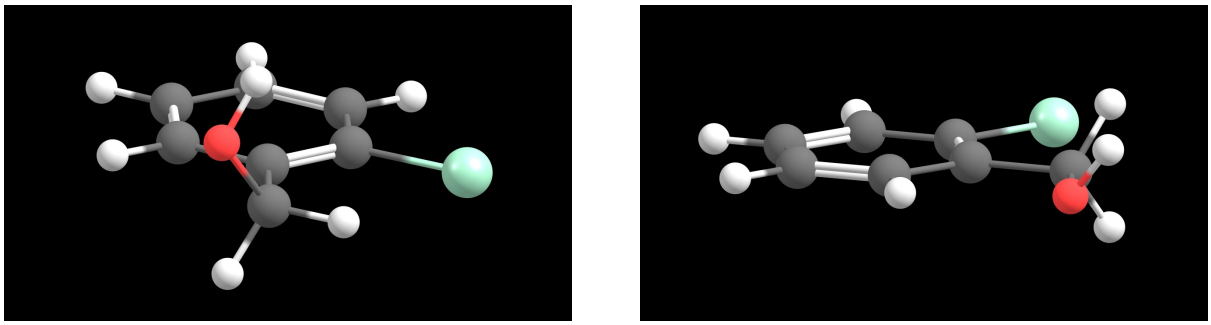


Fig. S1: Computed electronic energy order of the monomer conformers for B, Cl, Br, I calculated at B3LYP-D3(BJ)/def2-QZVP level (left) compared to results from calculations at DLPNO-CCSD(T)/aug-cc-pVQZ//B3LYP-D3(BJ)/def2-QZVP level (right).

1.5 Transitions states: Cl monomers

In fig. S2 the structures of the two transition states of the Cl monomer are shown. The respective xyz coordinates can be found in table S6 and table S7.



(a) G'g to Tg; low. frequ. $-54.63\,\mathrm{cm}^{-1}$ **(b)** Tg to Tt; low. frequ. $-235.88\,\mathrm{cm}^{-1}$

Fig. S2: Transition states for the Cl monomers G'g to Tg (a) and Tg to Tt (b) including lowest calculated frequency, calculated at B3LYP-D3(BJ)/def2-QZVP level. Depending on the pdf reader, the imaginary normal coordinate may be animated.

Tab. S6: xyz coordinates for the Cl transition state between G'g and Tg at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-0.12560725391299	2.46718365442167	0.32952085702289
C	0.87524287624216	1.51716747804520	0.44144624380472
C	-1.42758521680969	2.06624805609881	0.04765583074461
H	1.89171954891752	1.82056956374081	0.65112041441248
C	0.61636669206772	0.15341244060977	0.27744596732909
C	-1.71519247525959	0.72162313233251	-0.12151164699078
H	-2.71921640426390	0.39260422744577	-0.34223275144068
C	-0.69625193049880	-0.21848152660485	-0.00760144962511
H	0.10474902157712	3.51437647912596	0.46333312484983
C	1.76293501945022	-0.82161979853466	0.39539379045583
H	2.21314868324065	-0.73864478129525	1.38412734039236
H	1.41270942483532	-1.84505483315173	0.27413432542839
O	2.81981971369230	-0.53057291262237	-0.51906742151223
H	2.47489719151233	-0.59913207773368	-1.41357508548660
H	-2.21915909956154	2.79664613006764	-0.04077581509348
Cl	-1.12805140324279	-1.90188883716859	-0.24012566704117

Tab. S7: xyz coordinates for the Cl transition state between Tg and Tt at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-0.04522060363027	2.45548317419586	-0.02726127260654
C	0.93822827129485	1.47620641205937	0.02811619977353
C	-1.38468650828294	2.09521595922211	-0.08734474167142
H	1.98196672130306	1.74498164159543	0.07806659869446
C	0.60846265511637	0.12366751851149	0.02543386041027
C	-1.73886969308490	0.75260987001692	-0.09095110121048
H	-2.77379318466811	0.44924172378054	-0.13835893756193
C	-0.74373556666790	-0.21098325598128	-0.03330546786362
H	0.23642427576202	3.49884646330196	-0.02235198290229
C	1.66963699204900	-0.94761722228484	0.09501748613874
H	1.49275623155779	-1.56989487000448	0.97637849489755
H	1.57748917297166	-1.60469539226905	-0.77265738333834
O	2.97558327049199	-0.39052315572275	0.17841222258395
H	3.51872293642907	-0.75079294764508	-0.52256776008268
H	-2.15566362680780	2.85116713338862	-0.13108103555064
Cl	-1.21555480792404	-1.89905676124672	-0.04090739142321

1.6 NCI analysis of the Tt monomer.

In fig. S3 the NCI[S2] analysis, with a reduced density gradient (RDG) value of 0.5 au and the blue-green-red (attractive, van der Waals, repulsive) color scheme ranging from -0.04 to 0.02 au, of the B and Cl Tt monomer is compared. The additional observed attractive interaction between the benzyl group and the Cl (or halogen in general) could be a reason for the planarity of the ortho-halogenated benzyl alcohols.

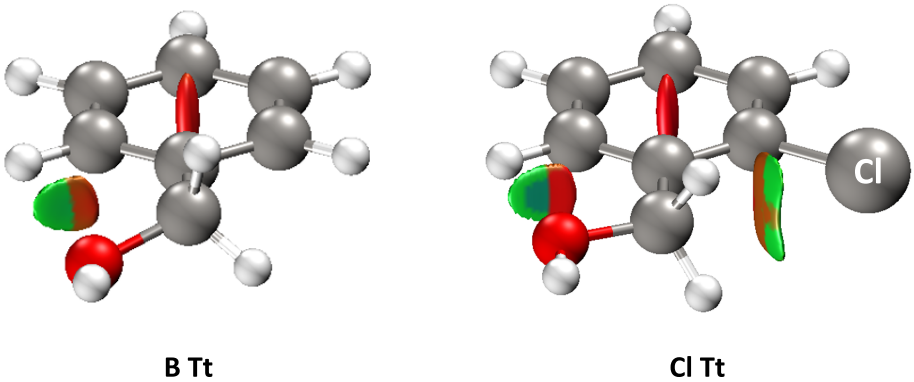


Fig. S3: Comparison between the B and Cl Tt monomers using noncovalent interaction analysis (NCI[S2]). The visualisation was done using MultiWFN[S3] and VMD[S4].

1.7 Dimer coordinates

The xyz files for the Cl dimer structures (fig. 9 in the main publication) are listed in table S8, table S9, table S10 and table S11.

Tab. S8: xyz coordinates for Cl Hom at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-1.80559300564391	0.01272881430551	-1.90912049605568
C	-2.24844229255701	0.62107034222368	-0.74280331664316
C	-1.19401842540587	-1.23074477369157	-1.84688766858839
H	-2.71668281737832	1.59518051988450	-0.78733480770527
C	-2.09652414186551	0.00916482406188	0.49924763974812
C	-1.02872012017784	-1.86586891734046	-0.62380189623559
H	-0.53899480114205	-2.82448907521848	-0.55734233621538
C	-1.48033708168561	-1.24147561396801	0.52577865213703
H	-1.92030327910670	0.51503342805130	-2.85788397980297
C	-2.56706653645900	0.69417656381962	1.75410009319505
H	-3.09825249329543	1.60662559814914	1.49612576708420
H	-3.25066001000079	0.04905648647605	2.30961425220060
O	-1.48994303132909	1.09964743291135	2.60795713909731
H	-1.09600375417798	0.30523705800854	2.98413370585822
H	-0.82774549475388	-1.70428880011075	-2.74585023557377
C	2.29020334128858	-1.25120748013698	0.80036612031520
C	1.76881566849137	0.01654044697360	1.01951253940885
C	2.55579371217629	-1.67846070193044	-0.49352376997864
H	1.57735953070071	0.36463936997107	2.02319079274209
C	1.49128053331332	0.88087985652340	-0.03538961851971
C	2.29676987144506	-0.83342979537859	-1.56425072174939
H	2.49756015507560	-1.14259861015689	-2.57901848663960
C	1.76847690519729	0.42521050429579	-1.32326016624750
H	2.48951890355633	-1.90231059202439	1.63938122472840
C	0.91719501070162	2.26122174453832	0.20716985294094
H	1.61068495497975	3.00642861330584	-0.18610800989510
H	-0.00490116203037	2.36213831509340	-0.37419449126120
O	0.70787766707046	2.57171907443687	1.56321453232967
H	-0.08201847089871	2.10886647255209	1.88573678021257
H	2.96611844133015	-2.66176046965359	-0.67476544100216
Cl	-1.24720655645316	-2.06002900752398	2.06072325776845
Cl	1.44543868172951	1.46507886388258	-2.69643110908173

Tab. S9: xyz coordinates for Cl HomA at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-2.28221205831985	-2.60029178723382	0.43553445586544
C	-2.48272452440721	-1.49114874389556	1.24681979179323
C	-0.99080202027648	-2.99317033784915	0.11336124293851
H	-3.48819084223227	-1.17439985797868	1.48847448711974
C	-1.41171316449374	-0.76011573117789	1.75518409161483
C	0.09616297240223	-2.28098793412944	0.60231221870290
H	1.10514292966487	-2.56343915918669	0.34562075761126
C	-0.12566814616706	-1.18100688213526	1.41380344160939
H	-3.13012546507962	-3.14765340724011	0.05019829718612
C	-1.64893878602198	0.45568388226700	2.60954129162658
H	-2.70314597209627	0.52486206693011	2.86479975196291
H	-1.07673014614212	0.39080858244882	3.53691087826391
O	-1.33243946679809	1.67650814791715	1.93038329989894
H	-0.37745590473558	1.70979558533577	1.80008434440803
H	-0.82168992574284	-3.84508441058605	-0.52895551803498
C	2.00019599253685	2.62519922761522	-0.42495617106960
C	0.64594616481614	2.39090908472901	-0.62598862317755
C	2.93898144289226	1.71386845297334	-0.88881491104774
H	-0.08923576816970	3.10434654185057	-0.28358475425079
C	0.19455860816242	1.24901337116841	-1.28456974335226
C	2.51785445620407	0.57914141970430	-1.56838433692622
H	3.23029446942686	-0.13645067911182	-1.95043352284358
C	1.16148073664032	0.36569390279325	-1.76210943017640
H	2.31982353125954	3.51999725337628	0.09025739860049
C	-1.28470679539688	0.97650145684374	-1.46208324642853
H	-1.53293748555076	1.00901141589050	-2.52429005982459
H	-1.49335157640776	-0.04395217951752	-1.12655715824879
O	-2.12266541334874	1.90857864085155	-0.81974254310311
H	-1.99020062299260	1.83519275743539	0.13889393951151
H	3.99468794023818	1.88324481607940	-0.73257825230502
Cl	1.26273065528043	-0.29032738830881	2.00311958762028
Cl	0.66777362103826	-1.05808421981200	-2.65637677511872

Tab. S10: xyz coordinates for Cl Het at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	0.65497040903212	-2.07530464861237	1.16563595398278
C	-0.10910087315635	-1.23364398750606	1.96082104799893
C	0.20571065900778	-2.42219934432776	-0.09944039920534
H	0.25068200461254	-0.94441990044816	2.93868560494375
C	-1.33345919263339	-0.73270650800435	1.52461908798940
C	-1.00744062295999	-1.93405145124414	-0.56621196808523
H	-1.36235585199507	-2.18181167392968	-1.55435522861839
C	-1.75833987726295	-1.10475703442966	0.24967095208503
H	1.60909535431363	-2.43359901961049	1.52098842809899
C	-2.14712239416141	0.17397548613914	2.40929243047359
H	-3.13889358248892	-0.25030012672847	2.57993328352618
H	-1.65515877005824	0.27740337161070	3.37297289917970
O	-2.27946376830536	1.50442822294803	1.89378872828859
H	-2.90105466787532	1.47782572794700	1.15866689392241
H	0.80293906293271	-3.05734582844232	-0.73682900294428
C	3.27475561330018	0.45011598361729	1.00338680005131
C	2.14367440273410	1.24008405393919	0.84789518964647
C	3.66881565655990	-0.40868124343075	-0.01443453737582
H	1.82857291067230	1.91763345325070	1.62702990853120
C	1.38187418485827	1.19333960035742	-0.31600339726758
C	2.92682478054305	-0.47347768160351	-1.18591806776834
H	3.21337720364074	-1.13315878982691	-1.99117209062617
C	1.80022799115629	0.32379150530488	-1.32050678918839
H	3.85011522363465	0.50893182280019	1.91667210747884
C	0.15939796361339	2.07019999086153	-0.48597042431468
H	0.33024294030069	2.74667025571181	-1.32703422154503
H	-0.69184528450813	1.44349956004761	-0.76524451330787
O	-0.13181673109343	2.85516325221799	0.64709059759865
H	-0.80245366898397	2.39986528166435	1.17948573777489
H	4.54997008482025	-1.02489486104125	0.09555019341998
Cl	-3.29108998546593	-0.50501259363129	-0.36563952524376
Cl	0.88066268639127	0.21530444026264	-2.80863644308467

Tab. S11: xyz coordinates for Cl HetA at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-2.96549032415165	-0.23936048706513	1.97813252031079
C	-1.73627802665211	-0.88651628403170	1.97732230750437
C	-3.73404219468248	-0.20536518527870	0.82146305413829
H	-1.13384793047759	-0.92503744903583	2.87255955145632
C	-1.24277814256415	-1.50418845695897	0.83127828918952
C	-3.27194539342594	-0.82876309756534	-0.33048202227515
H	-3.85547050664636	-0.82202730932587	-1.23892403570310
C	-2.04132600365422	-1.46769779653768	-0.31039206601849
H	-3.32365688739636	0.23364459509197	2.88160867797088
C	0.12223670905813	-2.15918247903751	0.82125236359028
H	0.01088533061641	-3.21910173685377	0.58691307525988
H	0.70896014619439	-1.72148094186626	0.00582862954728
O	0.80498572209472	-2.07269417148718	2.04763134156721
H	1.14704792544980	-1.16932544104708	2.14581549169316
H	-4.69169568726139	0.29526764210501	0.81170927118887
C	-0.50950525324809	1.30622482793051	-1.85723272404182
C	-0.35206847887894	1.41894005724146	-0.48303447088390
C	0.60348255250143	1.33206162335563	-2.68516512434921
H	-1.21845428701742	1.38167084049043	0.16125907068187
C	0.90823294233338	1.56092905034283	0.09395037828958
C	1.87257601940607	1.47836454754105	-2.13960536679895
H	2.74934739764370	1.50252276479865	-2.76867140888563
C	2.00624276057577	1.59414610179813	-0.76559525913586
H	-1.49693722159473	1.17970640683729	-2.27508562192528
C	1.05500559048547	1.67465711930373	1.58853951009252
H	1.54941451069341	2.61250340984191	1.85202327910743
H	0.07114294665655	1.66774487040480	2.04920891182455
O	1.76723402954298	0.57960278002547	2.17720117788616
H	2.68454780327282	0.62796081129234	1.88782164876481
H	0.49202752865030	1.23362266698041	-3.75532235768045
Cl	-1.47534004994019	-2.22338039678347	-1.78391786675899
Cl	3.62324645823732	1.79470233207007	-0.10607788167525

1.8 Calculated wavenumbers for Cl, Br and I dimers

A comparison between the calculated band positions of the Cl, Br and I Hom and Het dimers is shown in fig. S4.

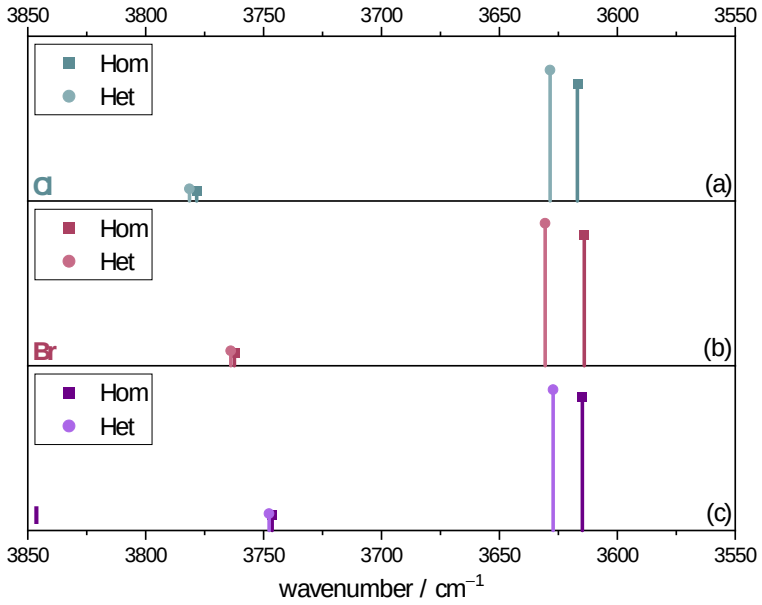
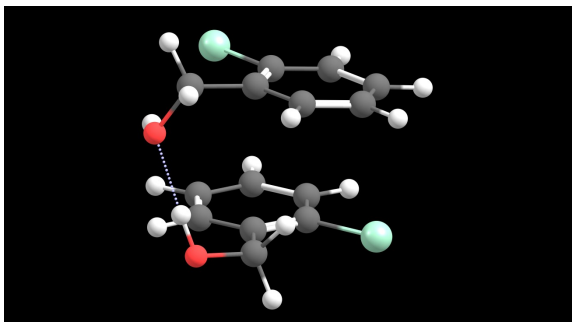


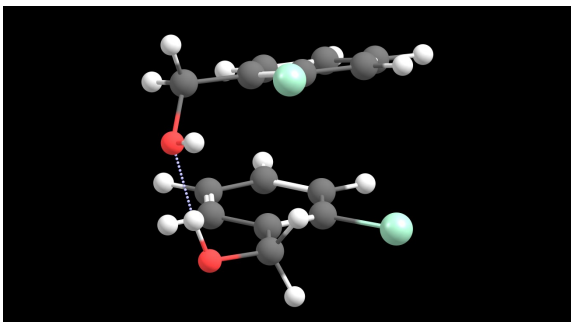
Fig. S4: Comparison between the calculated harmonic wavenumbers and intensities for the Hom and Het dimer conformers of Cl, Br, I, calculated at B3LYP-D3(BJ)/def2-QZVP level.

1.9 Transitions states: Cl dimers

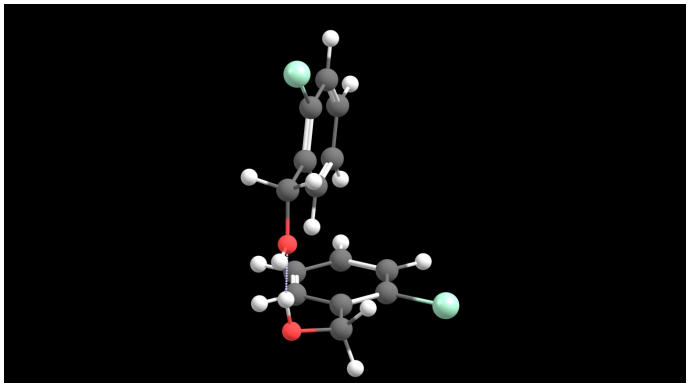
In fig. S5 the structures of the three transition states of the Cl dimer are shown. The respective xyz coordinates can be found in table S12, table S13 and table S14. The height of the barriers between the Cl dimers are shown in fig. S6 and a comparison between the barriers of Cl, Br and I dimers in fig. S7.



(a) HomA to Hom; low. frequ. $-17.78\,\mathrm{cm}^{-1}$



(b) HetA to Het; low. frequ. $-16.62\,\mathrm{cm}^{-1}$



(c) Het to Hom; low. frequ. $-22.36\,\mathrm{cm}^{-1}$

Fig. S5: Transition states for the Cl dimers HomA to Hom (a), HetA to Het (b) and Het to Hom (c) including the lowest calculated frequency, calculated at B3LYP-D3(BJ)/def2-QZVP level. Depending on the pdf reader, the imaginary normal coordinate may be animated.

Tab. S12: xyz coordinates for the Cl transition state between HomA and Hom at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-1.69451504219236	-2.62025564185144	0.20425224449548
C	-2.14558003738738	-1.56449748121505	0.98387055837894
C	-0.33358957906247	-2.87736330242587	0.11330665448974
H	-3.20479809777644	-1.35431692289495	1.04667818242790
C	-1.26081993293631	-0.75325474868517	1.69191313212661
C	0.57176094371646	-2.08419234910641	0.80413230950724
H	1.63368484252402	-2.26197050166489	0.73409724441554
C	0.09939792026059	-1.04090209496670	1.58345844852556
H	-2.40070256535335	-3.23014975926785	-0.33992812050704
C	-1.76805739384185	0.39522394028314	2.52186913732153
H	-2.85331050140740	0.36261331583093	2.57020915370398
H	-1.37955129737348	0.33128460128404	3.54028207630669
O	-1.44308583456845	1.67338193487399	1.96267146853430
H	-0.48481416536684	1.77374788896384	1.98635636556276
H	0.03009913953690	-3.68474987467791	-0.50489964609295
C	2.12539332589475	2.17652561585522	-0.42685875203150
C	0.74913306351155	2.21030072196522	-0.60826641734953
C	2.87275521463561	1.14361559671086	-0.97532802057118
H	0.16128939066371	3.01755170698424	-0.19647571853252
C	0.08644336911561	1.22363762852500	-1.33448660284351
C	2.24024448623518	0.15842071265724	-1.72182619158801
H	2.80274385530715	-0.64620545104886	-2.17120570578692
C	0.86603273330141	0.21509974401179	-1.89801521138663
H	2.61174494536606	2.95465869325973	0.14413025604367
C	-1.41922697824125	1.24377025618573	-1.49666243213286
H	-1.66655755071411	1.40827102230397	-2.54684983701448
H	-1.80747761658339	0.25405575442041	-1.23777446438203
O	-2.06517638658777	2.25670172186580	-0.76234161627671
H	-1.96233539785238	2.06864742645061	0.18447688080383
H	3.94306322952264	1.10286377155380	-0.83248238661818
Cl	1.26517082529263	-0.05785722110687	2.44776874955359
Cl	0.10522898969938	-1.02361525346226	-2.87547777036292

Tab. S13: xyz coordinates for the Cl transition state between HetA and Het at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	-0.82880425082705	1.63716920064072	-1.37807998796187
C	-0.40715818672928	1.81358304489793	-0.06786711414846
C	0.09369629212747	1.31509135576048	-2.36254709608330
H	-1.13233435809195	2.03182381448158	0.70293034397074
C	0.93403707993823	1.69074007044519	0.28736040421260
C	1.43833617804402	1.18570304933296	-2.03960081203872
H	2.16951554509666	0.93494361981893	-2.79285209396461
C	1.83875733040899	1.38197532974813	-0.72832017870941
H	-1.87671218983459	1.72637676286711	-1.62024949578549
C	1.36773463297717	1.89370763568842	1.71538343429505
H	2.08815899287828	2.71246334163584	1.78012847829808
H	0.50461003633799	2.15600378905489	2.32143151368482
O	1.92557951046643	0.72045611737075	2.31846427668243
H	2.78705092202962	0.56048229617742	1.91834797651519
H	-0.22681582156922	1.15336970826702	-3.38127684850079
C	-3.11200350610439	-0.23850965993339	1.67416665820595
C	-1.84536458289359	-0.78923988482122	1.82150336215215
C	-3.75679023709934	-0.29759222835041	0.44546525176588
H	-1.33831380298338	-0.75887252539287	2.77434314566528
C	-1.19199592925132	-1.40023457156816	0.75514555892127
C	-3.13147432831217	-0.91349955611148	-0.63076485881416
H	-3.61496768977860	-0.97580915286829	-1.59417731858531
C	-1.86526921144188	-1.45275779611799	-0.46339161181953
H	-3.59640098086110	0.23017307128568	2.51929337121173
C	0.20337393554040	-1.96609369696114	0.91329769142029
H	0.18472674718968	-3.03176932544357	0.67872415955150
H	0.85560645093694	-1.49697183776174	0.16886105668313
O	0.72841072482362	-1.83212887558914	2.21178022722248
H	1.08586770403743	-0.93546951913456	2.31344483179124
H	-4.74379445925136	0.12480915451805	0.32109687816962
Cl	3.55002476808868	1.23590100483459	-0.35579880891105
Cl	-1.09332995032798	-2.20027075644419	-1.84638611153255

Tab. S14: xyz coordinates for the Cl transition state between Het and Hom at B3LYP-D3(BJ)/def2-QZVP level.

atom	x	y	z
C	0.22026904588943	-1.70535815300804	0.15664892906094
C	-0.57317365762934	-0.63700635750357	0.55181634107913
C	-0.31339313868340	-2.98585649228052	0.11950615346339
H	-0.15032537328589	0.35003992362927	0.58295605808670
C	-1.90380214101209	-0.81580880373532	0.91440876418264
C	-1.63826512319288	-3.19385988511339	0.48171030870243
H	-2.07284640082994	-4.18179888085440	0.46228644064924
C	-2.41344861509292	-2.11373000073731	0.87366880886662
H	1.24942516249535	-1.52806654612817	-0.11825250664348
C	-2.77727269906314	0.33142582602089	1.33951907547822
H	-3.66877228620059	0.36022570792469	0.70755083240157
H	-3.11367941679333	0.17269390425479	2.36842825055746
O	-2.06789178686555	1.56742120303435	1.23895023399837
H	-2.67744531271474	2.28313895767752	1.43121289074536
H	0.29349475894857	-3.82533111388685	-0.18817679712552
C	3.51522381062125	0.31512009777380	0.85191416629359
C	2.51973125279679	1.28280683812219	0.83392498146253
C	3.94552716671741	-0.26179424847153	-0.33609083347162
H	2.17283989710333	1.73498049883038	1.75082342154084
C	1.93177294826921	1.69565848395341	-0.35914245966331
C	3.37858800275435	0.13478902961812	-1.53984782976939
H	3.69694749694482	-0.29968431810184	-2.47547085553313
C	2.38616911400231	1.10451666442049	-1.53693135836687
H	3.95218977883740	0.01155699110470	1.79252804240334
C	0.83864657030587	2.74534710219803	-0.36891884936574
H	1.22968126252234	3.66167537871488	-0.81624731934873
H	0.02249811756411	2.40900321430633	-1.01279216009945
O	0.36268581362825	3.07518074534808	0.92005980068199
H	-0.36414380624454	2.47756569870792	1.13980560223882
H	4.71852781253645	-1.01702339446120	-0.33223110584485
Cl	-4.08023261146235	-2.40148614526633	1.32953878340026
Cl	1.69371776136956	1.58658925357691	-3.07179757139671

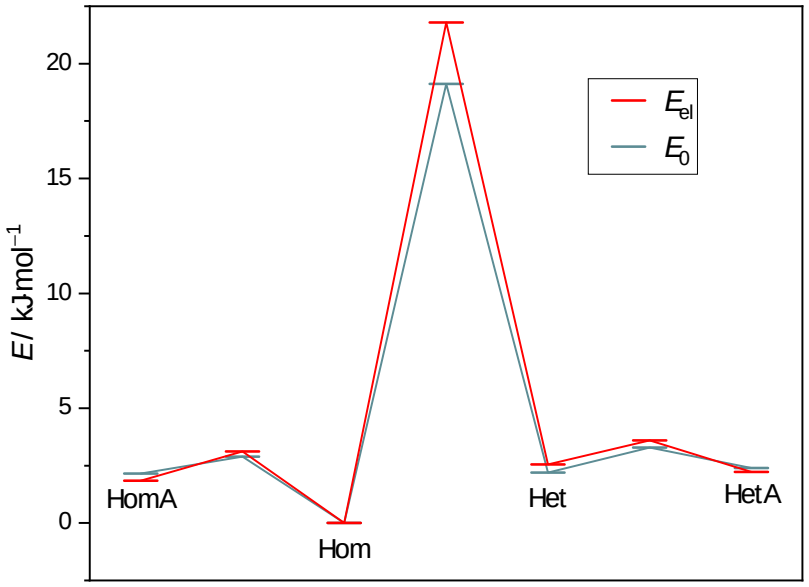


Fig. S6: Cl dimer energies and calculated transition state energies at B3LYP-D3(BJ)/def2-QZVP level with (E_0) and without ZVPE (E_{el}).

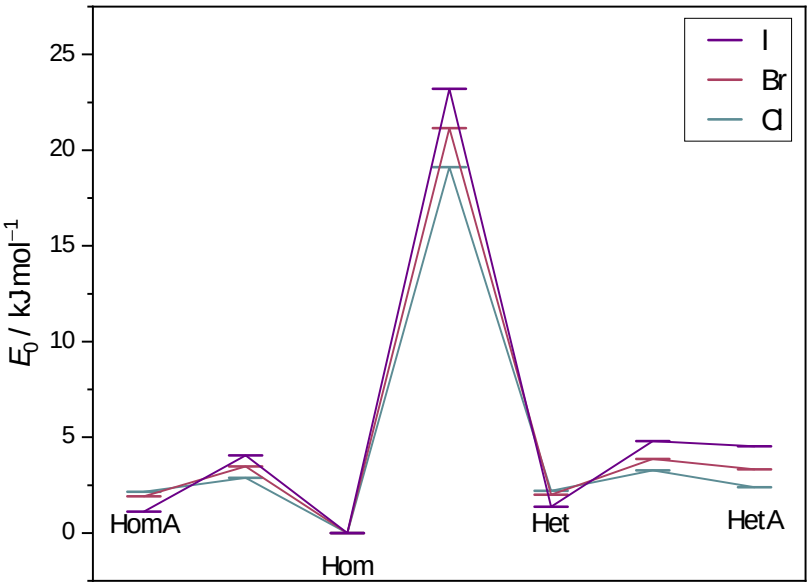


Fig. S7: Relative ZPVE-corrected energies and transition barriers between the four most stable dimers of Cl, Br, I, calculated at B3LYP-D3(BJ)/def2-QZVP level.

2 Experimental results

2.1 Measurement conditions

Tab. S15: Details for the measurement conditions of the shown spectra including the carrier gas, the temperature of the substance chamber T_{Subst}, the temperature of the nozzle T_{Nozzle} and the number of averaged scans #.

Substance	**Carrier gas**	T_{Subst} / °C	T_{Nozzle} / °C	#	Figure
2-Chlorobenzyl alcohol	He	70	90	482	11b, 13a
2-Chlorobenzyl alcohol	He	80	100	149	12b
2-Chlorobenzyl alcohol	He+Ar	80	100	175	12a
2-Bromobenzyl alcohol	He	90	110	375	13b
2-Iodobenzyl alcohol	He	110	130	325	13c

2.2 Experimental and calculated band positions

In table S16 the experimentally observed band positions and assignments to the computed conformations are shown. Scaled harmonic band positions for monomers and dimers are also listed and, if applicable, compared to the experiment.

Tab. S16: Experimental band positions (ν), calculated band positions at B3LYP-D3(BJ)/def2-QZVP level (ω_{calc}), scaled band positions ($\omega_{\mathrm{scal}} = \omega_{\mathrm{calc}} \cdot 0.96$), calculated IR intensity (I_{calc}) and difference between experimental and scaled band positions ($\Delta\omega = \omega_{\mathrm{scal}} - \nu$). D is short for H-bond donor and A short for H-bond acceptor. The deviations between experiment and scaled harmonic theory are very systematic, supporting the proposed assignments.

Substance	**Assignment**	**Label**	ν cm^{-1}	ω_{calc} cm^{-1}	ω_{scal} cm^{-1}	I_{calc} $\mathrm{km\,mol}^{-1}$	$\Delta\omega$ cm^{-1}
Cl	Monomer	G'g	3636	3799.5	3647.5	33	+11.5
		Tg	-	3818.9	3666.1	33	-
		Tt	3687	3849.6	3695.6	54	+8.6
	hom Dimer	Tg-G'g$_{\mathrm{D}}$	3499	3617.0	3472.2	425	−26.8
		Tg-G'g$_{\mathrm{A}}$	-	3778.4	3627.3	38	-
		Tg-G'g-a$_{\mathrm{D}}$	-	3624.1	3479.1	307	-
		Tg-G'g-a$_{\mathrm{A}}$	-	3759.1	3608.7	64	-
	het Dimer	Tg-Gg'$_{\mathrm{D}}$	-	3628.6	3483.5	476	-
		Tg-Gg'$_{\mathrm{A}}$	-	3781.4	3630.1	44	-
		Tg-Gg'-a$_{\mathrm{D}}$	-	3614.2	3469.6	470	-
		Tg-Gg'-a$_{\mathrm{A}}$	-	3778.4	3627.3	54	-
Br	Monomer	G'g	3626	3788.0	3636.5	36	+10.5
		Tg	-	3819.3	3666.5	35	-
		Tt	3688	3849.7	3695.7	56	+7.7
	hom Dimer	Tg-G'g$_{\mathrm{D}}$	3498	3614.0	3469.4	436	−28.6
		Tg-G'g$_{\mathrm{A}}$	-	3762.3	3611.8	44	-
		Tg-G'g-a$_{\mathrm{D}}$	-	3622.9	3478.0	311	-
		Tg-G'g-a$_{\mathrm{A}}$	-	3748.2	3598.3	66	-
	het Dimer	Tg-Gg'$_{\mathrm{D}}$	3511	3630.6	3485.4	475	−25.6
		Tg-Gg'$_{\mathrm{A}}$	-	3763.9	3613.3	50	-
		Tg-Gg'-a$_{\mathrm{D}}$	-	3612.7	3468.2	489	-
		Tg-Gg'-a$_{\mathrm{A}}$	-	3759.8	3609.4	64	-
I	Monomer	G'g	3613	3774.6	3623.6	39	+10.6
		Tg	-	3818.5	3665.8	36	-
		Tt	3686	3849.4	3695.4	57	+9.4
	hom Dimer	Tg-G'g$_{\mathrm{D}}$	3498	3614.9	3470.3	445	−27.7
		Tg-G'g$_{\mathrm{A}}$	-	3746.3	3596.4	51	-
		Tg-G'g-a$_{\mathrm{D}}$	-	3619.9	3475.1	309	-
		Tg-G'g-a$_{\mathrm{A}}$	-	3733.0	3583.7	69	-
	het Dimer	Tg-Gg'$_{\mathrm{D}}$	3510	3627.2	3482.1	470	−27.9
		Tg-Gg'$_{\mathrm{A}}$	-	3747.6	3597.7	56	-
		Tg-Gg'-a$_{\mathrm{D}}$	-	3618.2	3473.5	511	-
		Tg-Gg'-a$_{\mathrm{A}}$	-	3742.4	3592.7	74	-

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